Reconciling Reported VOC Emissions with Ambient Measurements

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December 12, 2007

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 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 ISC.**

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

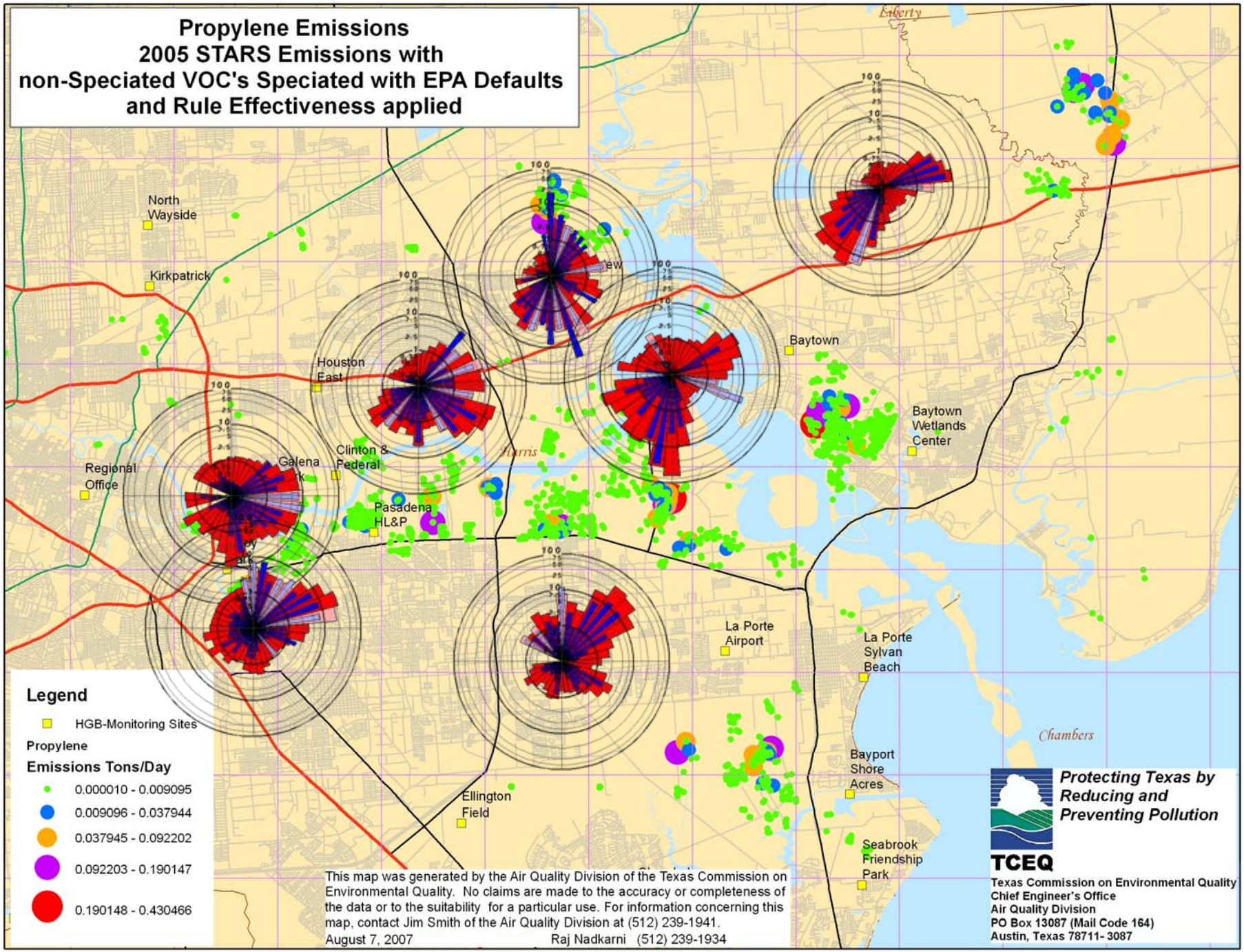
The ISC Model (Cont.)

- **We ran ISC for each hour in 2005 using archived meteorological data, provided that wind direction was constant for at least six hours:**
  - **Sinuosity (shortest path length/actual path length) > .95 (straight line sinuosity = 1.0).**
  - **Wind Direction varies < 30° over six hours.**

- **We used the emissions data created for the 2005 CAMx modeling runs:**
  - **2005 STARS extract**
  - **Complete speciation**
  - **Rule-effectiveness adjusted**
  - **Note: does not capture most temporal variability in point source hydrocarbon emissions.**

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

Propylene Emissions
2005 STARS Emissions with non-Speciated VOC's Speciated with EPA Defaults and Rule Effectiveness applied



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

ISC Results

- **Comparing the ISC-modeled and monitored concentrations at the Auto-GC sites indicates discrepancies between what we would expect to see (ISC-modeled concentrations) and what we actually are seeing (monitored concentrations).**

- **The wind roses generally point to areas from whence these discrepancies may arise, but don't indicate distances.**

- **This approach does not directly address how well reported emissions agree with actual emissions.**

PSCF

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

- **For each location and hour, six-hour back trajectories were calculated, with locations output every five minutes. Each trajectory then consists of 12*6=72 individual points.**

