Reconciling Reported HRVOC Emissions with Ambient Measurements, Update

Jim Smith
Southeast Texas Photochemical Modeling Technical Committee
August 19, 2009
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

<table>
<thead>
<tr>
<th>Case</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>Day-specific emissions; replicate what actually happened</td>
</tr>
<tr>
<td>Baseline Case</td>
<td>Typical emissions; used in RRF to predict future design values</td>
</tr>
<tr>
<td>Future Base Case</td>
<td>Apply future growth + on-the-books controls to estimate future ozone</td>
</tr>
<tr>
<td>Control Strategy Testing</td>
<td>Determine control strategies that will effectively reduce ozone</td>
</tr>
<tr>
<td>SIP</td>
<td>Document modeling procedures</td>
</tr>
</tbody>
</table>
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 $\geq 0.95$. 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 $\leq 15^\circ$ 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.
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

Auto GC

“Not High” Traj.

PSCF = 1/5 = .2

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

Air Quality Division  •  Emission Reconciliation  •  J. Smith: August 19, 2009  •  Page 16
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 Value = 0.68

Auto GC

0.68 ppbC
0.68 ppbC
2.35 ppbC
0.21 ppbC

0.21
0.68
2.35
0.68
2.35
0.68
0.68
0.68
2.35
0.21
2.35
0.21
0.68
0.21
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

ppbC

<0.1
0.1–0.2
0.2–0.4
0.4–0.7
0.7–1.0
1.0–1.5
1.5–2.0
2.0–3.0
3.0–4.0
4.0–5.0
5.0–7.0
7.0–10.0
>10.0

Emissions (Tons/Day)

0.867
0.434
0.217
0.108
0.054
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

ppbC

<0.1
0.1 – 0.2
0.2 – 0.4
0.4 – 0.7
0.7 – 1.0
1.0 – 1.5
1.5 – 2.0
2.0 – 3.0
3.0 – 4.0
4.0 – 5.0
5.0 – 7.0
7.0 – 10.0
>10.0

Emissions (Tons/Day)

0.867
0.434
0.217
0.108
0.054
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, WDMMax 15, 2 Km Grid, Iteration 1
Cells with at least 100 Trajectory Points, Unreconciled Area Sources

ppbC

- <0.1
- 0.1 – 0.2
- 0.2 – 0.4
- 0.4 – 0.7
- 0.7 – 1.0
- 1.0 – 1.5
- 1.5 – 2.0
- 2.0 – 3.0
- 3.0 – 4.0
- 4.0 – 5.0
- 5.0 – 7.0
- 7.0 – 10.0
- >10.0

Emissions (Tons/Day)

- 0.867
- 0.434
- 0.217
- 0.108
- 0.034
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.
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.
## Emission Reconciliation Summary

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Propene</td>
<td>10.03</td>
<td>25.07</td>
<td>149.8%</td>
<td>9.65</td>
<td>21.92</td>
<td>127.1%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>10.96</td>
<td>18.72</td>
<td>70.8%</td>
<td>10.10</td>
<td>15.80</td>
<td>56.4%</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>2.22</td>
<td>3.02</td>
<td>35.7%</td>
<td>1.53</td>
<td>1.97</td>
<td>28.3%</td>
</tr>
<tr>
<td>1-Butene</td>
<td>2.59</td>
<td>3.96</td>
<td>52.8%</td>
<td>2.70</td>
<td>3.13</td>
<td>16.2%</td>
</tr>
<tr>
<td>t-2-Butene</td>
<td>0.58</td>
<td>1.38</td>
<td>135.4%</td>
<td>0.50</td>
<td>1.55</td>
<td>210.9%</td>
</tr>
<tr>
<td>c-2-Butene</td>
<td>0.33</td>
<td>0.74</td>
<td>126.8%</td>
<td>0.54</td>
<td>0.86</td>
<td>58.1%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>26.72</strong></td>
<td><strong>52.89</strong></td>
<td><strong>97.9%</strong></td>
<td><strong>25.02</strong></td>
<td><strong>45.23</strong></td>
<td><strong>80.7%</strong></td>
</tr>
</tbody>
</table>
CAMx HRVOC Model Performance - Wallisville

Unreconciled Emissions

June, 2005

AQS-1

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 31
CAMx HRVOC Model Performance - Wallisville

Reconciled Emissions

June, 2005

AQS-1

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 32
CAMx HRVOC Model Performance - Wallisville

10X Flare HRVOC Sensitivity

June, 2005 AQS-1

ETH Concentrations (ppb)  
OLE Concentrations (ppb)  
IOLE Concentrations (ppb)

June, 2005

AQS-1

ETH Concentrations (ppb)  
OLE Concentrations (ppb)  
IOLE Concentrations (ppb)
CAMx HRVOC Model Performance – Deer Park

Unreconciled Emissions

June, 2005

Unreconciled Emissions

AQS-1

Air Quality Division  •  Emission Reconciliation  •  J. Smith: August 19, 2009  •  Page 34
CAMx HRVOC Model Performance – Deer Park

