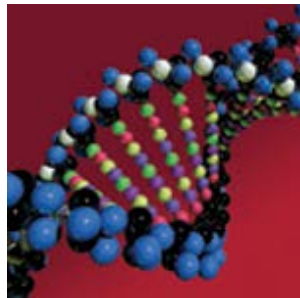


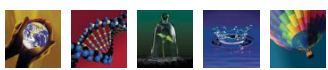
# Oil and Gas Source Contributions to Denver/North Front Range Ozone and VOC using CAMx/OSAT and CMB/PMF



Ralph Morris, Edward Tai and Tim Sturtz  
ENVIRON International Corporation  
Novato, California

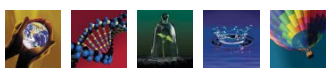
Western Met, EI and AQ Modeling Workshop  
Boulder, Colorado

June 21, 2011



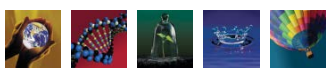
# Background

- 2008 Denver ozone State Implementation Plan (SIP) used a June-July 2006 photochemical modeling database to demonstrate attainment of the 1997 8-hour ozone NAAQS (0.08 ppm) by 2010
- During June-July 2006, CDPHE/APCD collected VOC measurements on several days
  - Evaluation of the CAMx photochemical grid model using the VOC measurements found that it underestimated the observed VOC concentrations



# Background

- Post 2008 Denver ozone SIP, RAQC performed two studies:
  - Phase I: 2015/2020 Ozone Projections
    - For comparison with current (0.075 ppm) and potential new (0.060-0.070 ppm) ozone NAAQS
  - Phase II: Investigate Ways to Improve Model Performance
- As part of the Phase II Model Improvements the VOC measurements and modeling results were analyzed to determine whether we could identify any shortfalls in the VOC emissions inventory



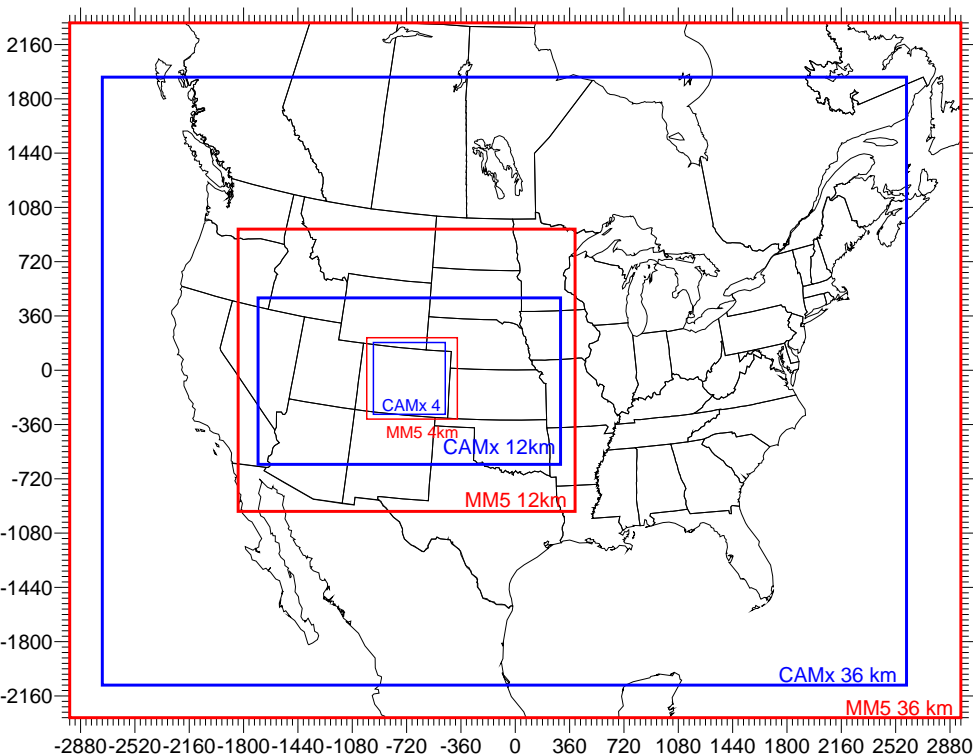
# Outline of O&G Ozone/VOC Contribution

- VOC model performance evaluation
- Meteorological analysis on high and low observed VOC days
- Modeled ozone sensitivity to oil and gas (O&G) VOC emissions
- Receptor Modeling VOC Source Apportionment
  - Chemical Mass Balance (CMB)
  - Positive Matrix Factorization (PMF)
- Deterministic Source-Oriented PGM VOC Source Apportionment Modeling
  - Comparison with Receptor Modeling VOC Source Apportionment modeling



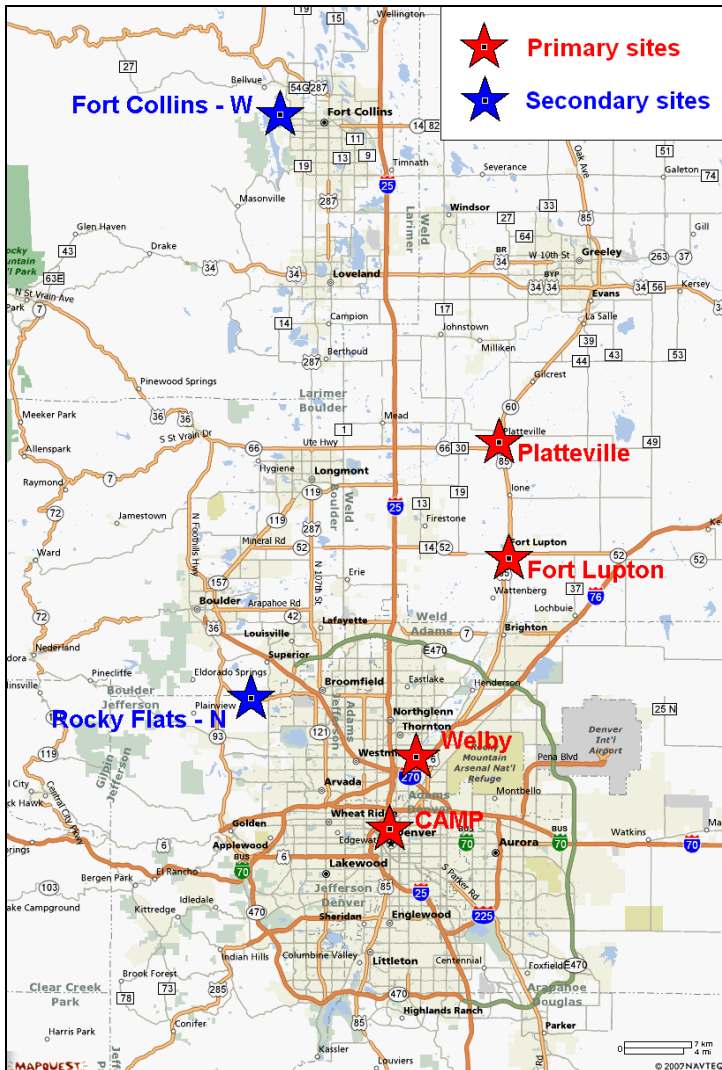
# MM5/SMOKE/CAMx Modeling System

- 2008 Denver Ozone SIP
- 36/12/4 km domains



- June-July 2006
- 36 km CONUS domain
  - Used to generate BCs for 12 km domain
  - 36 km BCs from GEOS-Chem global chemistry model
- CAMx 12/4 km domains run with two-way grid nesting
  - Sensitivity, Source Apportionment and Control Strategy runs on 12/4 km domains
- 2006 Base Case
- 2010 Base Case
- 2010 Source Apportionment
- 2010 Control Strategy

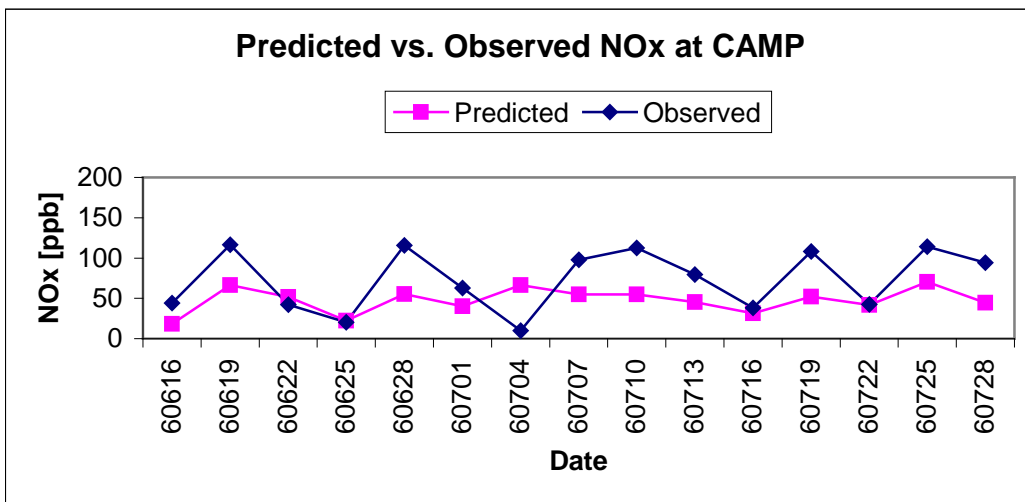
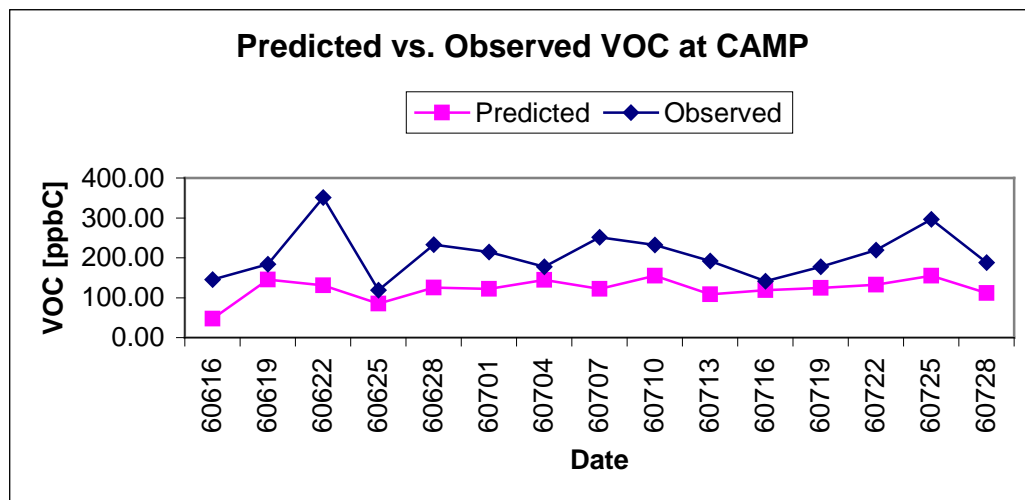
# VOC Model Performance Evaluation