- **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.**

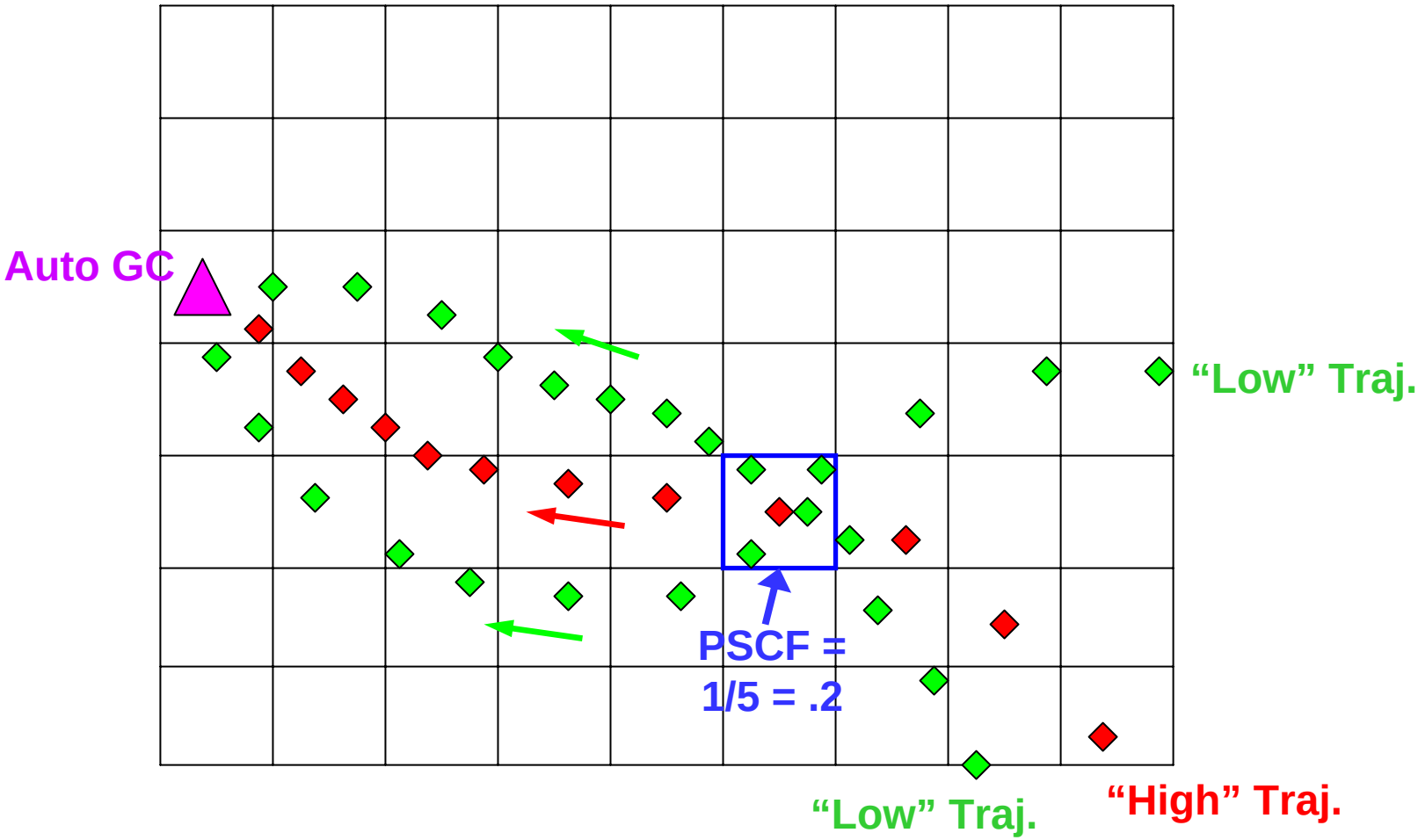
PSCF (Cont.)

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

- **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

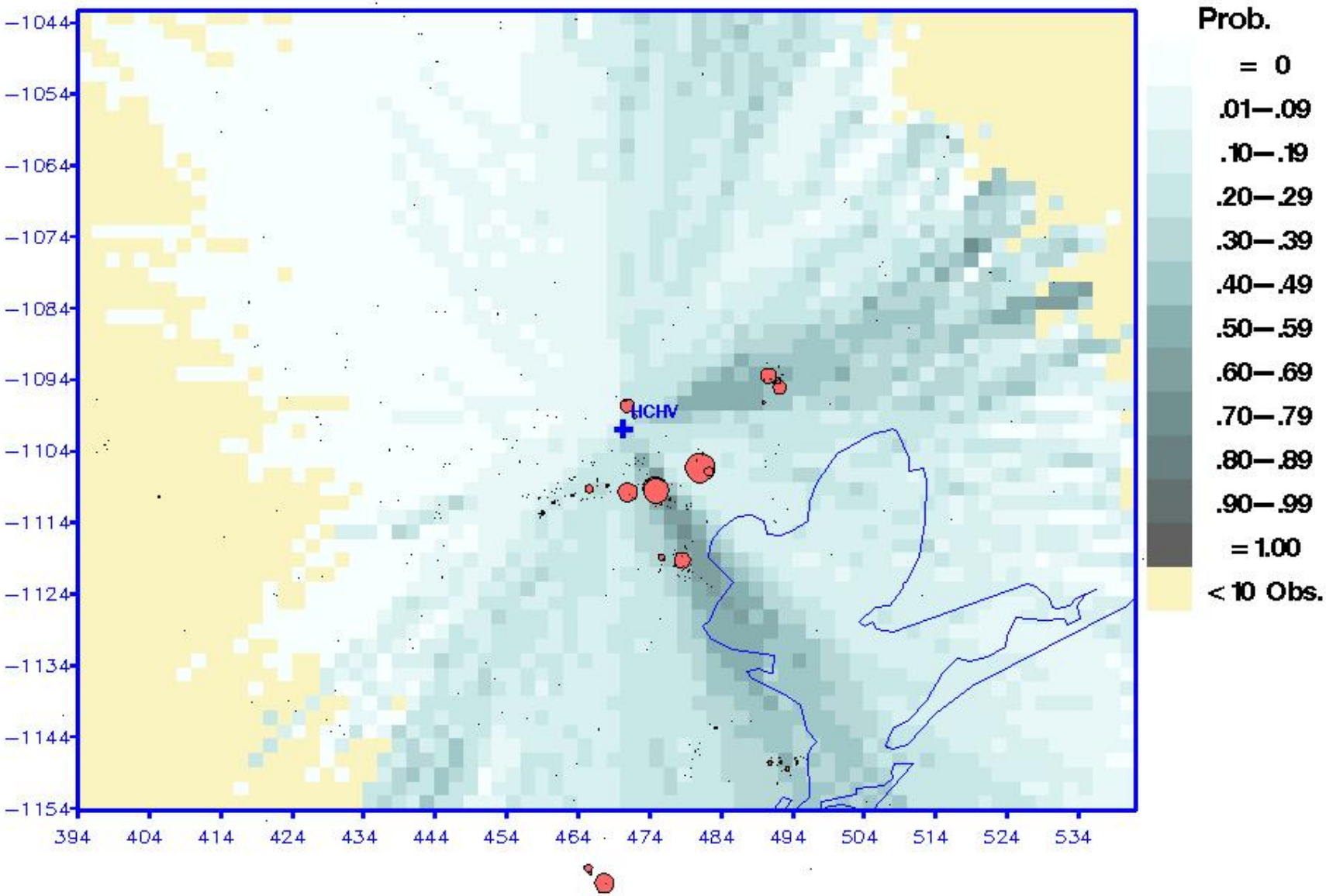


PSCF (Cont.)

