Comparison of Ambient Measurements to Emissions Representations in Modeling: Source Apportionment Results

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Presentation Outline

- Background
- Summary of EI reconciliation results
- Summary of source apportionment analyses:
    - Intro to receptor modeling
    - Dual model approach (PMF & CMB)
    - Sites and data quality
    - Source profiles
    - Results

Background (1 of 2)

Project Objective:

To provide corroborative evidence, with sufficient justification, that can potentially explain disagreements between modeled and observed pollutant concentrations.

Background (2 of 2)

Overview of Approach:

- Perform EI reconciliation with pollutant ratios (TNMOC/NO_x, CO/NO_x)
- Perform EI reconciliation with speciated VOCs (TNMOC composition)
- Perform VOC source apportionment (e.g., CMB, PMF)

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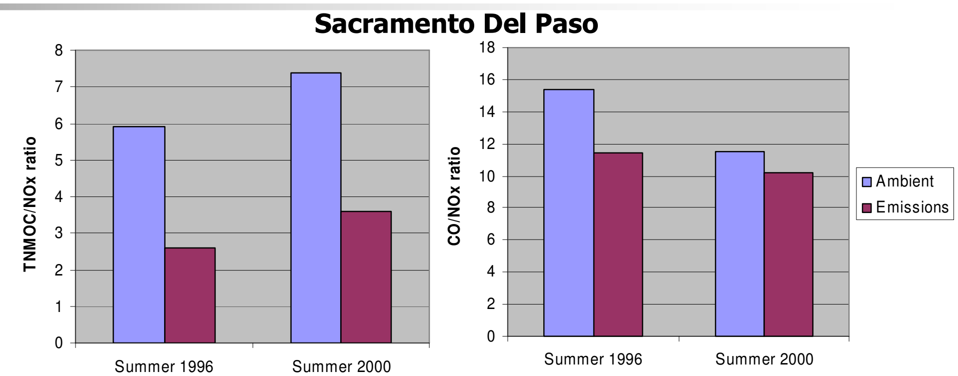
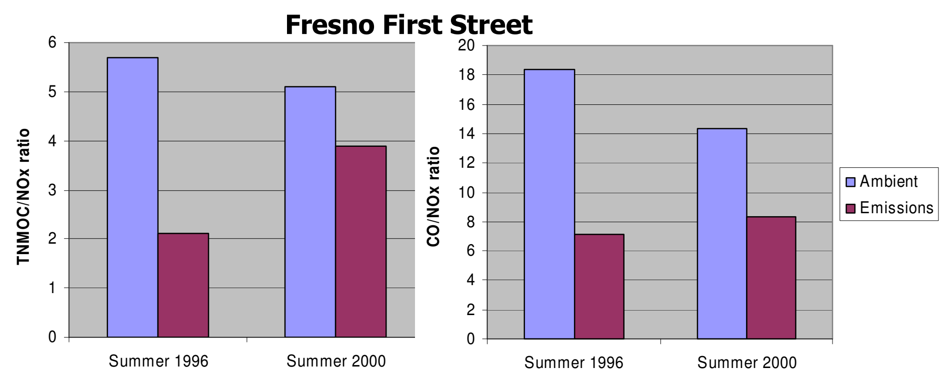
EI Reconciliation Results (1 of 5)

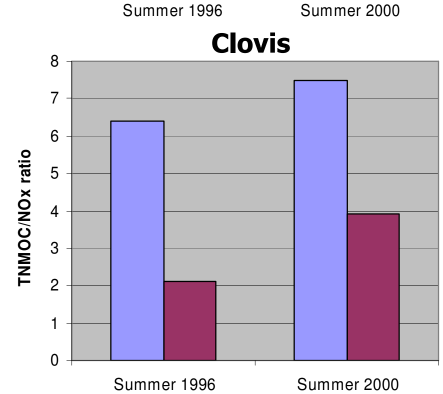
- Overall, the emissions data show better agreement with ambient data than previous emission inventories have.

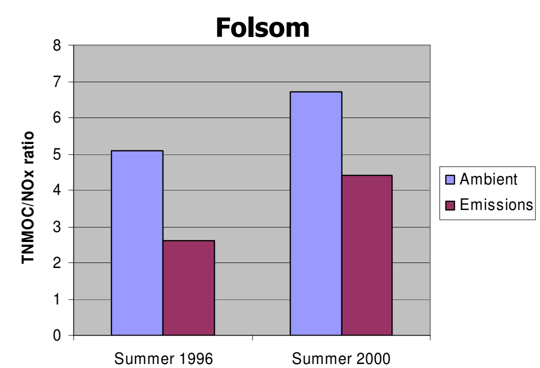
Air Basin	Ambient ratio/Emissions ratio			
	DRI 1990	DRI 1995	DRI 2000	STI 2000*
Sacramento	2.2	1.6	1.7	1.4 - 2.4
Fresno	3.6	2.6	1.9	1.4 - 7.2
Kern	--	3.9	2.9	2.6 - 4.3

*This column shows the range of results from all sites evaluated in each air basin—including both urban and rural sites.



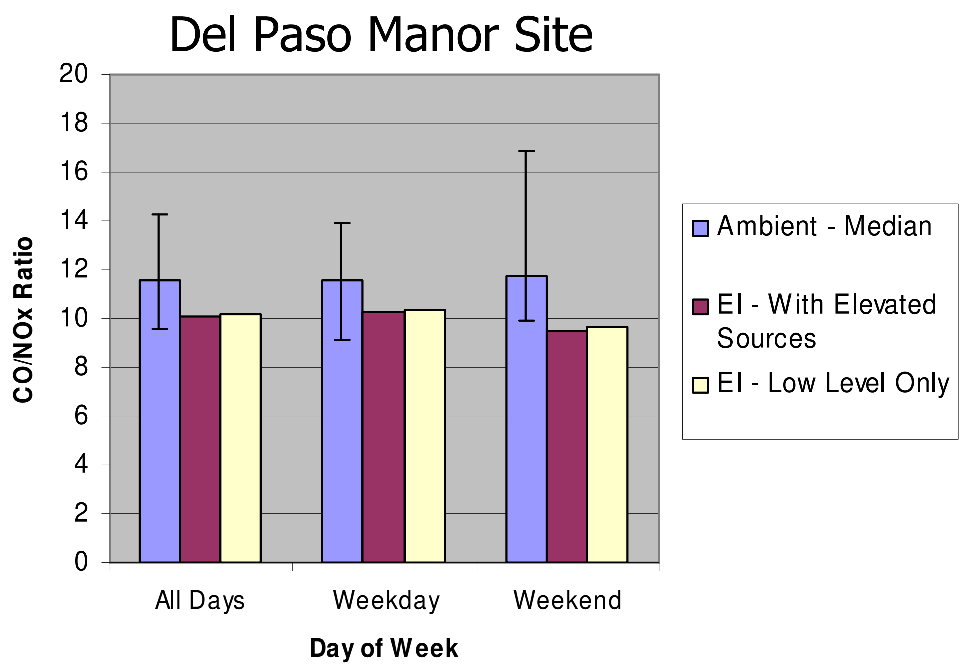






EI Reconciliation Results (2 of 5)