- Morning samples at CAMP and Welby Denver Sites
  - Represents on-road mobile sources
- Morning samples at Fort Lupton and Platteville Weld Co. sites
  - Represents O&G sources
- Converted VOC species to CB05 species to be consistent with CAMx. Dropped EtOH and MeOH CB05 species as not sampled.
  - VOC comparisons are actually sum of CB05 VOC species including ethane but without EtOH and MeOH (more like TNMOG than VOC)



# VOC and NO<sub>x</sub> Model Performance at CAMP

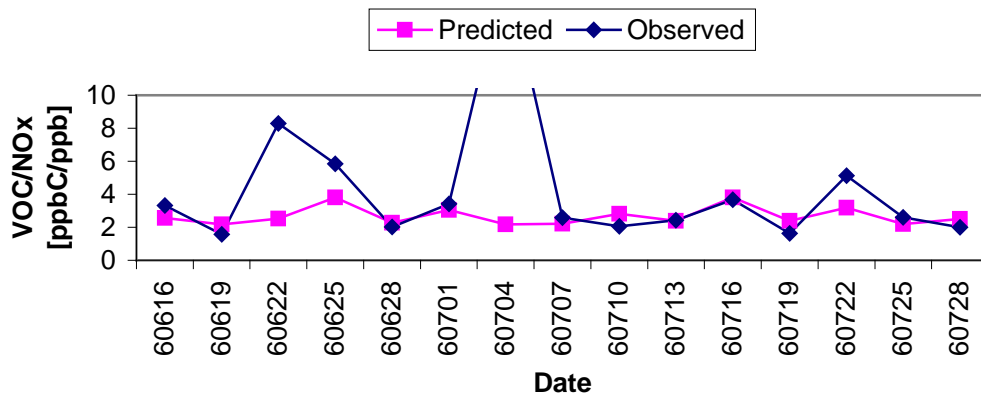


- Morning 5-8am MST VOC and NO<sub>x</sub> comparisons
- VOC and NO<sub>x</sub> underestimated by approximately a factor of 2 on average with some exceptions
- July 4 very low NO<sub>x</sub>
- CAMP monitor by roadway (Broadway) so underestimation expected since model is 4 km x 4 km x 36 m grid cell volume average

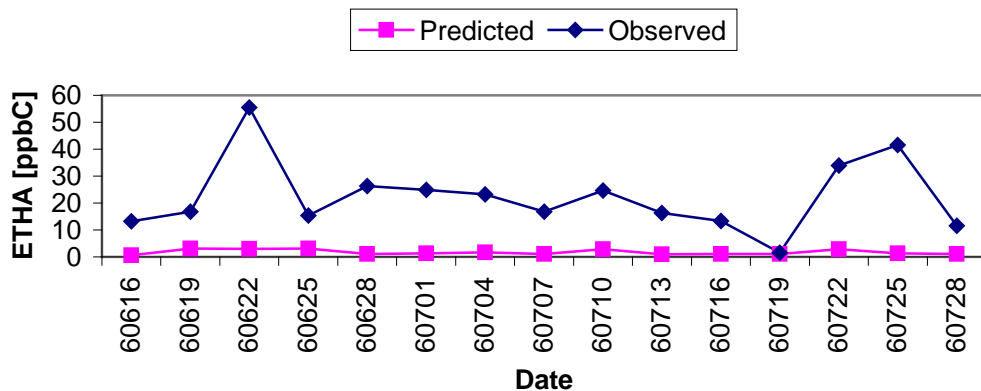


# VOC/NO<sub>x</sub> ratios and Ethane at CAMP

Predicted vs. Observed VOC/NO<sub>x</sub> Ratio at CAMP



Predicted vs. Observed ETHA at CAMP

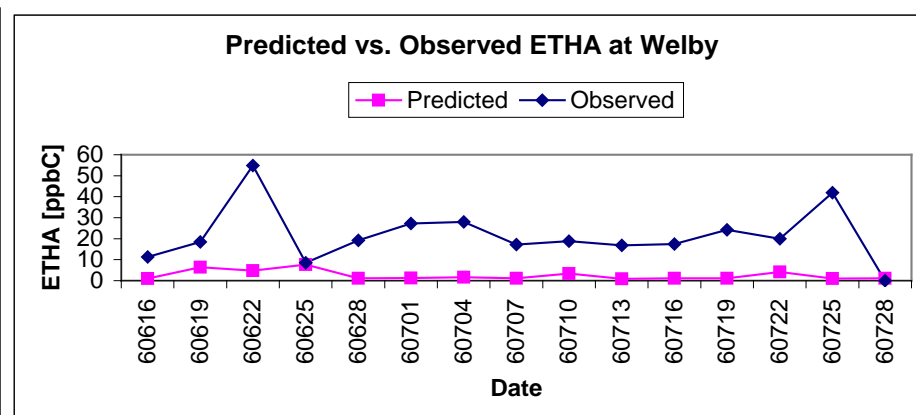
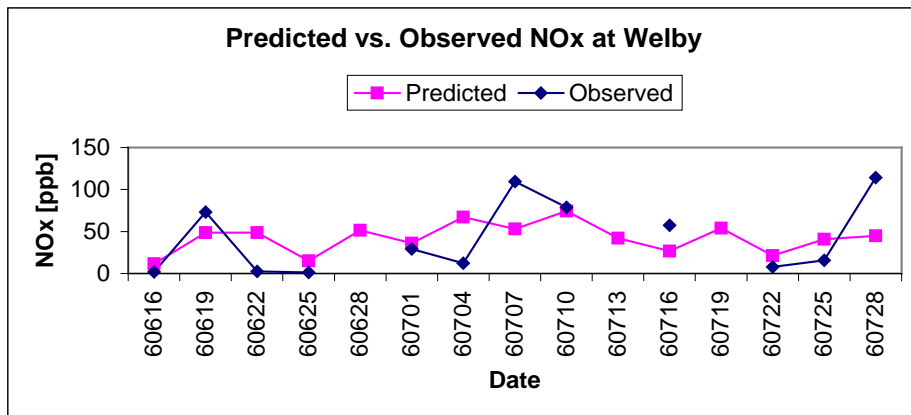
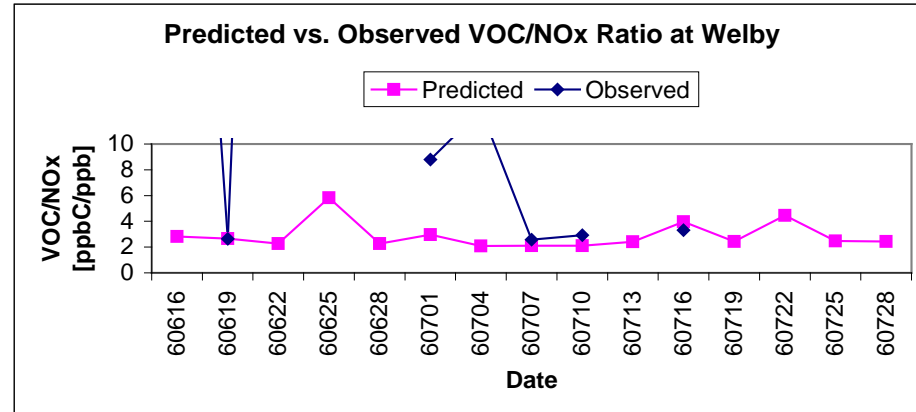
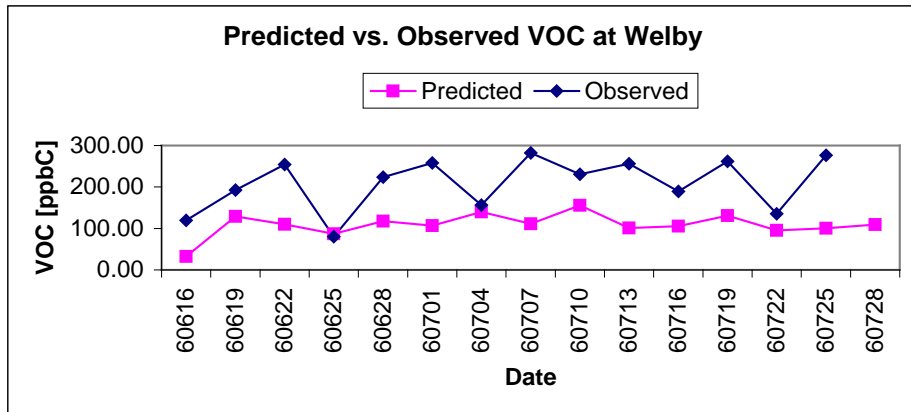