- **The analysis shown in the following slide used data from 2005 and 2006, and only excluded "very curvy" trajectories (S < 0.8 or angle > 120°).**
  - **PSCF does not require "steady state" or "straight-line winds" assumptions as does the ISC analysis.**

Potential Source Contribution Function for Propene

Sites: HCHV, 2005/6 Data



PSCF Results

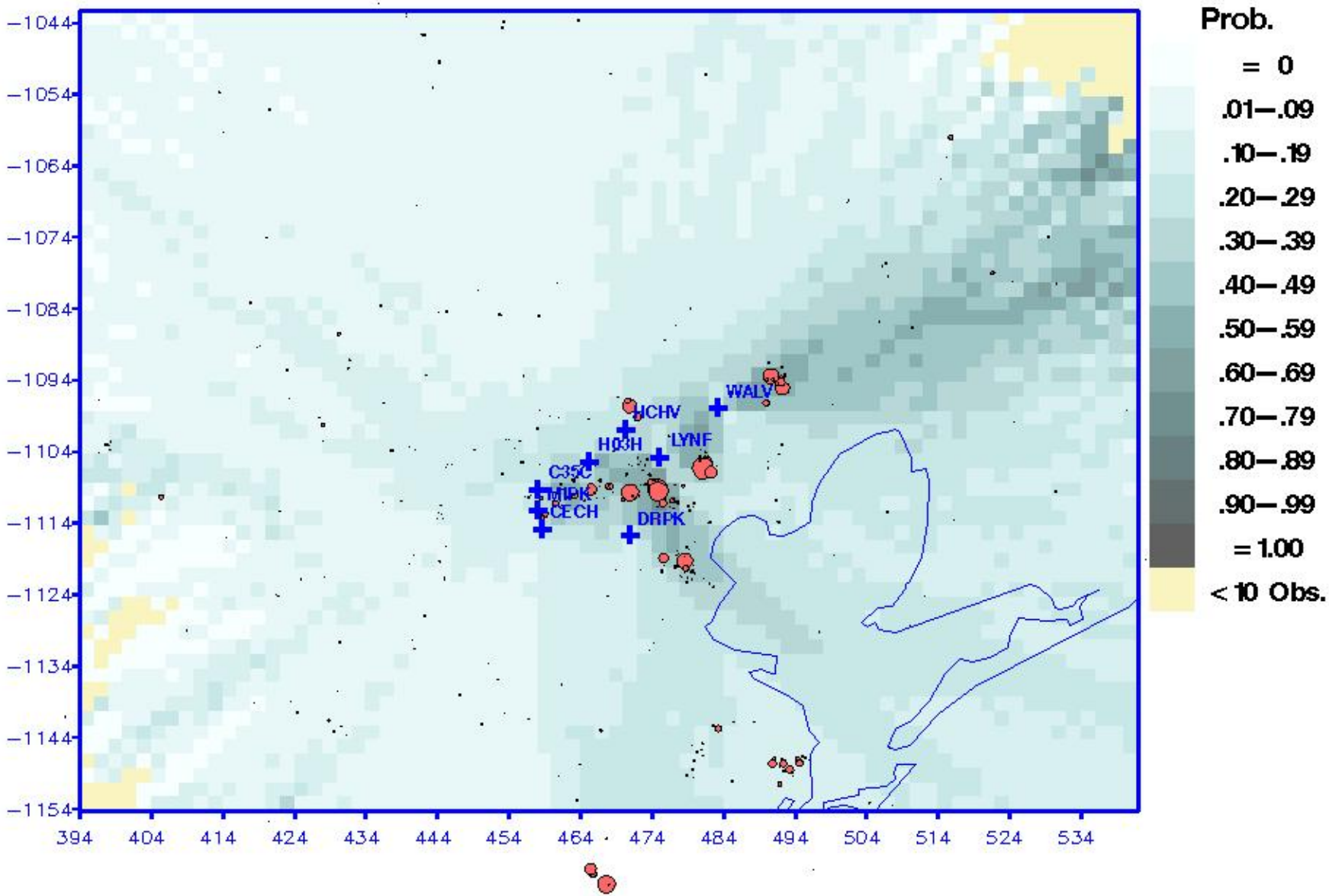
- **Analysis shows that when wind comes from E or SE, probability of seeing “high” propene concentrations is > 50%.**

- **Method points towards known sources, but also shows long “tails” beyond sources (artifact).**