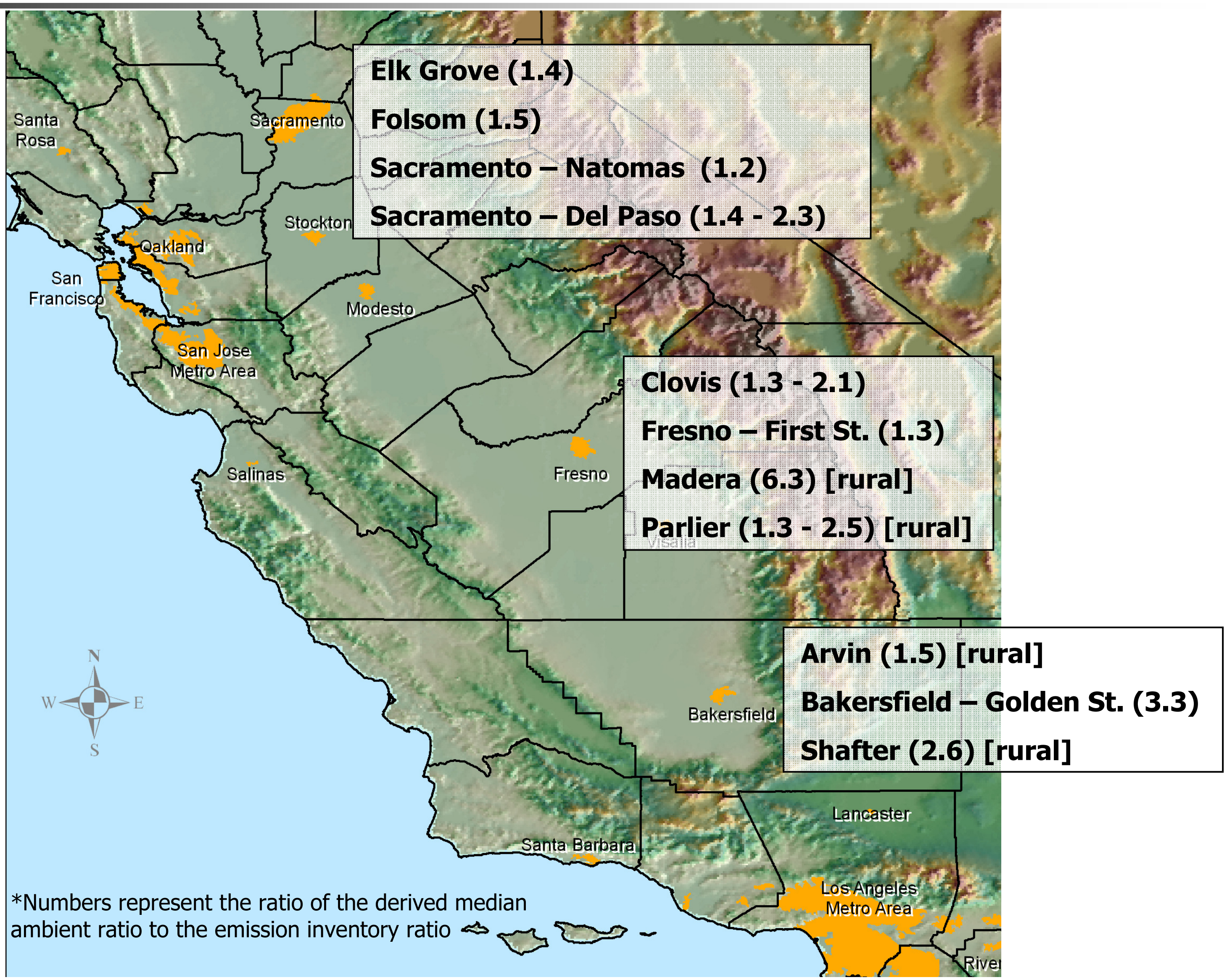
- At some sites, the emissions data correlate with ambient data as closely as could be expected given analyses limitations*.



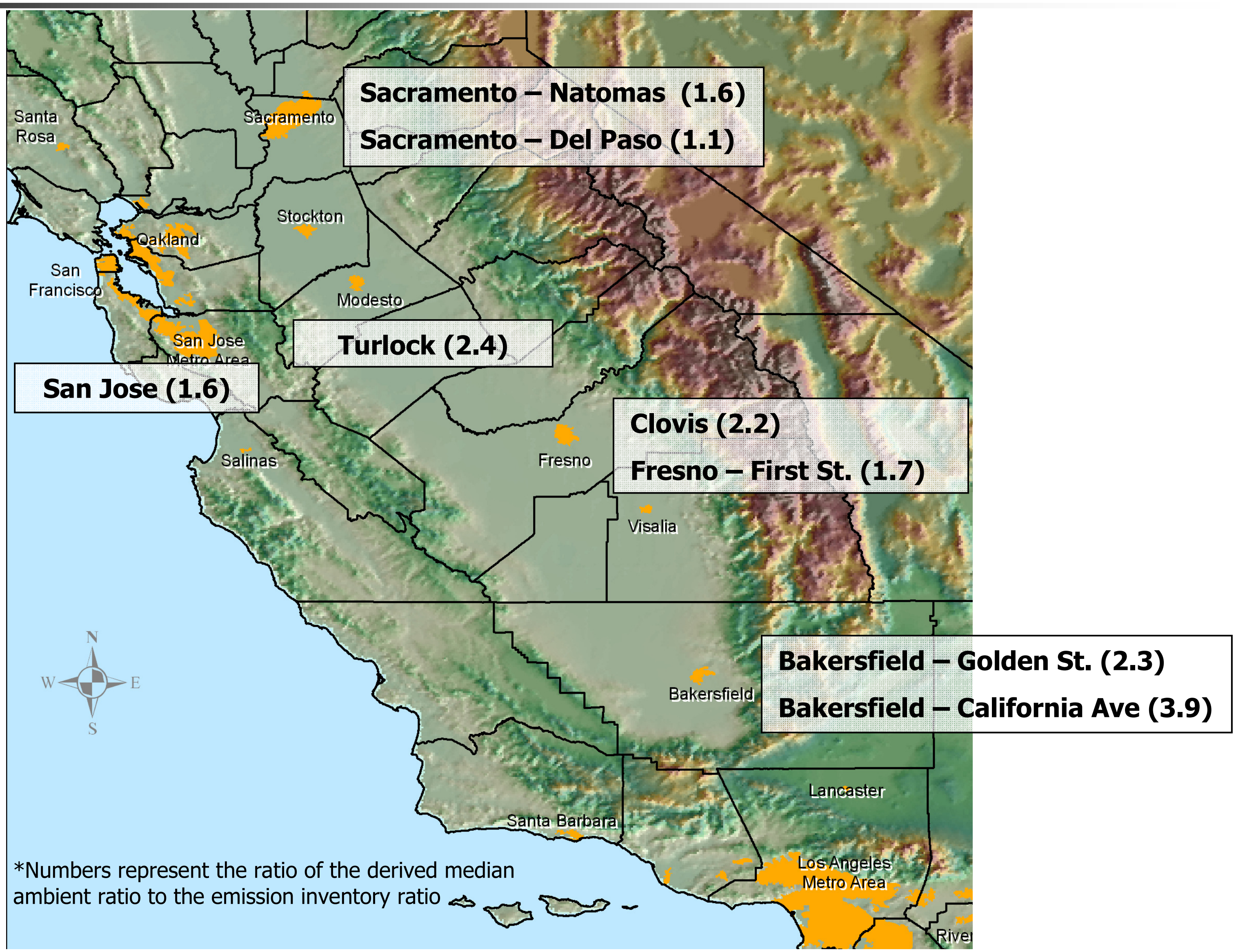
* "ARB staff believes that an assessment such as this should only be expected to produce ambient/emissions ratios that are within approximately +/- 25 to 50% of 1.0." (ARB, 1997)