- VOC and NO<sub>x</sub> both emitted by mobile sources so share dispersion
- VOC/NO<sub>x</sub> ratio comparisons better metric for evaluating inventory
- Very good agreement between predicted and observed VOC/NO<sub>x</sub> ratios on most days
- Ethane greatly underestimated





# VOC Performance at Welby

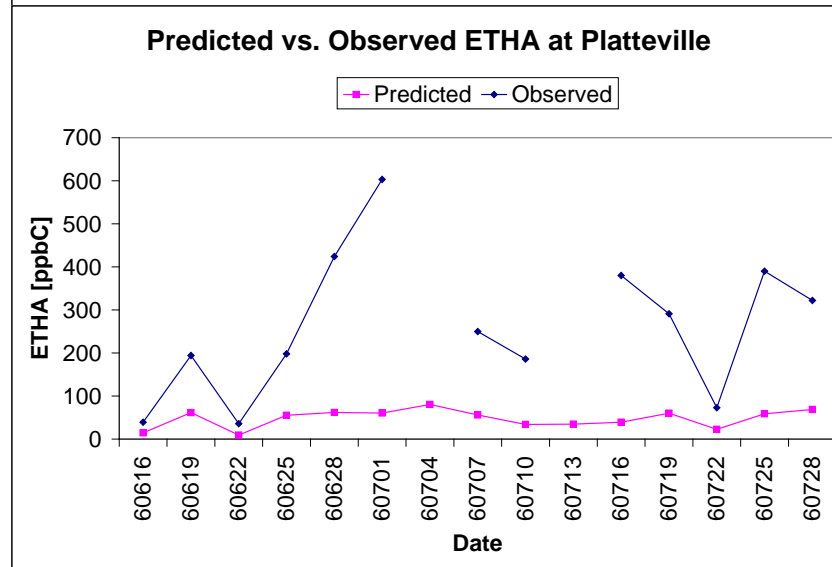
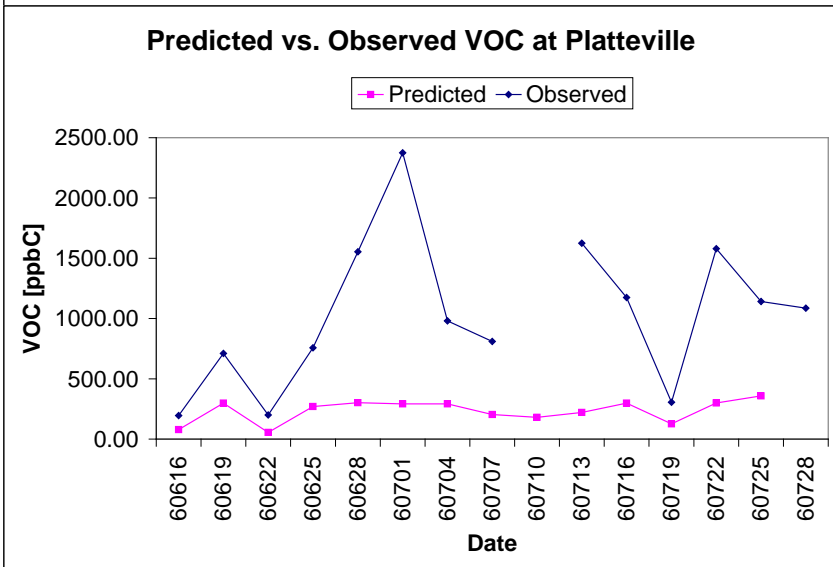
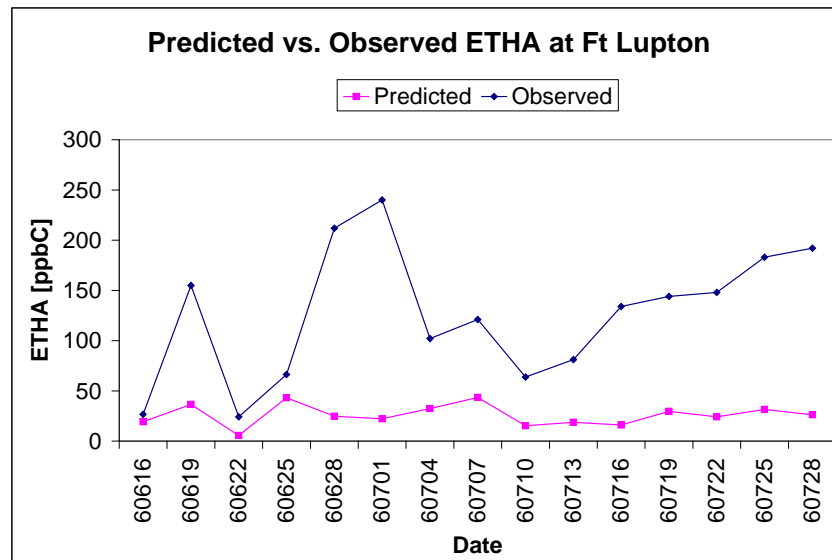
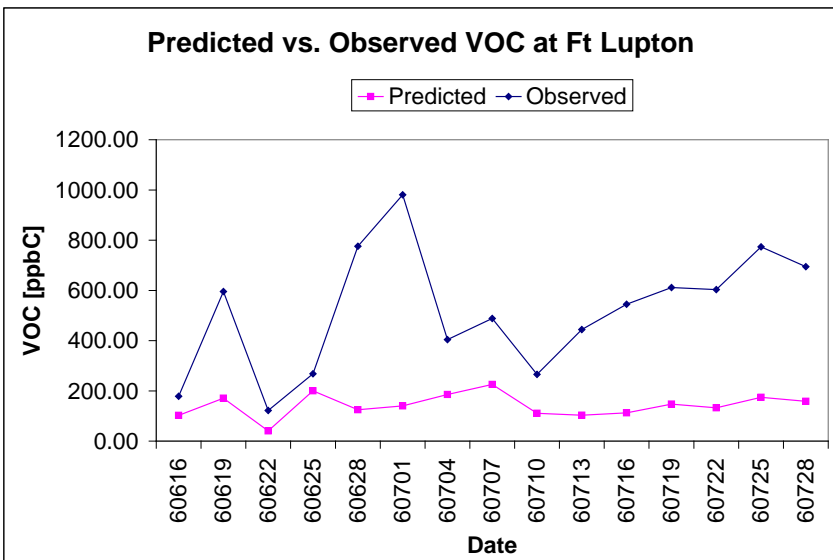


- More variability at Welby than CAMP, VOC underestimated
- Very low NO<sub>x</sub> on some days, missing on others
- VOC/NO<sub>x</sub> good agreement for four days