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

Potential Source Contribution Function for Propene

Sites: C35C CECH DRPK H03H HCHV LYNF MIPK WALV, 2005/6 Data



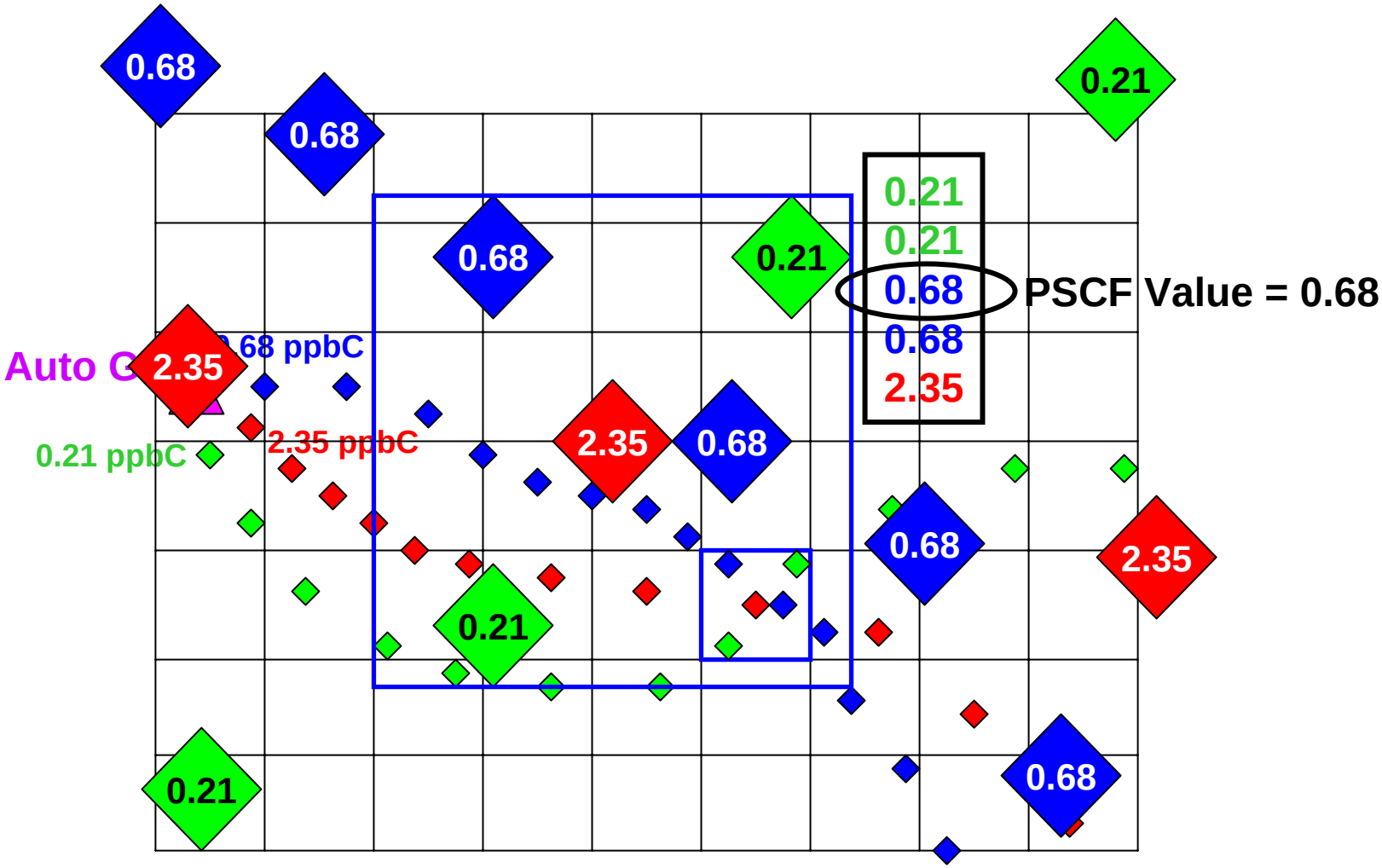
PSCF – Type 2

- **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 2005 "straight" trajectories used in the ISC analysis discussed earlier.**