EI Reconciliation Results (3 of 5)

TNMOC/NOx Ratios

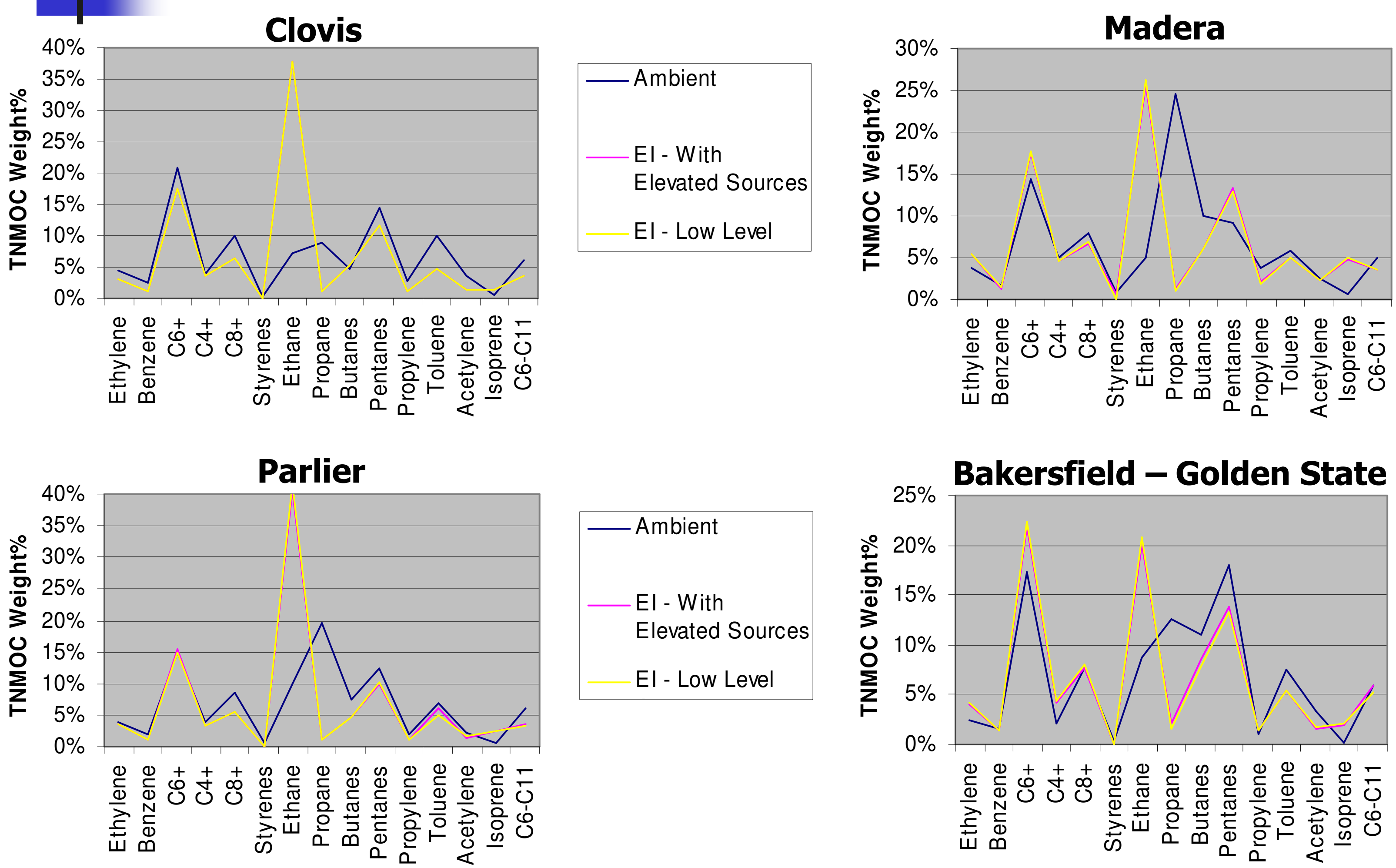


EI Reconciliation Results (4 of 5)



*Numbers represent the ratio of the derived median ambient ratio to the emission inventory ratio

EI Reconciliation Findings (5 of 5)



Ethane: livestock emissions spatially allocated using population density.

Summary of Findings

- EI generally under-predicts pollutant ratios
- Urbanized Sacramento area:
  - Good agreement on weekdays
  - Poorer agreement on weekends
- Urbanized Fresno area:
  - Good agreement on weekdays and weekends
- Urbanized Bakersfield area:
  - Poor agreement on weekdays and weekends

Recommendations

- Improve accuracy of weekend emission estimates.
- Correct spatial distributions of emissions (e.g., from livestock waste).
- Further investigate the poor agreement in Kern County.
- Collect more ambient data at Bay Area sites to enable more robust evaluations.

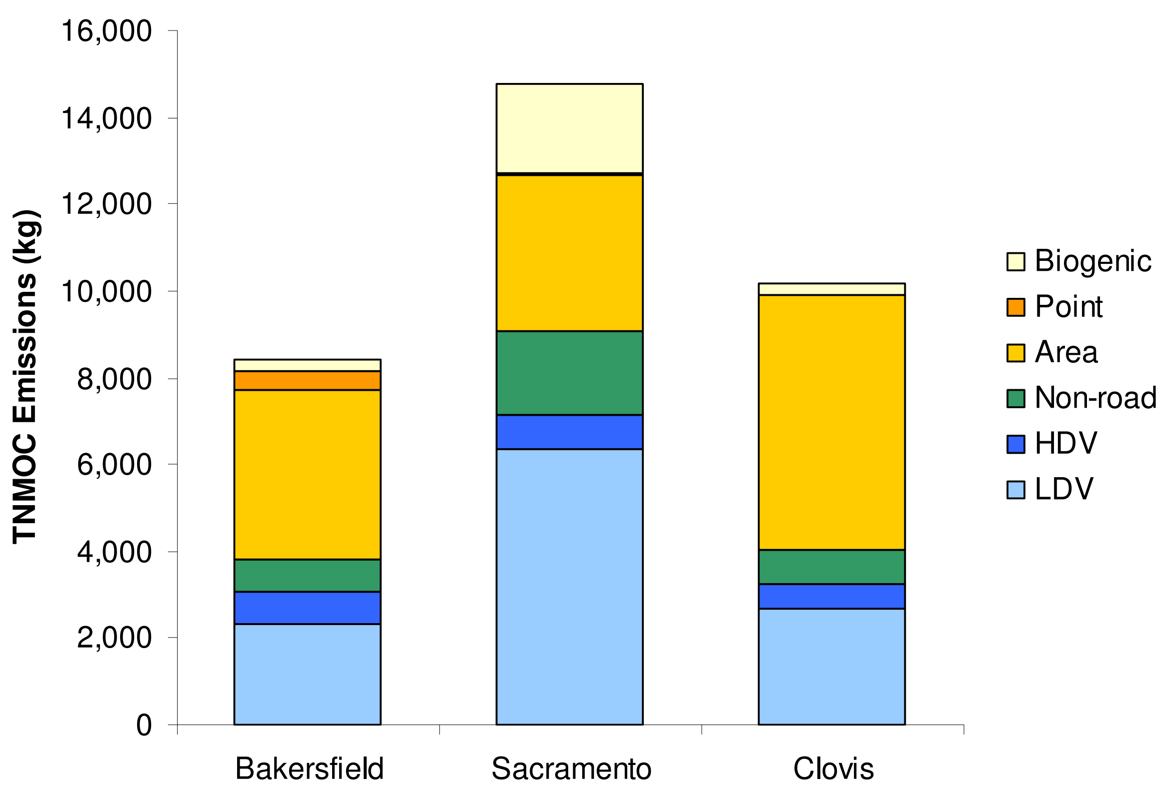
Source Apportionment Overview

- To further reconcile the emission inventory and ambient data, receptor modeling was conducted with Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) on ambient speciated VOC data at three sites:
  - Sacramento Del Paso (SDP)
  - Clovis (CLO)
  - Bakersfield Golden State (BGS)
- Results by broad source category were compared to emission inventory data.
- Focus on 2000 data, though larger dataset was needed for PMF (1998-2000).