# VOC and Ethane Underestimated at Weld Co Sites

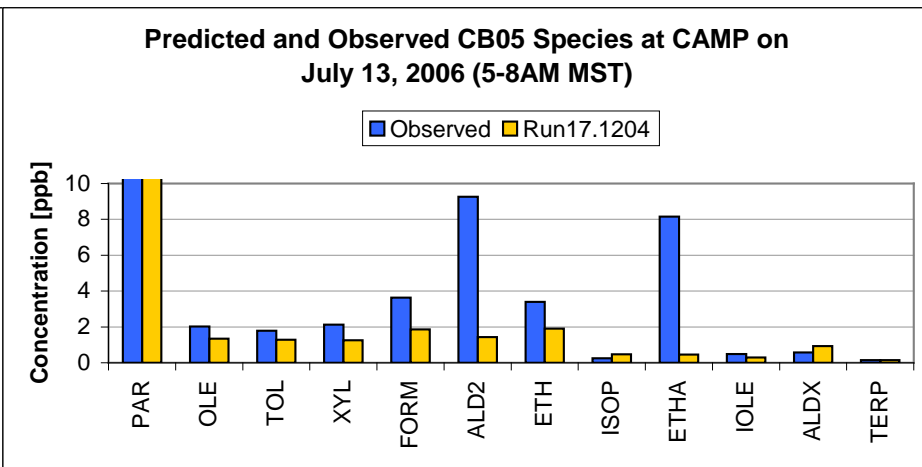
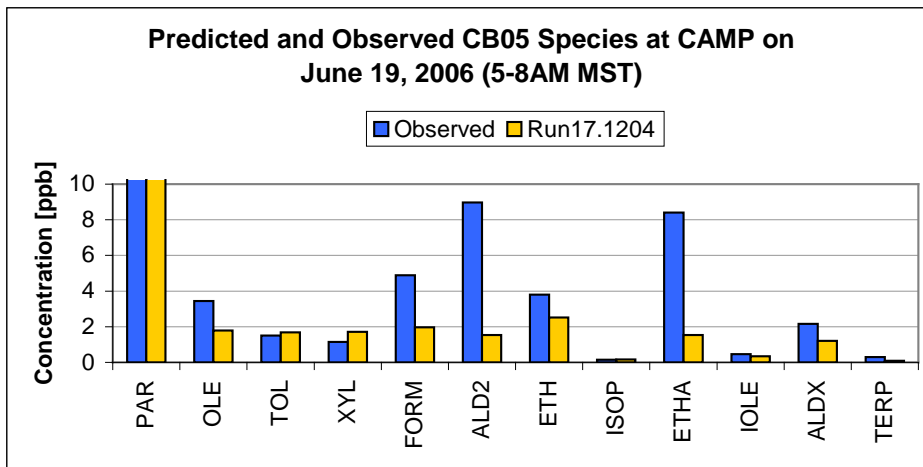
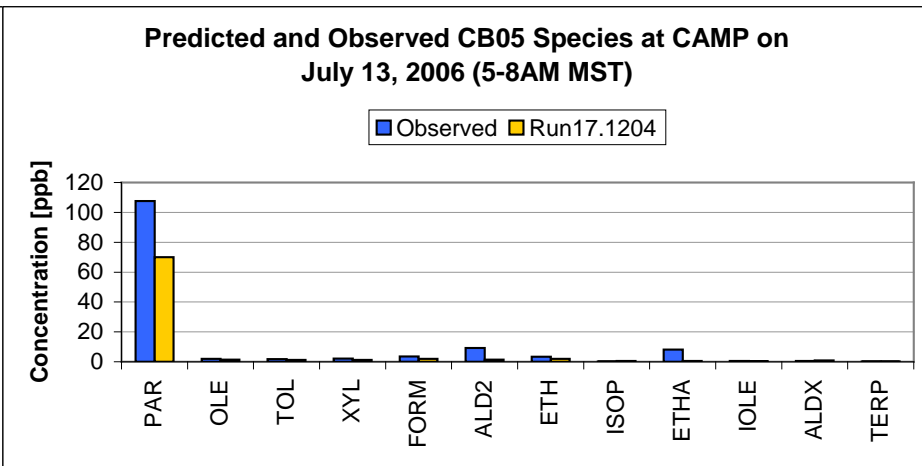
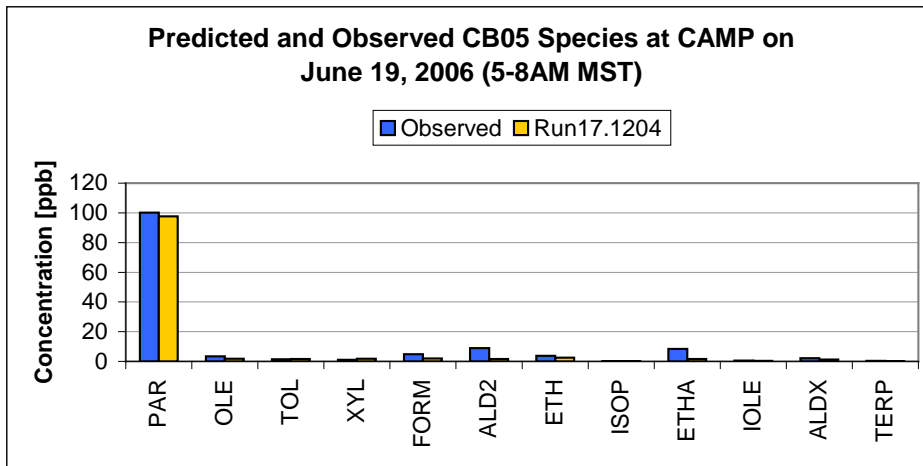
No NO<sub>x</sub> measurements





# Example Speciated VOC Comparisons

CAMP w/ PAR (top) w/o PAR (bottom)



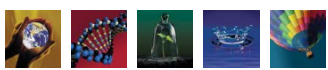
Similar underestimate in Weld County only PAR and Ethane underestimation even greater



# Weld County PAR and Ethane Underestimate

- Observed PAR 2-5 times greater than predicted
- Observed Ethane ~5 times greater than predicted

Site	Date	Observed (ppbC)	Predicted (ppbC)	Difference (ppbC)	Difference (%)
<b>PAR</b>					
Ft. Lupton	June 19	403	119	284	-70%
Ft. Lupton	July 13	321	67	254	-79%
Ft. Lupton	July 28	455	105	350	-77%
Platteville	June 19	484	224	260	-54%
Platteville	July 28	779	267	512	-66%
<b>ETHA</b>					
Ft. Lupton	June 19	88	18	70	-80%
Ft. Lupton	July 13	41	9	32	-77%
Ft. Lupton	July 28	96	13	83	-77%
Platteville	June 19	97	31	66	-68%
Platteville	July 28	161	34	127	-79%



# Conclusions VOC Model Evaluation

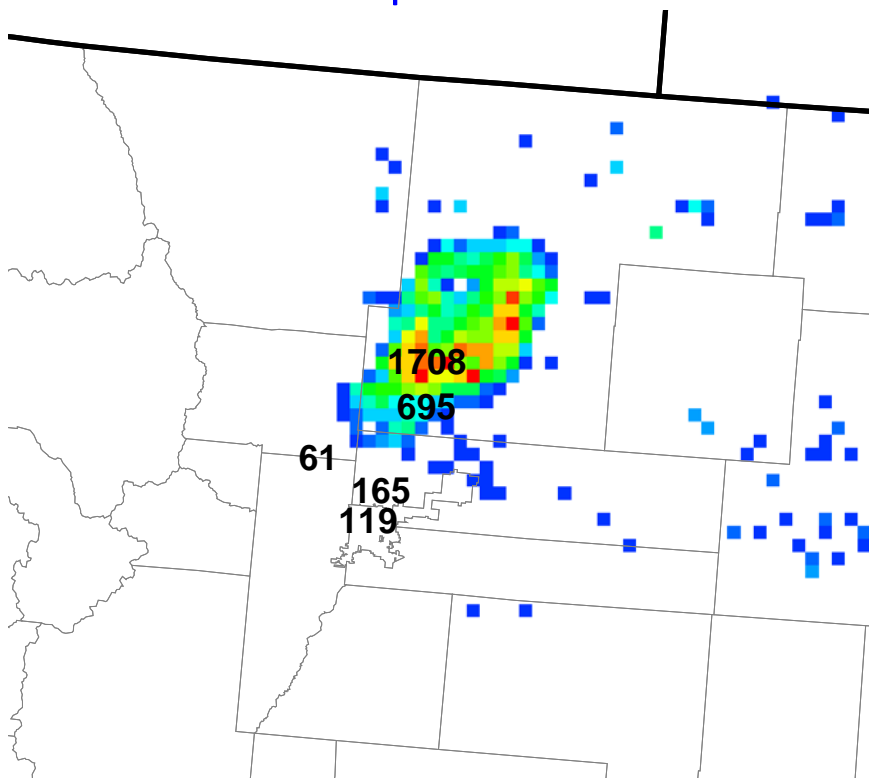
- Model underestimates VOC
  - For some VOC species underestimation is greater (e.g., ethane and acetaldehyde)
- Modeled 4 km x 4 km x 36 m volume average versus surface point measure confounds analysis
  - Underestimation expected at CAMP roadside monitor
  - Also expected because dealing with surface emissions under morning non-uniform mixing conditions
- Good VOC/NO<sub>x</sub> ratio comparison at CAMP suggest mobile source VOC may be about right (assuming mobile NO<sub>x</sub> is correct)
- Large underestimation of PAR and Ethane at Weld County suggests O&G VOC emissions may be underrepresented
  - Again, volume average predictions vs. surface point measurements precludes making a definitive statement in this regard
- Differences in VOC species fractions for some species
  - More aromatics (TOL & XYL) in model than observed
  - More higher aldehydes and biogenic species in model than observed
  - Less ethane in model, especially in Denver (missing ethane emissions?)



# Meteorological Analysis of High & Low VOC Days

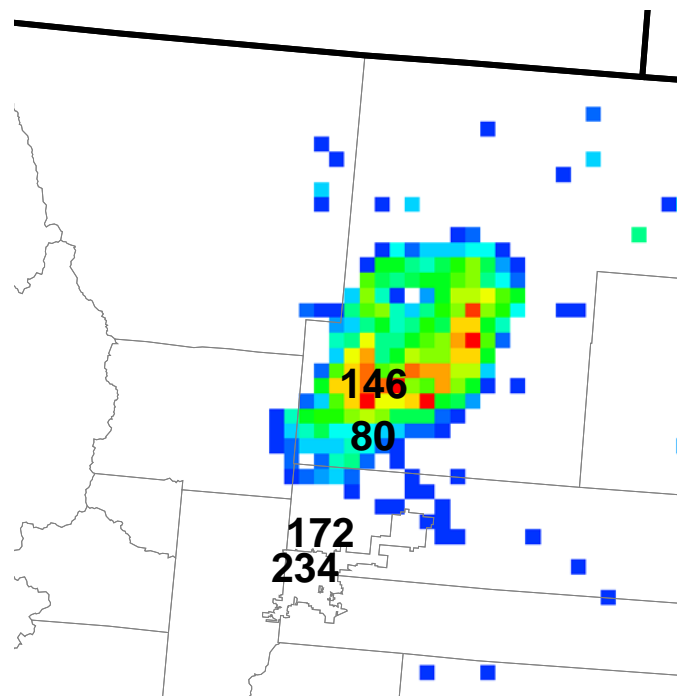
- High VOC Day (Jul 1, 2006)

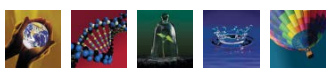
- Platteville PAR very high (1,708 ppbC) over highest D-J Basin O&G emissions area
- Slow wind speeds



- Low VOC Day (Jun 22, 2006)

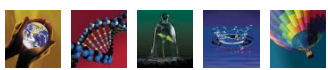
- Low PAR (80-234 ppbC) with fast wind speeds, little residence time in Weld County





# Conclusions VOC and Meteorological Analysis

- Days when back trajectories have longer residence time over Weld County O&G sources VOC underestimation bias is the greatest
  - Especially for PAR and ETHA, source signatures for O&G emissions
- Lower VOC days have little residence time over Weld County and faster wind speeds
- Suggests O&G VOC may be under-represented
- Not definitive due to modeled volumetric average versus observed surface point measurement