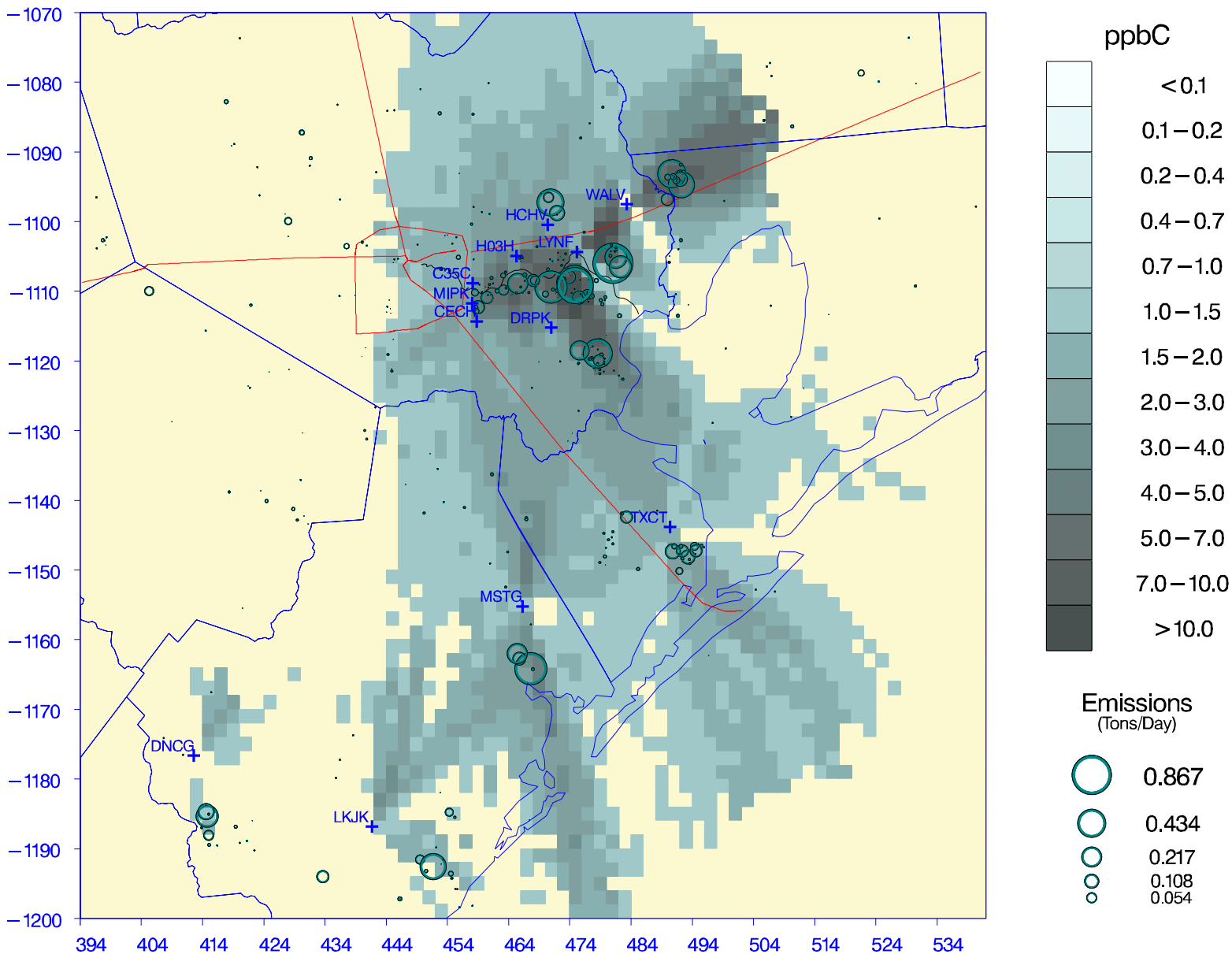
PSCF Type 2 Illustration



PSCF for Monitored Propene

Twelve HGB Area Sites

Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 1.0 ppbC



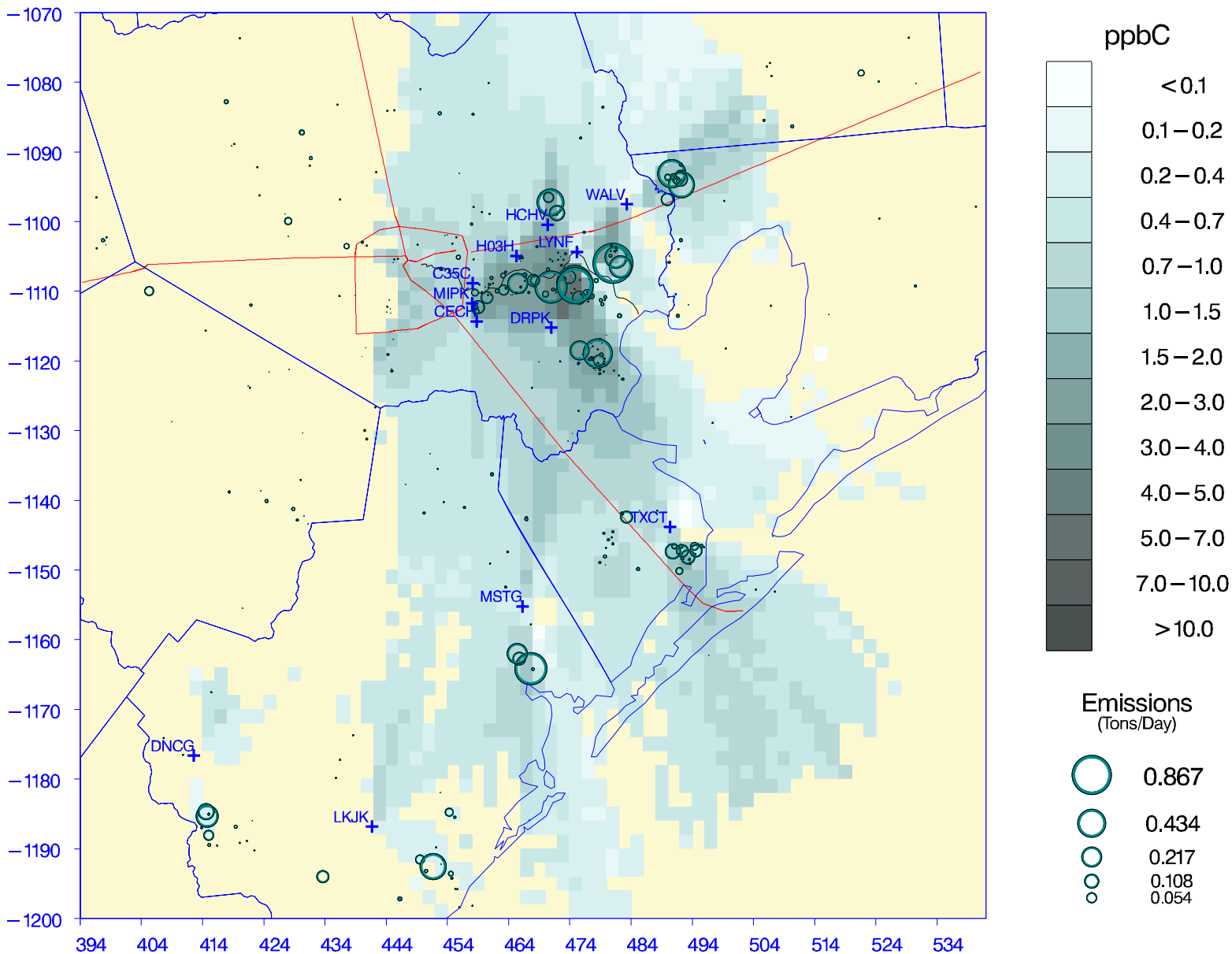
PSCF – Type 2 (Cont.)

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

PSCF for ISC Modeled Propene

Twelve HGB Area Sites

Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 1.0 ppbC



PSCF – Type 2 (Cont.)

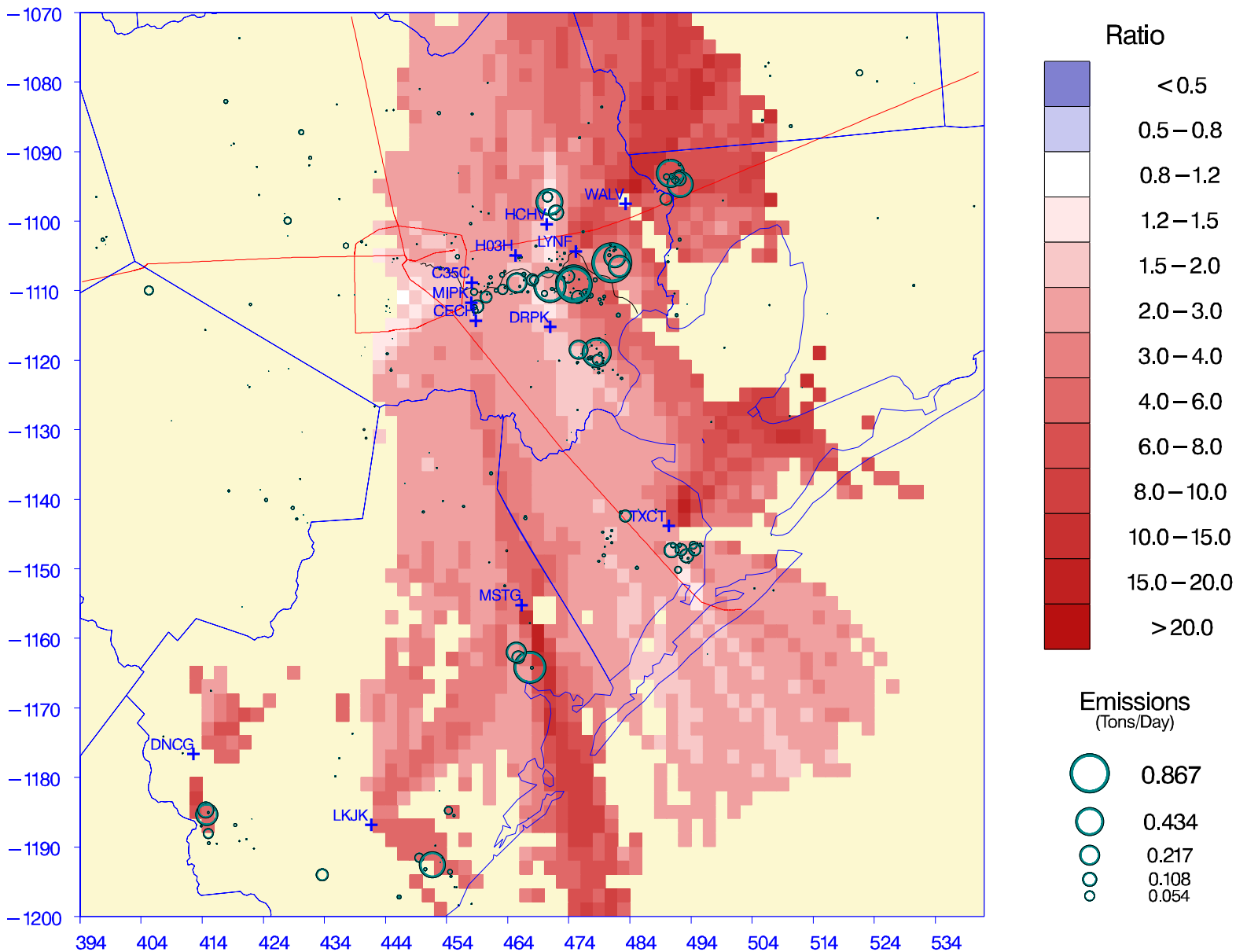
- **The monitored data generally shows higher median concentrations than ISC indicates would be expected, based on the reported emissions.**