Review of Initial Comparisons

- Among the 3 Tier 1 sites, TNMOC concentrations were highest at BGS (45% higher than at CLO; 75% higher than at SDP)
- In the EI, TNMOC emissions are lowest at BGS and highest at SDP
- The EI reconciliation showed good agreement between emissions and ambient data at SDP, so TNMOC emissions are likely underpredicted at CLO and BGS.

Summary of 0500 to 1000 PDT TNMOC emissions by source category



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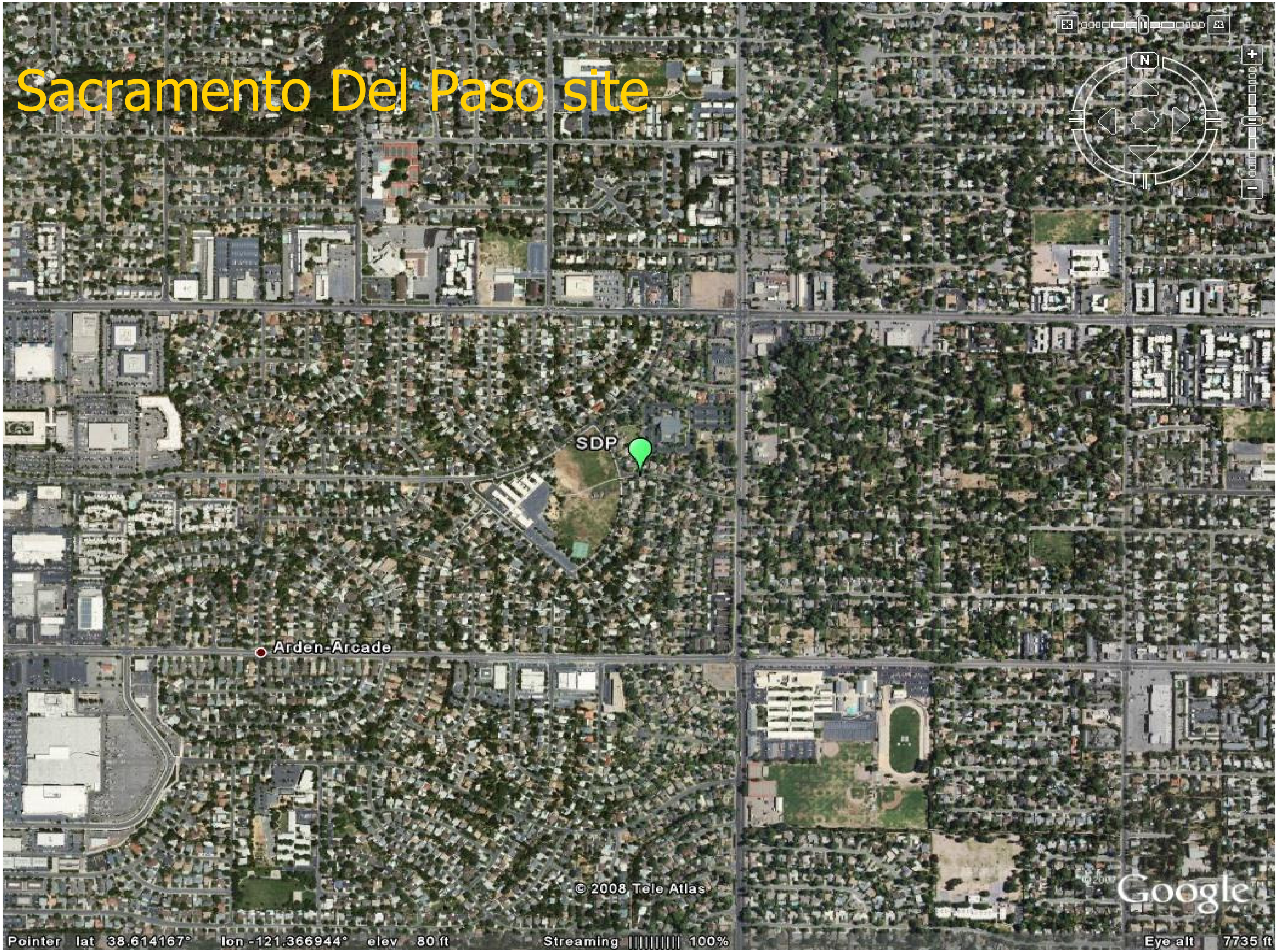
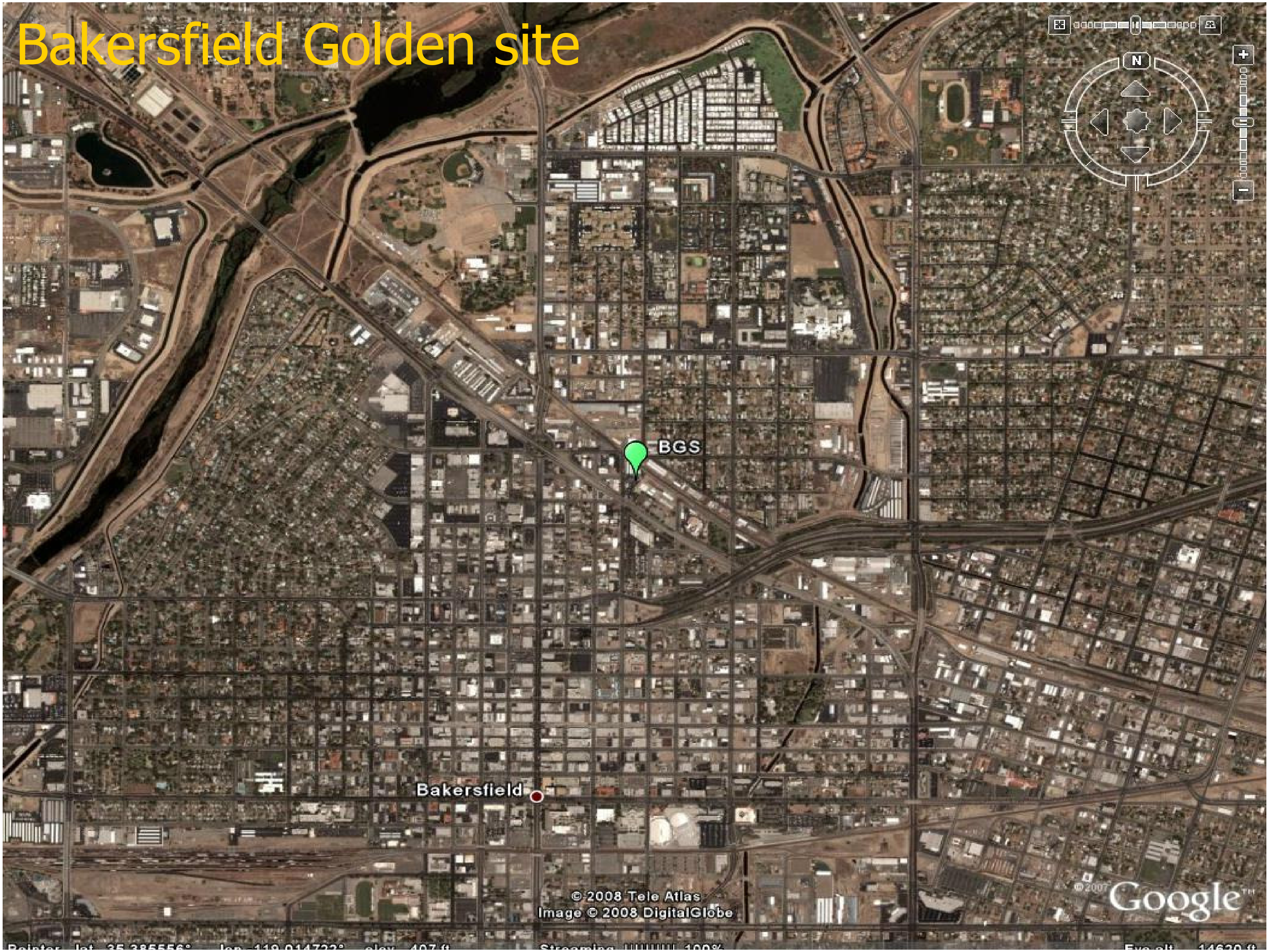
Sacramento Del Paso site