# O&G VOC Sensitivity Test

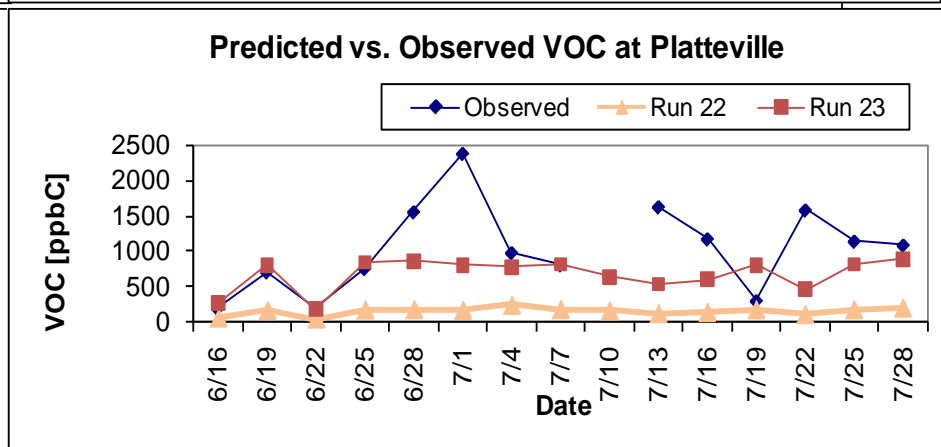
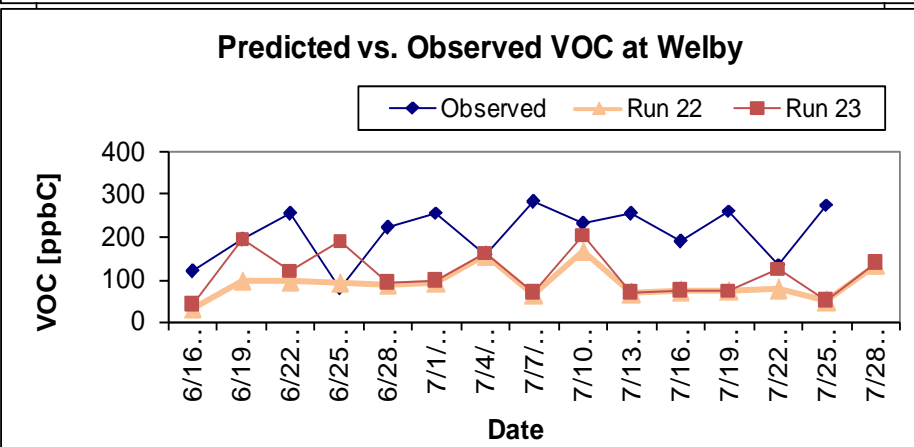
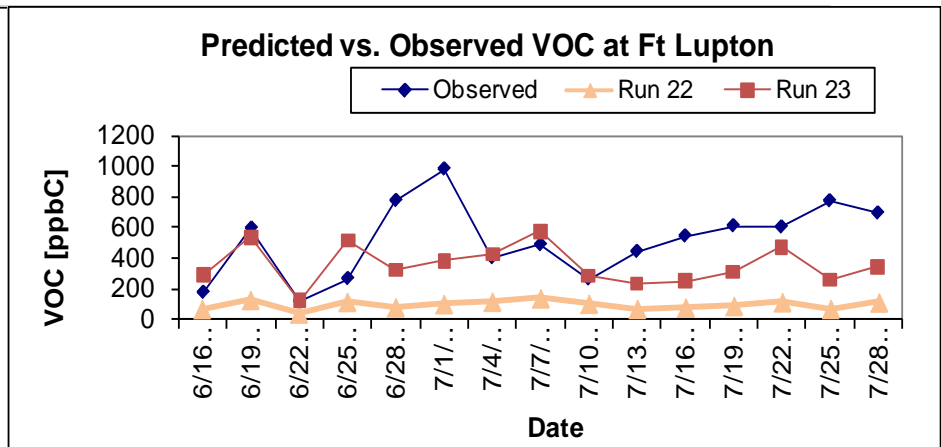
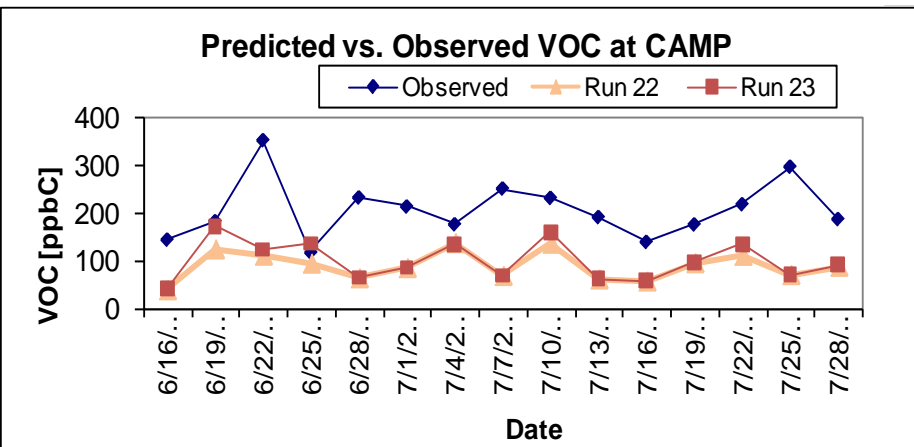
- Analysis suggests of a possible understated O&G VOC emissions in D-J Basin
  - Known missing O&G related mobile source emissions
  - Importance unknown, being investigated in ongoing Piceance Pilot Project (P3)
- Performed CAMx 5 time O&G VOC emissions sensitivity test
  - 5xVOC was an arbitrary adjustment
  - Does not mean we believe O&G VOC emissions are underestimated by a factor of 5
  - Wanted to chose a factor so that ozone signal is above model noise
- Examine ozone and VOC model performance





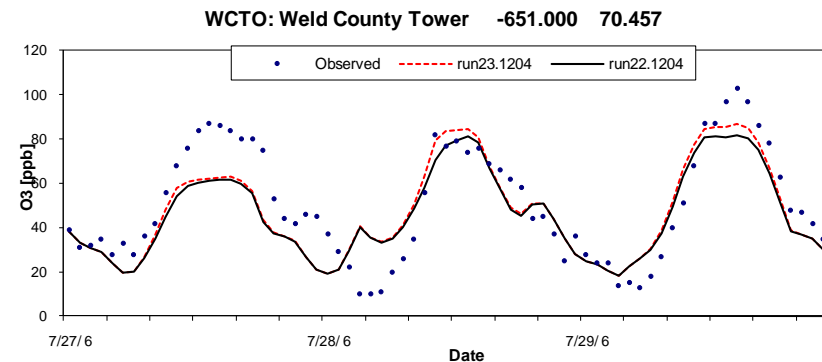
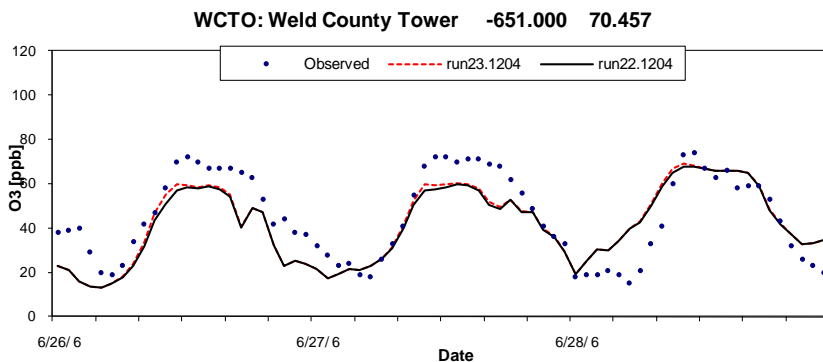
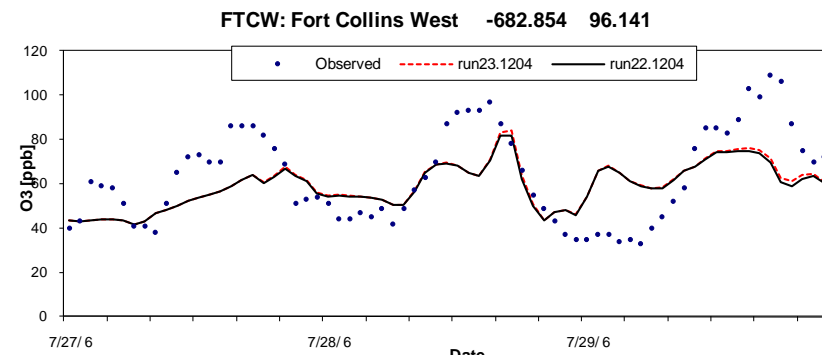
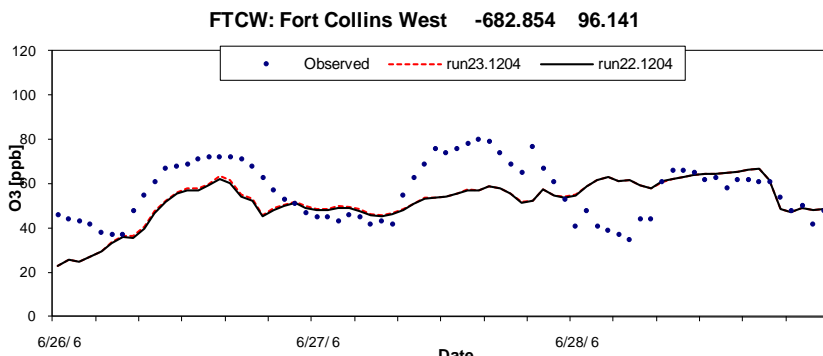
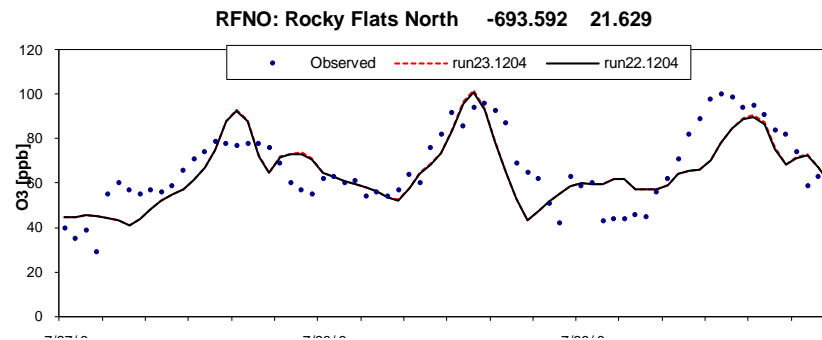
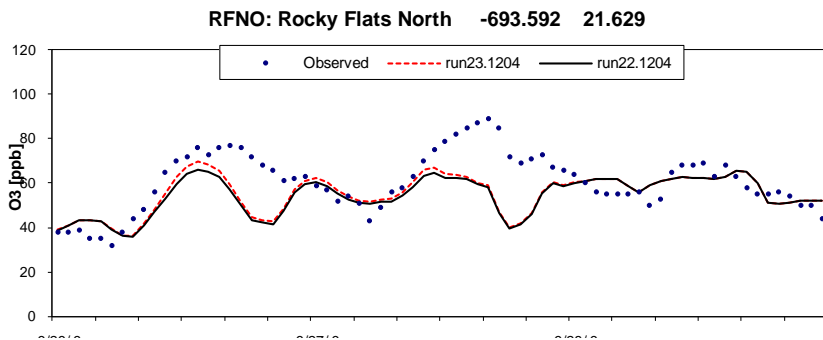
# 5xVOC O&G Sensitivity Test (Run23) vs. Base Case (Run22) VOC Model Performance