Reconciled Emissions

**ETH Concentrations (ppb)**

**OLE Concentrations (ppb)**

**IOLE Concentrations (ppb)**

---

June, 2005

AQS-1
CAMx HRVOC Model Performance – Lynchburg Ferry

Unreconciled Emissions

June, 2005

ETH Concentrations (ppb)

OLE Concentrations (ppb)

IOLE Concentrations (ppb)

AQS-1

ETH

OLE

IOLE
CAMx HRVOC Model Performance – Lynchburg Ferry

10X Flare HRVOC Sensitivity

June, 2005

AQS-1

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 39
CAMx HRVOC Model Performance – NOAA P3
All Flights August 31 – October 12, 2006,
HG 2-Km Subgrid

Unreconciled Emissions

ETH

Modeled vs. P3 Observed ETH Mixing Ratios
Reg10_No_PSCF

OLE

Modeled vs. P3 Observed OLE Mixing Ratios
Reg10_No_PSCF

IOLE

Modeled vs. P3 Observed IOLE Mixing Ratios
Reg10_No_PSCF
CAMx HRVOC Model Performance – NOAA P3
All Flights August 31 – October 12, 2006,
HG 2-Km Subgrid

Reconciled Emissions

**ETH**

Modeled vs. P3 Observed ETH Mixing Ratios
Reg10

**OLE**

Modeled vs. P3 Observed OLE Mixing Ratios
Reg10

**IOLE**

Modeled vs. P3 Observed IOLE Mixing Ratios
Reg10
CAMx HRVOC Model Performance – NOAA P3
All Flights Aug. 31 – Oct. 12, 2006,
HG 2-Km Subgrid

10X Flare HRVOC Sensitivity

ETH

Modeled vs. P3 Observed ETH Mixing Ratios
Reg10_FlareHRVOC10X

OLE

Modeled vs. P3 Observed OLE Mixing Ratios
Reg10_FlareHRVOC10X

IOLE

Modeled vs. P3 Observed IOLE Mixing Ratios
Reg10_FlareHRVOC10X
CAMx Formaldehyde Model Performance

Unreconciled Emissions

Moody Tower, AQS-1  Lynchburg Ferry, AQS-1  NOAA P3

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 43
CAMx Formaldehyde Model Performance

Reconciled Emissions

Moody Tower, AQS-1  Lynchburg Ferry, AQS-1  NOAA P3
CAMx Formaldehyde Model Performance

10X Flare HRVOC Sensitivity

Moody Tower, AQS-1  |  Lynchburg Ferry, AQS-1  |  NOAA P3

Modeled vs. P3 Observed FORM Mixing Ratios
Reg10_FlareHRVOC10X
CAMx Formaldehyde Model Performance

Formaldehyde Concentration (ppb) at Layer 2 (20060815-20060914)

Unreconciled vs. Reconciled

Reconciled vs. 10X Flare HRVOC

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 46
CAMx Ozone Model Performance

Reconciled Emissions

June, 2005

AQS-1

Bayland Park

Deer Park

Wallisville

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 48
CAMx Ozone Model Performance

10X Flare HRVOC Sensitivity

June, 2005 AQS-1

Bayland Park

Deer Park

Wallisville

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 49
CAMx Ozone Model Performance

Unreconciled Emissions

Modeled vs. Observed: Hourly Values (20060815-20060814)

O3 Concentrations (ppb)

Moody Tower, AQS-1

Modeled vs. P3 Observed O3 Mixing Ratios

Reg10_No_PSCF

NOAA P3

Air Quality Division  •  Emission Reconciliation  •  J. Smith: August 19, 2009  •  Page 50
CAMx Ozone Model Performance

Reconciled Emissions

Modeled vs Observed: Hourly Values (20060815-20060914)
camx15l_0805_hgbh2_bc06cc01_reg10sl_200608ep1_eoa_oemis_biodata neutrality_newvocfeu_greil_hg1hpa_01:

O3 Concentrations (ppb)

Moody Tower, AQS-1

Modeled vs. P3 Observed O3 Mixing Ratios
Reg10

NOAA P3

Air Quality Division  •  Emission Reconciliation  •  J. Smith: August 19, 2009  •  Page 51
CAMx Ozone Model Performance

10X Flare HRVOC Sensitivity

Modeled vs Observed: Hourly Values (20060615-20060614)

Moody Tower, AQS-1

NOAA P3

Air Quality Division • Emission Reconciliation • J. Smith: August 19, 2009 • Page 52
CAMx Ozone Model Performance Summary

Episode Mean 1-Hour Ozone Relative Bias
Reg 10 Base Case With and Without PSCF-Based Emission Reconciliation

Episode Mean 1-Hour Ozone Relative Error
Reg 10 Base Case With and Without PSCF-Based Emission Reconciliation

Episode Mean 1-Hour Unpaired Peak
Modeled and Observed \( \text{O}_3 \)
Reg 10 Base Case With and Without PSCF-Based Emission Reconciliation

Episode Mean 8-Hour Unpaired Peak
Modeled and Observed \( \text{O}_3 \)
Reg 10 Base Case With and Without PSCF-Based Emission Reconciliation
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