Fresno Clovis site

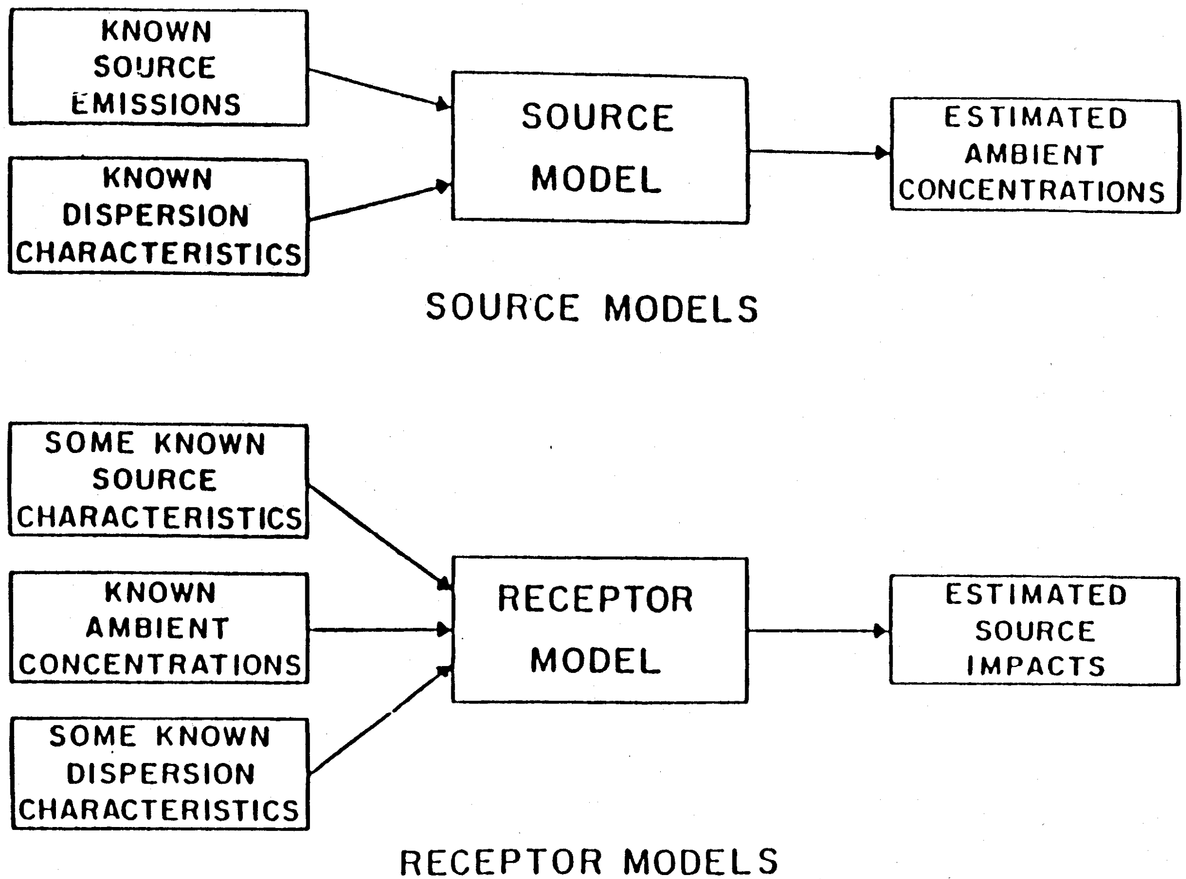
Bakersfield Golden site



Introduction to Receptor Modeling (1 of 4)

Source Model vs. Receptor Model

- The source model uses source emissions as inputs and calculates ambient concentrations
- The receptor model uses ambient concentrations as inputs and calculates source contributions



Adapted from Watson, 1979, *Dissertation*; Watson and Chow 2005

Introduction to Receptor Modeling (2 of 4)

How Multivariate Receptor Models Work

Receptor models require the input of time series of multiple species to extract information from all sample data simultaneously.

Strengths

- Use real ambient data to drive the model
- Quantify sources in every sample
- Give goodness-of-fit diagnostics for a robust analysis of how well the identified sources represent the data

Weaknesses

- Sources need to be independent to be isolated
- Meteorology and atmospheric reactivity can obscure source signatures
- Consistent identifying/naming of the factors can be difficult

Introduction to Receptor Modeling (3 of 4)

Chemical Mass Balance (CMB)

- CMB is a receptor model that uses information from both the receptor and the sources to quantify source contributions to ambient pollutant levels.
- CMB solves a series of linear equations that represent the linear sum of the product of source profile abundances and source contributions.
- CMB can be applied to a single sample.

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Introduction to Receptor Modeling (4 of 4)

Positive Matrix Factorization (PMF)

- An advantage of using PMF over CMB is that source profiles do not have to be known before running PMF.
- The only required inputs are ambient concentrations, but a large number of samples and species is needed.
- The disadvantage of PMF is that factors that account for the variance in the data are produced; typically, these factors are representative of a source or group of sources, but they can be difficult to interpret.

Data Issues

- 3-hour speciated VOC data samples were examined
- CMB: only data from the 0500 PDT samples in 2000 were examined; this is sufficient for a robust CMB analysis
- PMF: more data are required for a robust analysis, so data from 1996-2000 were examined, but only results from 2000 at 0500 PDT were used to compare to CMB and the EI
- Data in 2000 had previously been truncated or rounded, so there is a loss of precision in these data that cannot be recaptured
- Focus on morning data to minimize the impact of photochemistry complicating the analyses.
- Mass that was unidentified from the chemical analysis of the collected cannisters was not examined in the receptor models. This mass is part of TNMOC, but *completely of unknown origin and chemical composition*. Based on trends with tracer species we could potentially associate this mass with specific sources, but this would require significant extra effort outside of this project.