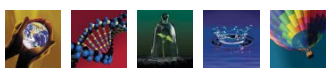
- Little change at CAMP/WELB
- Much better VOC performance at FTLP/PLAT





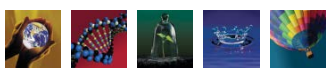
# 5xVOC O&G Sensitivity Test (Run23) vs. Base Case (Run22) Ozone Model Performance





# Conclusions: 5xVOC O&G Sensitivity Test

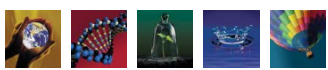
- No or very small improvements (few ppb at most) in ozone performance on some days/sites
- Significant improvements in VOC at Weld County sites
  - At Platteville, factor of 6 average VOC under-prediction reduced to factor of 1.5
- Caveat regarding modeled volume average vs. surface point measurement
- O&G largest VOC source in Weld County
  - Missing mobile source VOC related to O&G
  - Condensate largest source of O&G VOC in D-J Basin
    - Reg 7 assumes 95% VOC control of large condensate tanks with 100% Rule Effectiveness
    - 80% Rule Effectiveness would increase VOC from these sources by ~5x



# Receptor Model VOC Source Apportionment

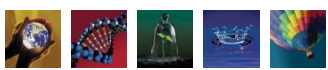
- Chemical Mass Balance (CMB)

- User inputs VOC source profiles (fingerprints) with key fitting species for each source type and speciated VOC measurements
- CMB estimates VOC source contributions using least squares solution to set of linear equations
- Can't input too many VOC source profiles or use source profiles that are too similar (co-linear)
- VOC species not in CMB input VOC source profiles are “unidentified” fraction



# Receptor Model VOC Source Apportionment

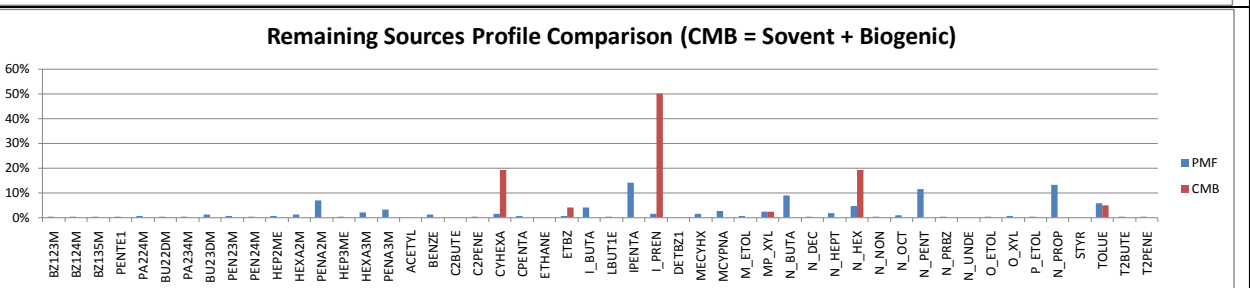
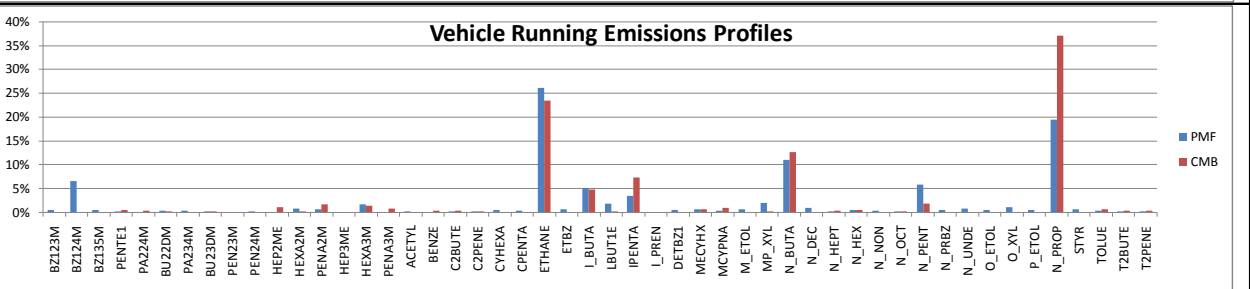
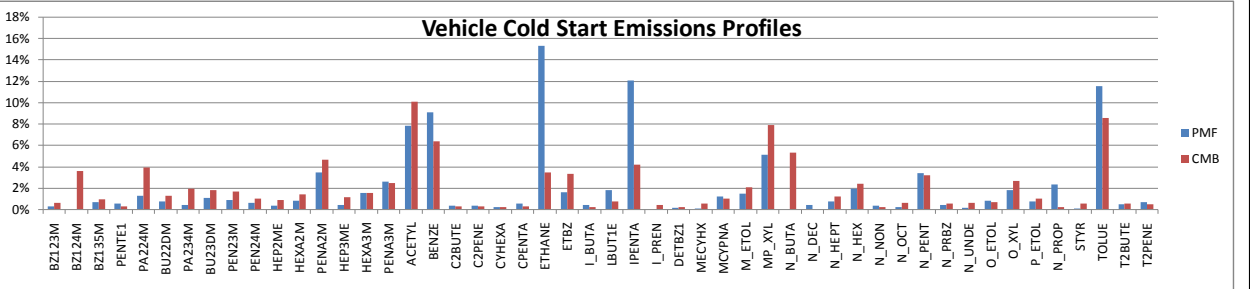
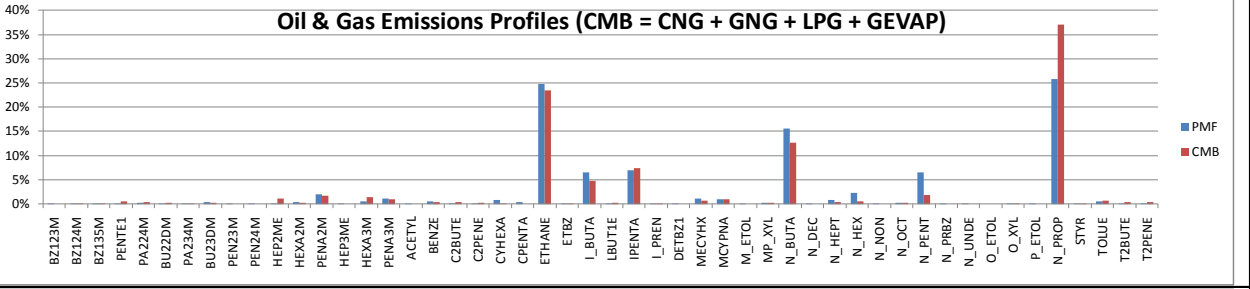
- Positive Matrix Factorization (PMF)
  - Solves similar equations as CMB only does not use any a priori knowledge about VOC source profiles
  - Outputs a set of N factors of VOC speciation profiles
  - User examines factors and tries to relate them to VOC profiles for specific source categories
  - Needs many VOC samples in order to solve for factors
  - Advantage over CMB is that it is not constrained by prior knowledge of VOC source profiles
  - Disadvantage is that factors may be difficult to interpret or represent multiple source categories



# Preliminary CMB and PMF VOC Source Apportionment

- Input VOC Source Profiles for CMB:
  - Compressed Natural Gas (CNG)
  - Geogenic Natural Gas (GNG)
  - Liquid Petroleum Gas (LPG)
  - Gas Evaporative (Gas Evap)
  - Vehicle Exhaust (Gasoline Combustion)
  - Biogenic
    - Oil and gas sources include combination of CNG, GNG, LPG and Gas Evap
- Preliminary PMF using 4 Factors and just CMB VOC fitting species
  - Compare CMB VOC source profiles for PMF Factors to help identify Factors