- **Taking the ratio by grid cell of the monitor-based medians to the ISC-modeled medians provides an emission reconciliation factor (ERF) for each grid cell.**

PSCF Ratio (Mon/ISC) for Propene

Twelve HGB Area Sites

Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 1.0 ppbC



PSCF – Type 2 (Cont.)

- **Applying the ERF to the reported emissions by grid cell produces reconciled emissions which can be further analyzed.**

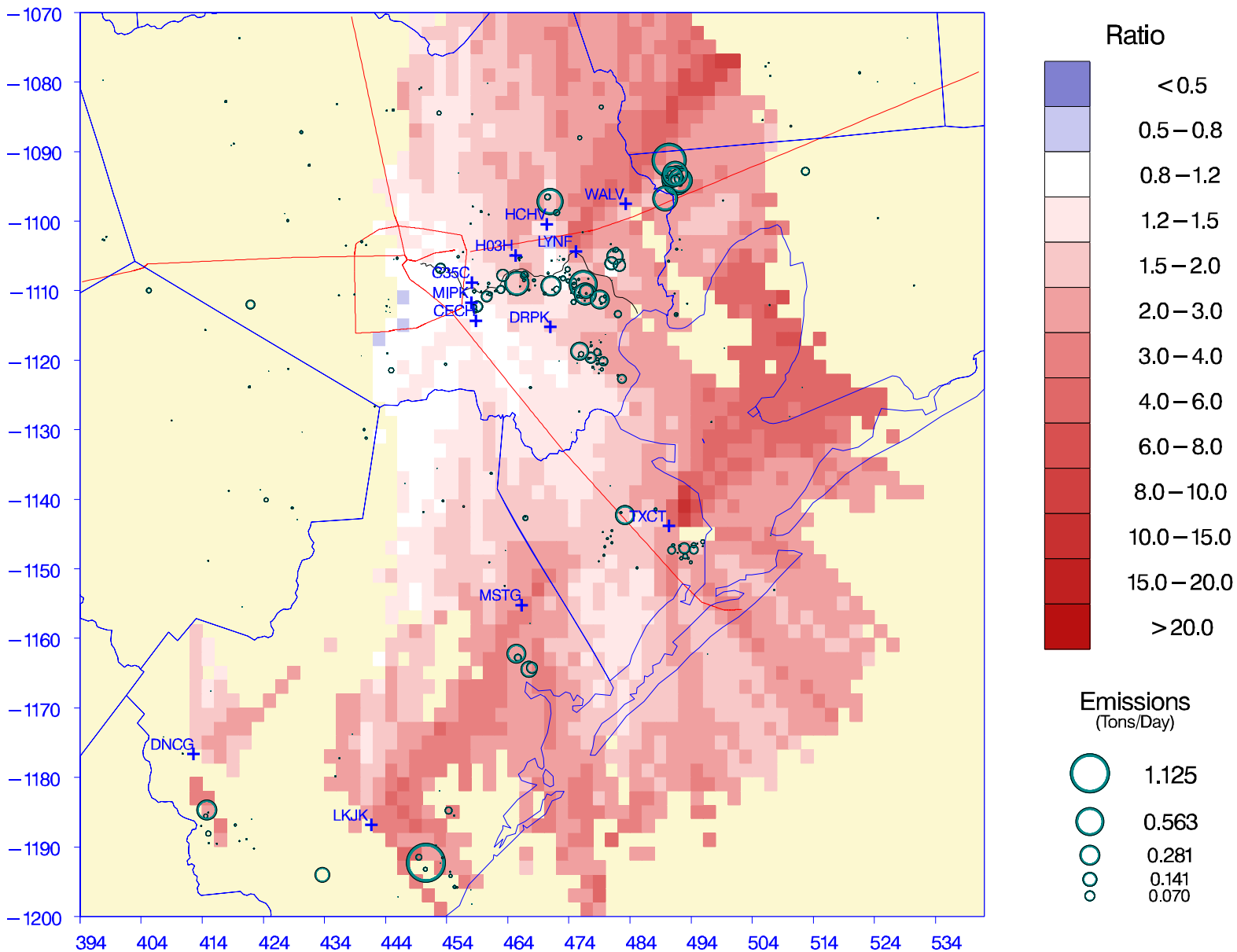
- **Summarized across the 8-County Area (and assuming all the reconciliation is due to point sources), propene emissions increase from 10.032 tpd to 36.765 tpd after reconciliation. The overall emission reconciliation factor is 3.665.**