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Use of Source Profiles

- The more accurate and appropriate the profiles are, the higher the confidence in the results based on them.
- In CMB, source profiles are used explicitly in the model, where the ambient data are forced to fit a combination of source profiles.
- In PMF, source profiles are used for comparison with PMF-derived factor profiles, which in theory should approximate source profiles or represent atmospherically transformed profiles (e.g., aged "carryover" emissions).

Source Profile Data

- Source profile information were obtained from ARB and other studies in California:
  - ARB (US EPA, 2006), all source types but diesel
  - Watson et al., 2001; all source types
  - Uncertainties developed based on Fujita et al., 1995
- As part of sensitivity analyses, similar profiles (i.e., gasoline mobile) were used one by one to understand which would yield the best results.
- Only mobile profiles measured after 1996 were used, to capture any changes due to RFG and to use profiles from the same period as the ambient data.

Evaluation of Results

- In both models, the results can be objectively evaluated:
  - How well total mass and the mass of each species is predicted by the solution;
  - The shape of the scaled residual distributions for each species;
  - Independence of sources from each other;
- In both models, results also need to make physical sense (i.e., mobile sources are predicted in nearly all samples), sources cannot contribute negative mass, and PMF factor profiles should be reasonably close to actual source profiles.

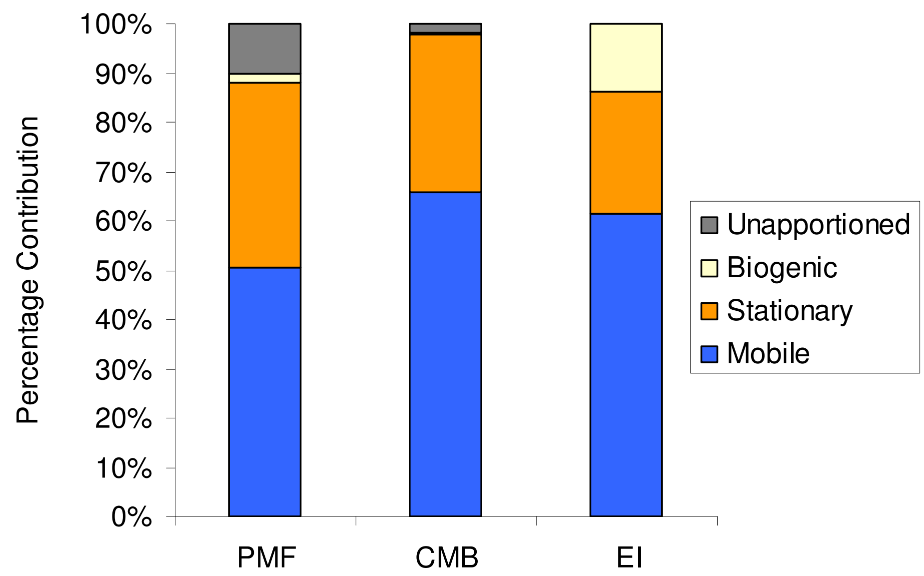
Summary of Results (1 of 8)

- Mobile sources were quantified with both CMB and PMF at each site; Tracers included acetylene, benzene, toluene, etc. Mobile sources showed a decrease in mass on weekends compared to weekdays at all sites.
- Biogenic sources were quantified using isoprene as a tracer, though this is highly reactive and often below detection, and was only a minor contributor to total mass.
- Solvents, coatings and refinery activity were also identified, with aromatics, mid-length alkanes and light alkanes, respectively, as tracers.
- Ethane and propane can also be part of aged air masses that have no link to their original source, so this may influence the quantification of refinery activity.

Summary of Results (2 of 8)

Sacramento

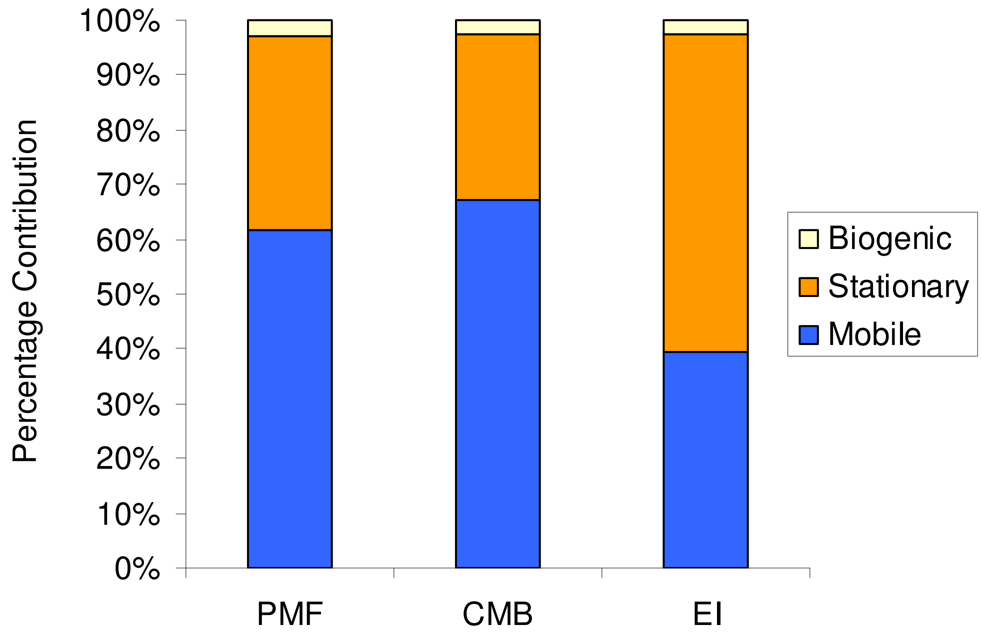
- CMB and PMF yielded similar results, showing most of the mass due to mobile sources.
- The EI estimate of mobile sources (61%) fell within the range of mobile source TNMOC contributions from the PMF (50%) and CMB analyses (66%).
- The contribution of biogenic emissions to TNMOC was higher in the EI than in the source apportionment analyses.
- These results corroborate the findings from the EI reconciliation work, which indicated that the EI and ambient data showed relatively good agreement at the Sacramento site.



Summary of Results (3 of 8)

Clovis

- Clovis had mediocre agreement between the EI and ambient data.
- The EI estimate of mobile sources is much lower than the mobile source contributions from CMB and PMF.
- An adjustment of the EI to reflect more mobile source influence would likely result in better agreement between the EI and ambient data at Clovis.