# Comparison of preliminary CMB/PMF



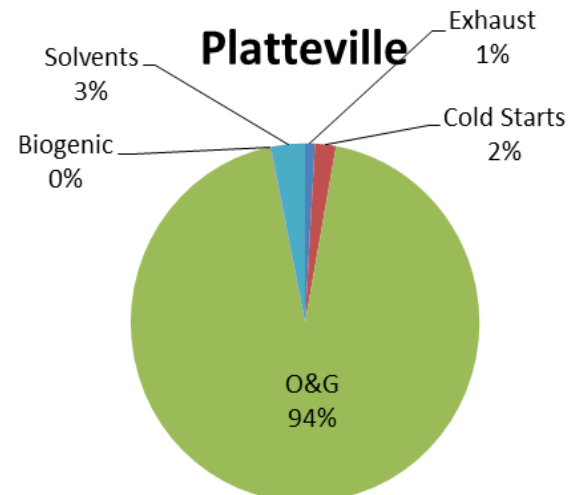
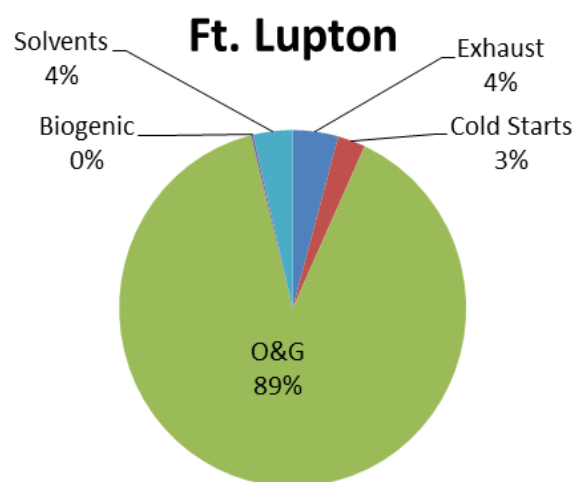
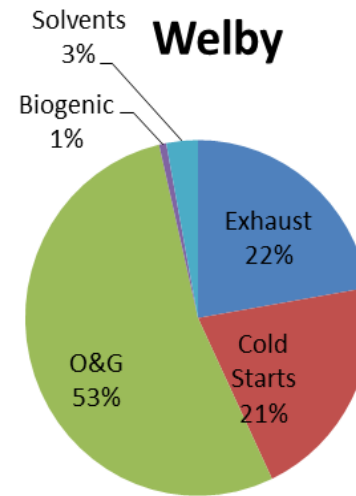
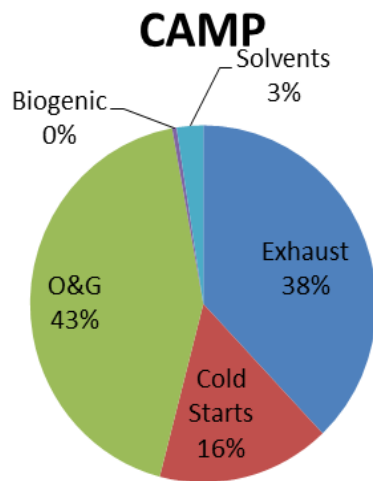
- Very good match between first three PMF factors and Oil and Gas, Vehicle Cold Start and Vehicle Running Exhaust VOC profiles
- Fourth factor compared with Biogenic+Solvent, but not a very good match.
- PMF able to distinguish between vehicle cold start and exhaust



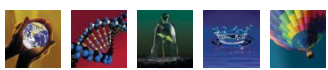
# Revised CMB VOC Source Apportionment

## Similar to Preliminary CMB

- Add Vehicle Cold Start (CS) and Solvent (Sol) category
- Group CNG, LPG GNG and Gas Evap into O&G source category

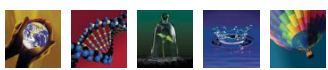






# Revised PMF VOC Source Apportionment

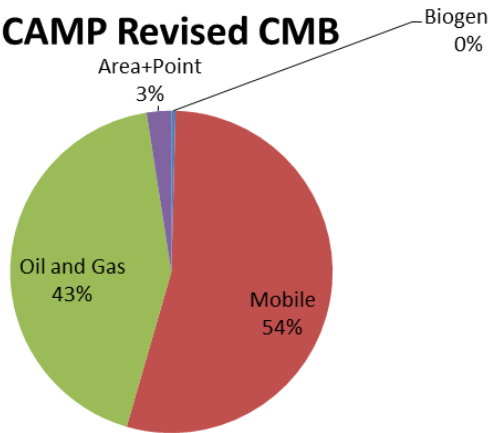
- Use all VOC species in measurements
  - As opposed to just CMB fitting species used in the preliminary PMF modeling
  - CMB biogenic VOC profiles uses isoprene as main fitting species
    - VOC measurements had low isoprene, but did have monoterpene ( $\alpha$ -pinene &  $\beta$ -pinene)
- Revised PMF four factors identified as follows:
  - Oil and Gas (high ethane, isobutane, isopentane, n-butane and propane)
  - Gasoline Combustion (Mobile) (high acetylene and ethylene)
  - Biogenic Sources (high  $\alpha$ -pinene &  $\beta$ -pinene)
  - Area/Point Source (high 1-dodecane, n-dodecane and n-undecane)



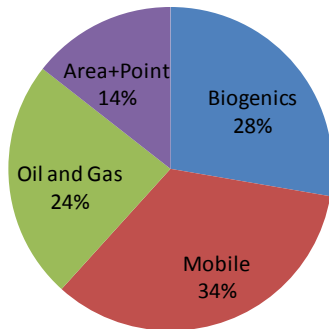
# Emissions-Based VOC Source Apportionment Modeling and Comparison to Receptor Modeling

- Use CAMx Ozone Source Apportionment Technology (OSAT) to track VOC emissions for major source categories:
  - Mobile Sources (on-road plus non-road)
  - Biogenic Sources
  - Oil and Gas Sources
  - Area/Point Sources
- Extract 5-8am MST CAMx/OSAT VOC at four sites
- Compare CAMx/OSAT VOC source apportionment with Revised CMB and PMF VOC Source Apportionment
  - Relative (%) and Absolute (ppbC) comparisons

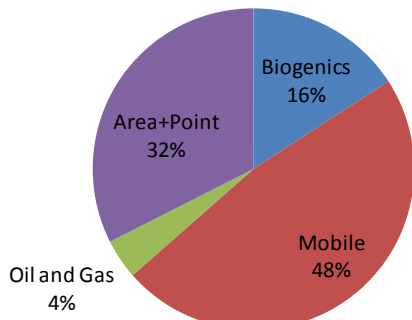
## CAMP Revised CMB



## CAMP Revised PMF 2



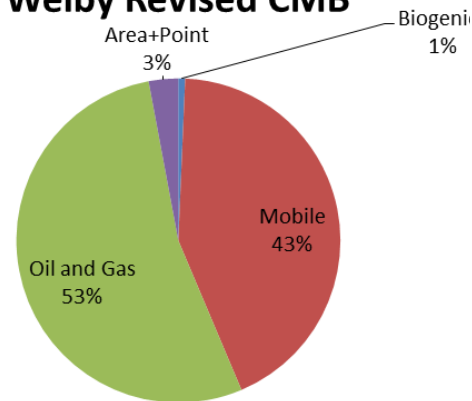
## CAMP CAMx OSAT



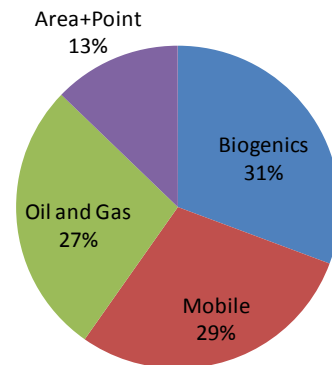
# VOC Source Apportionment at CAMP

- All three techniques estimate Mobile is largest contributing source category (54%, 34% & 48%)
- CMB & PMF estimate more O&G (43% & 24%) than OSAT (4%)
  - This is likely due to some of CMB/PMF O&G fraction being in OSAT Mobile and Area/Point categories (e.g., home heating)
- Biogenic high in PMF (28%) and OSAT (16%), nonexistent in CMB

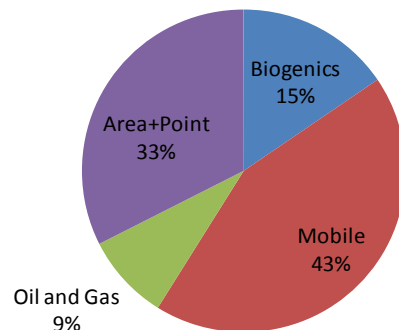
### Welby Revised CMB



### Welby Revised PMF

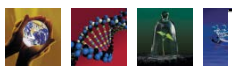


### Welby CAMx OSAT

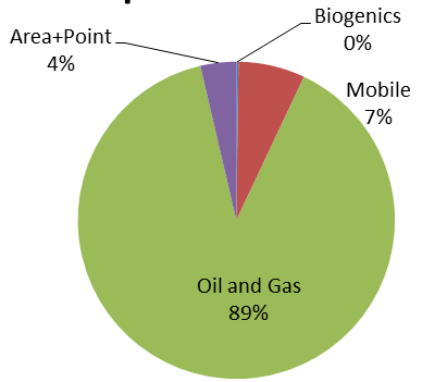


# VOC Source Apportionment at WELB

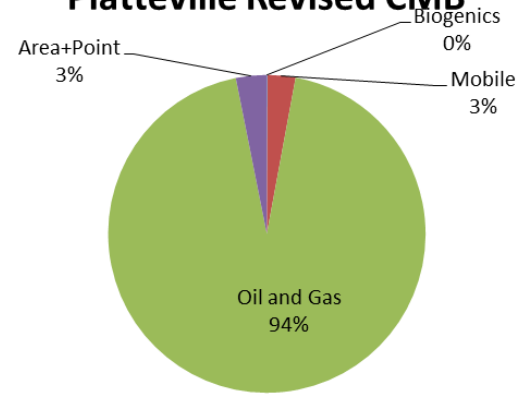
- High mobile VOC contribution for CMB, PMF & OSAT (43%, 29% & 43%)
- O&G higher in CMB & PMF (53% & 27%) than OSAT (9%)
- PMF estimates twice the biogenic VOC contribution (31%) compared to OSAT (15%), with CMB essential no biogenic contribution (1%)