- **Some more pollutants follow:**

PSCF Ratio (Mon/ISC) for Ethene

Twelve HGB Area Sites

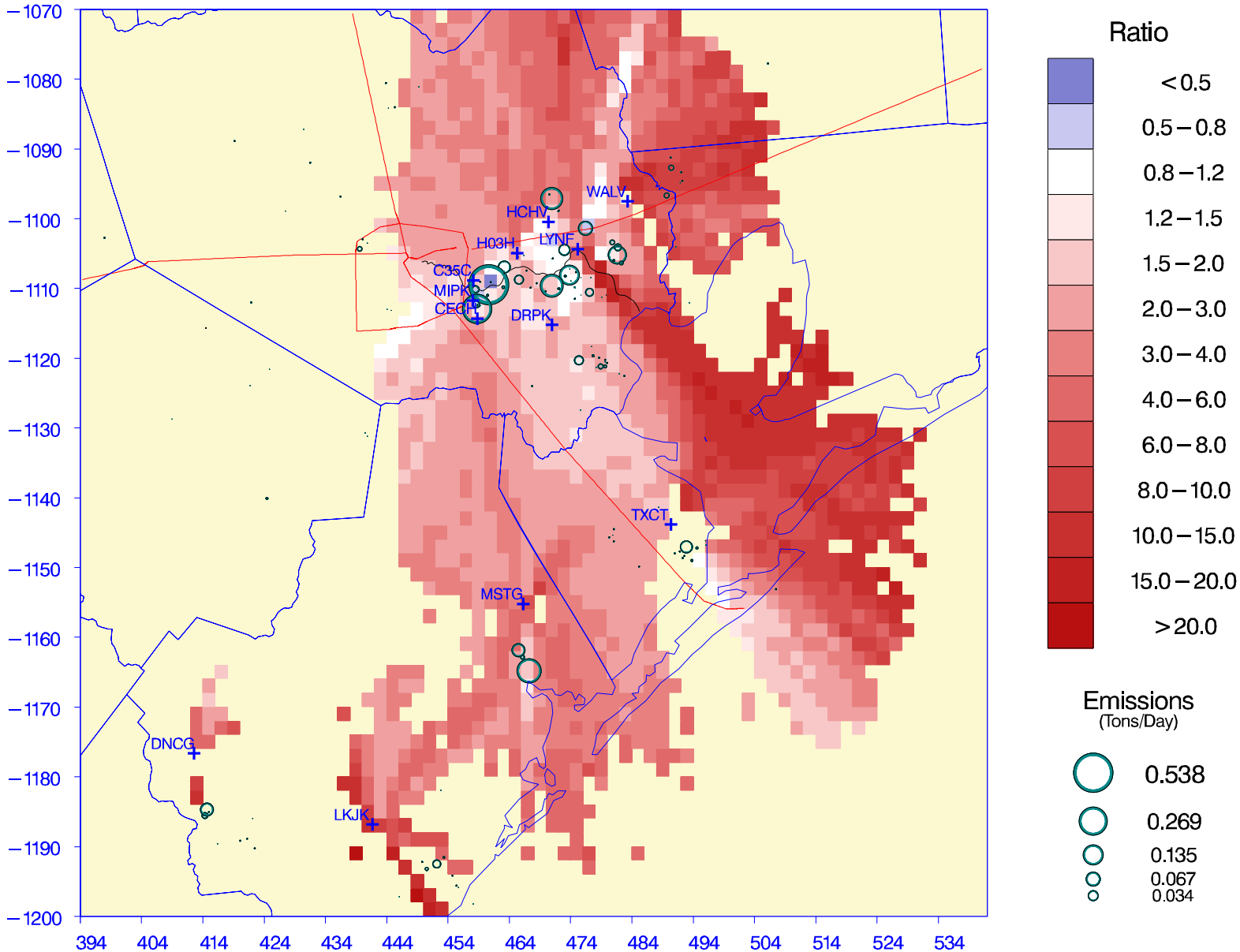
Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 1.0 ppbC



PSCF Ratio (Mon/ISC) for 1,3 – Butadiene

Twelve HGB Area Sites

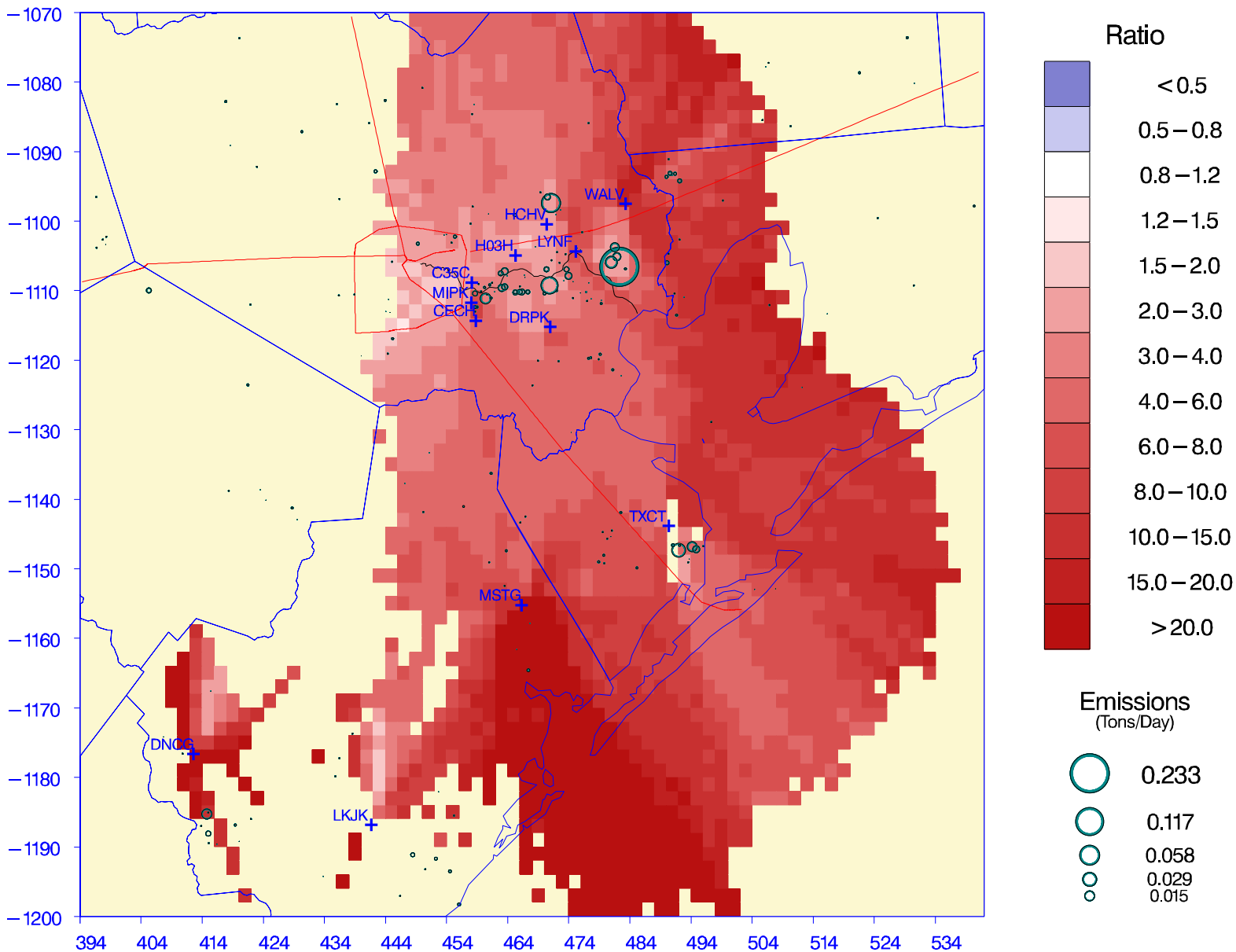
Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 0.2 ppbC