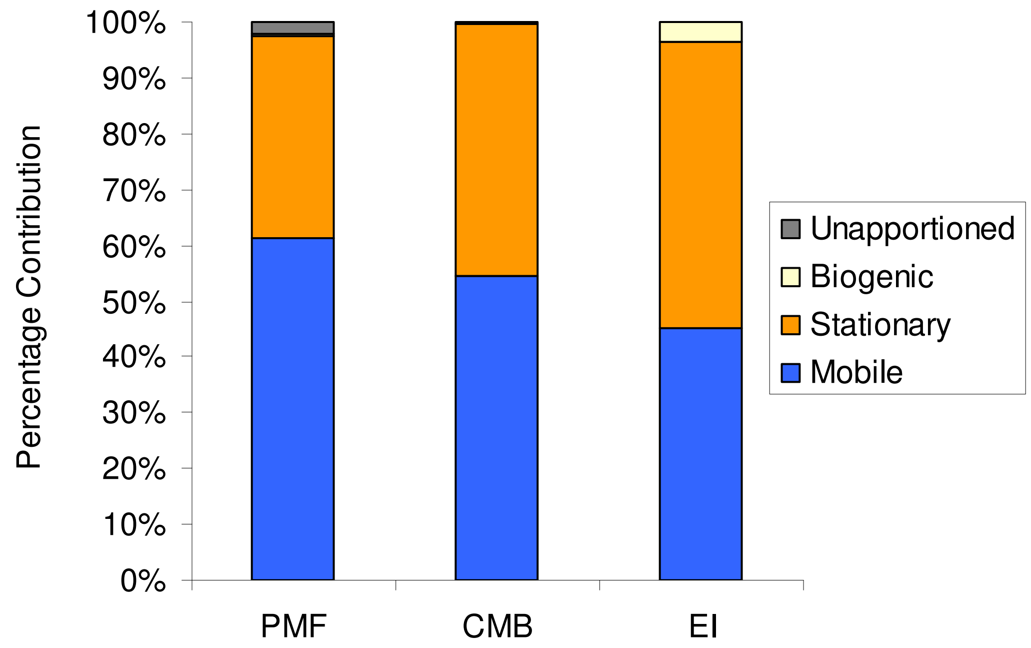


Summary of Results (4 of 8)

Bakersfield

- At Bakersfield, the EI compared poorly with the ambient data, with ambient TNMOC/NOx ratios being 3 to 4 times higher than EI-derived ratios.

- The EI shows less than half of the TNMOC attributed to mobile sources, while the CMB/PMF results suggest that mobile sources account for over half of the identified TNMOC mass.



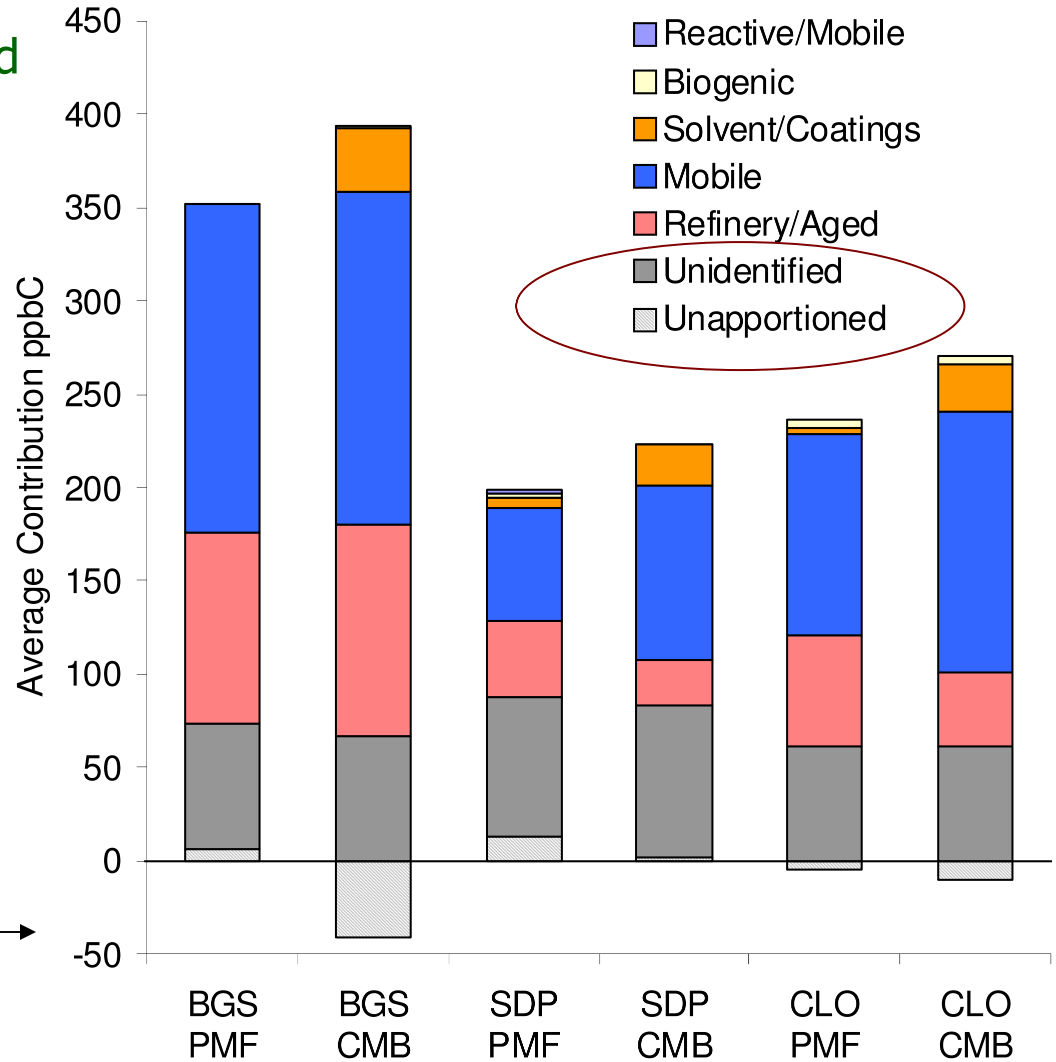
Summary of Results (5 of 8)

Results for 3-hr VOC samples collected during summer 2000 at 0500 PDT.

Mass that could not be accounted for by the source apportionment model is *unapportioned*.

Unidentified mass is the difference between TNMOC and the sum of Photochemical Assessment Monitoring Stations (PAMS) target compounds; this mass was not included in the source apportionment models