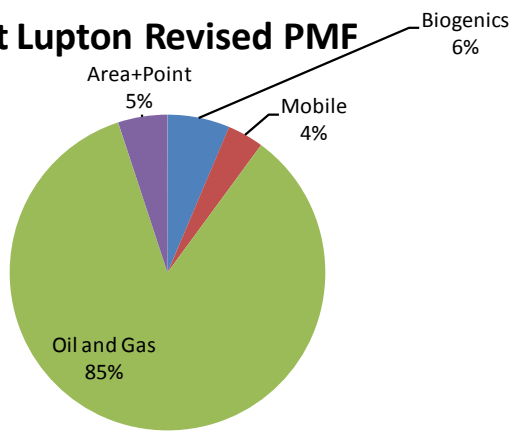
### Ft Lupton Revised CMB



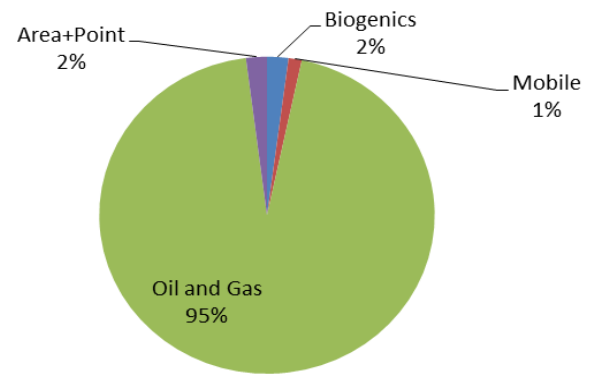
### Platteville Revised CMB



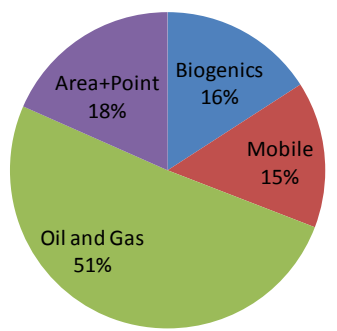
### Ft Lupton Revised PMF



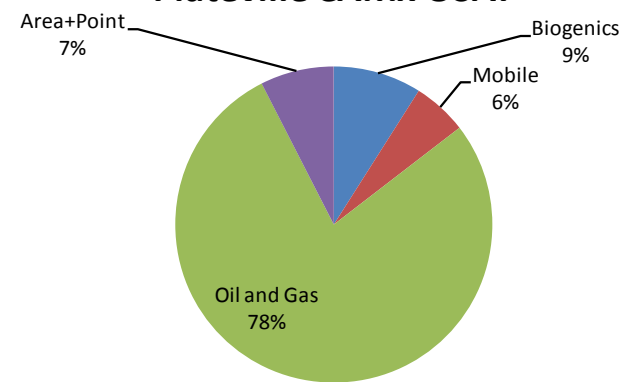
### Platteville Revised PMF

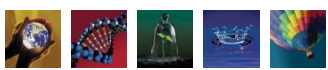


### Fort Lupton CAMx OSAT



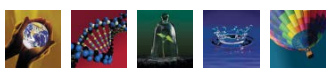
### Plateville CAMx OSAT





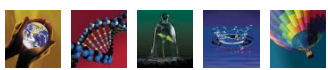
# Biogenic and Area/Point Source Comparisons

- PMF estimates more biogenic VOC than CAMx/OSAT
  - PMF biogenic factor to just biogenic as includes non-biogenic VOC species (e.g., ethane)
  - CMB essentially no biogenic as does not include monoterpenes
- CMB and PMF vs. CAMx/OSAT Area/Point comparison inconclusive
  - PMF fourth factor called Area/Point but identification less clear than other factors



# Conclusions: VOC Source Apportionment Modeling

- Comparison of monitored-based CMB/PMF and emissions-based OSAT VOC source apportionment inconclusive:
  - Is CAMx VOC underestimation bias due to missing VOCs or differences between modeled volume average and surface point measurement
  - VOC source categories in CMB, PMF and OSAT represent different sources
    - CAMx/OSAT precisely defined from pre-merged emission files
    - PMF not precise as they represent mathematical factors
    - CMB has large unidentified due to species not in CMB VOC source profiles
    - Mobile and O&G sources have cross-over species
- Results consistent with O&G VOC emissions being understated

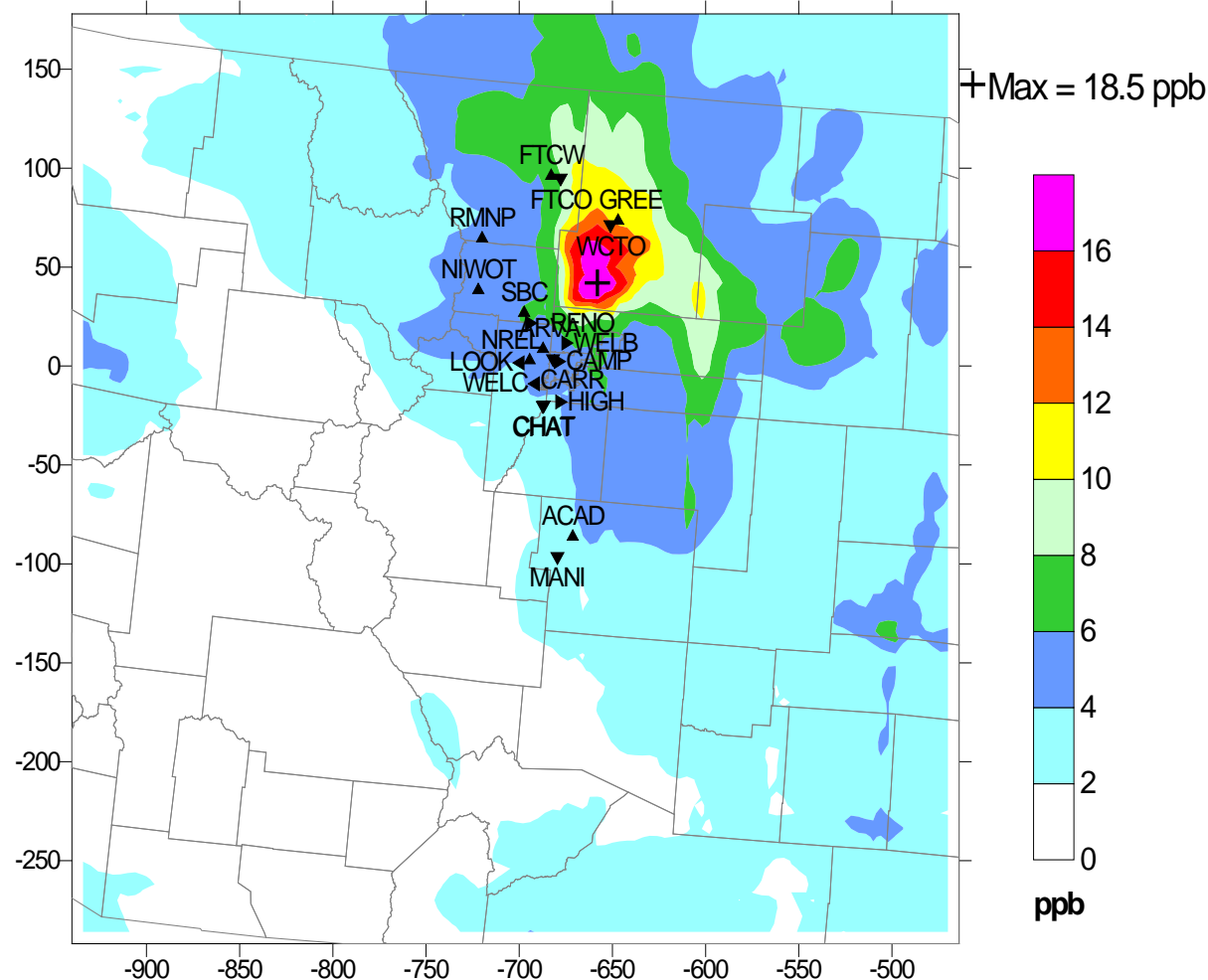


# What About Ozone?

- Maximum Ozone Contributions due to O&G Sources using CAMx/APCA

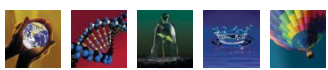
- Using 2006 Base Case emissions inventory with likely understated O&G VOCs

- ~ 6 ppb at RFNO
- ~8 ppb at FTCW
- Max = 19 ppb in Weld County



Denver June + July, 2006 Episode  
Highest 1-hour Ozone Contribution from Oil and Gas  
CAMx Run 24.1204.apca





# Acknowledgements

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  - Dennis McNally and Cyndi Looms of Alpine