PSCF Ratio (Mon/ISC) for t−2−Butene

Twelve HGB Area Sites

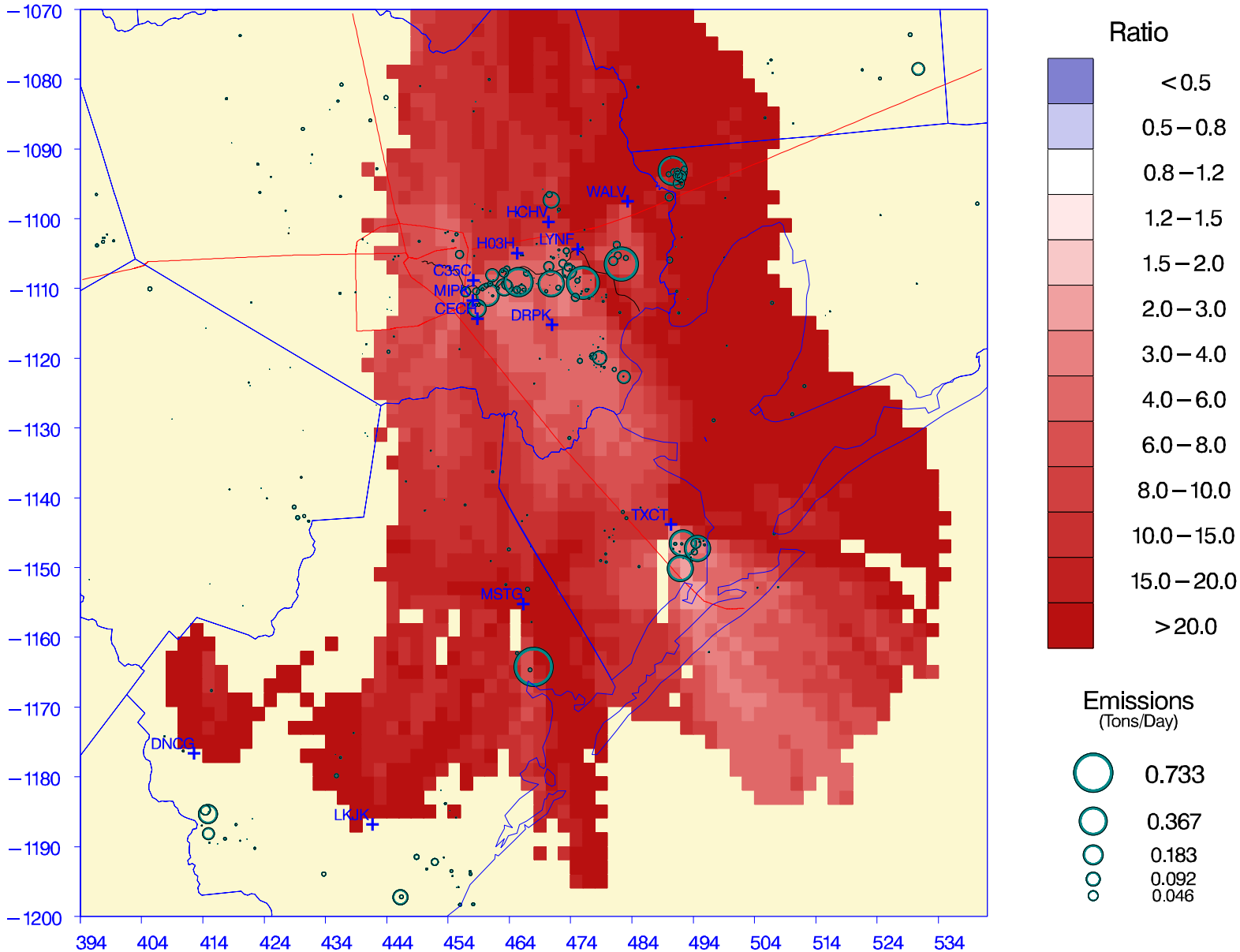
Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 0.2 ppbC



PSCF Ratio (Mon/ISC) for isoButane

Twelve HGB Area Sites

Cells with at least 300 Trajectory Points and Median Monitored Mixing Ratio > 2.0 ppbC



Reconciliation Summary

Pollutant	Reported Emissions (tpd)	Reconciled Emissions (tpd)	Ratio
Propene	10.032	36.765	3.665
Ethene	10.962	24.341	2.220
1,3-Butadiene	2.223	3.376	1.519
1-Butene	2.593	5.686	2.193
t-2-Butene	0.585	1.920	3.282
c-2-Butene	0.328	0.804	2.451
n-Butane	32.178	63.874	1.985
isoButane	6.965	48.683	7.321

Next Steps

- **Repeat ISC analysis for 2006.**
- **Run PSCF for 2006, calculate new ERFs.**
- **Create new (reconciled) base emissions for 2005 and 2006.**
- **Re-run ISC using reconciled emissions.**

Next Steps

- **Perform goodness-of-fit analysis: Which emissions best fit observed data when input to ISC?**
  - **Unreconciled (reported) emissions**
  - **Constant multiplier applied to all sources**
  - **Reconciled emissions, i.e. reported emissions multiplied by grid-cell specific reconciliation factors.**

- **Finally, run CAMx with reconciled emissions and test model performance vs. unreconciled emissions (target date mid-December).**

- **Update analysis when 2006 STARS data become available.**

Issues

- **No chemistry in ISC implies a high bias in the modeled concentrations. Discrepancies between ISC-Modeled and Measured concentrations are probably larger than shown in the table, especially for very reactive compounds.**

- **High background levels of some compounds could cause ISC to be biased low, especially for less-reactive compounds.**

- **For now, reconciliation is applied only to point sources, but area & mobile sources may contribute to observed discrepancies.**

Issues (Cont.)

- **Routine inventory data does not include hour-to-hour variability for point sources.**

- **Limiting analyses to straight trajectories may cause unanticipated biases.**