Negative values indicate that mass was overestimated, on average

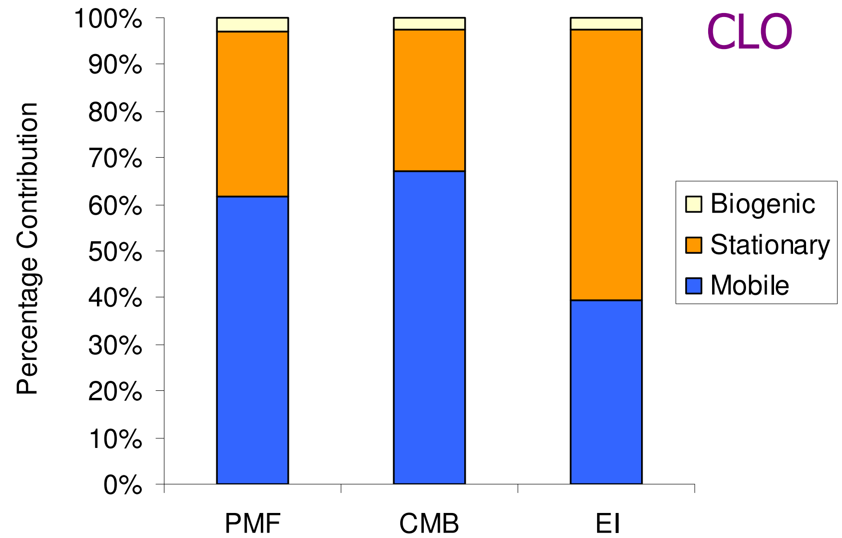


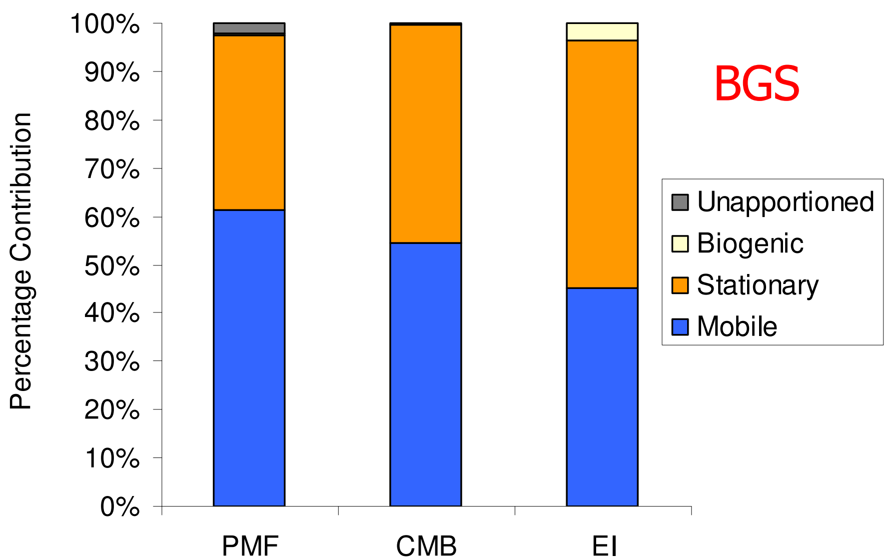
Summary of Results (6 of 8)

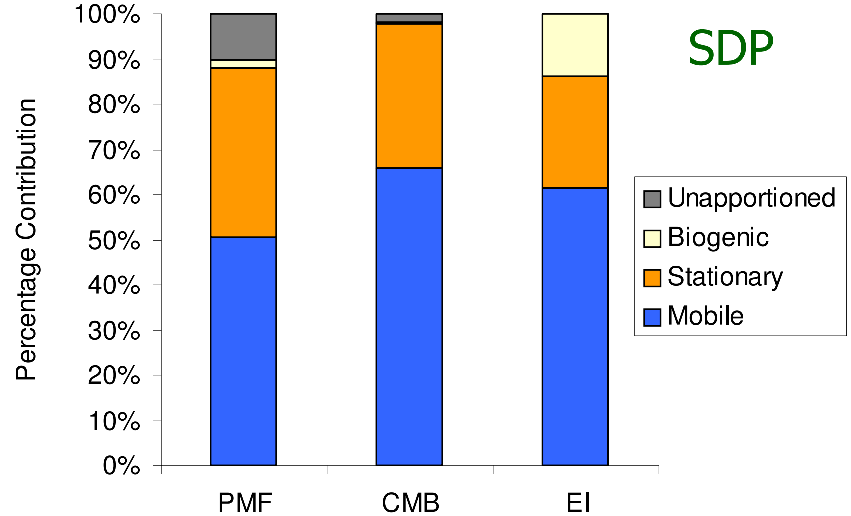
Average apportioned mass, year-2000 emission inventory, 0500-1000 PDT

With the exception of biogenics, the mobile-to-stationary mix in Sacramento is consistent between analyses.

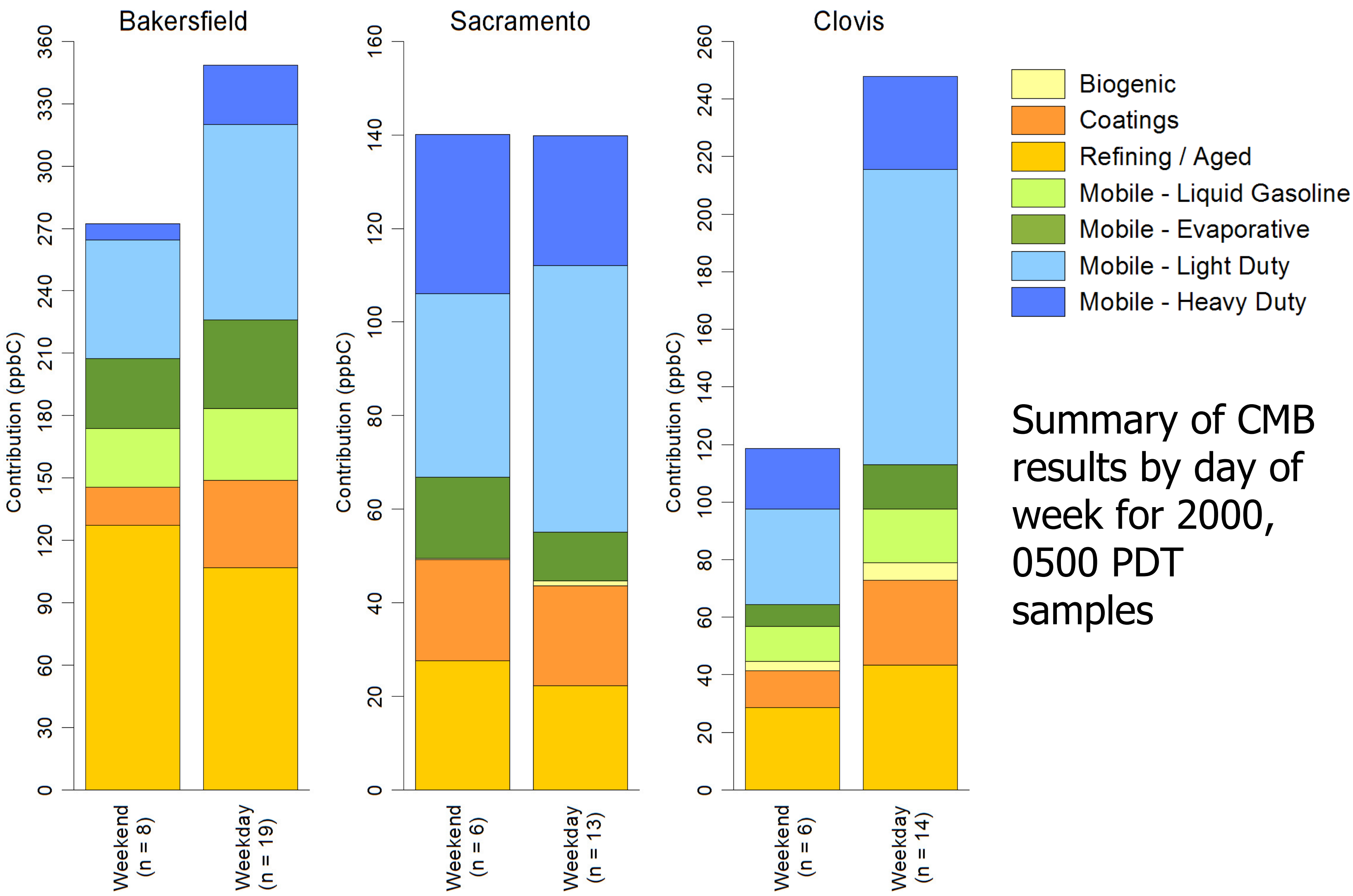
At Clovis and Bakersfield, mobile sources appear to be underestimated.





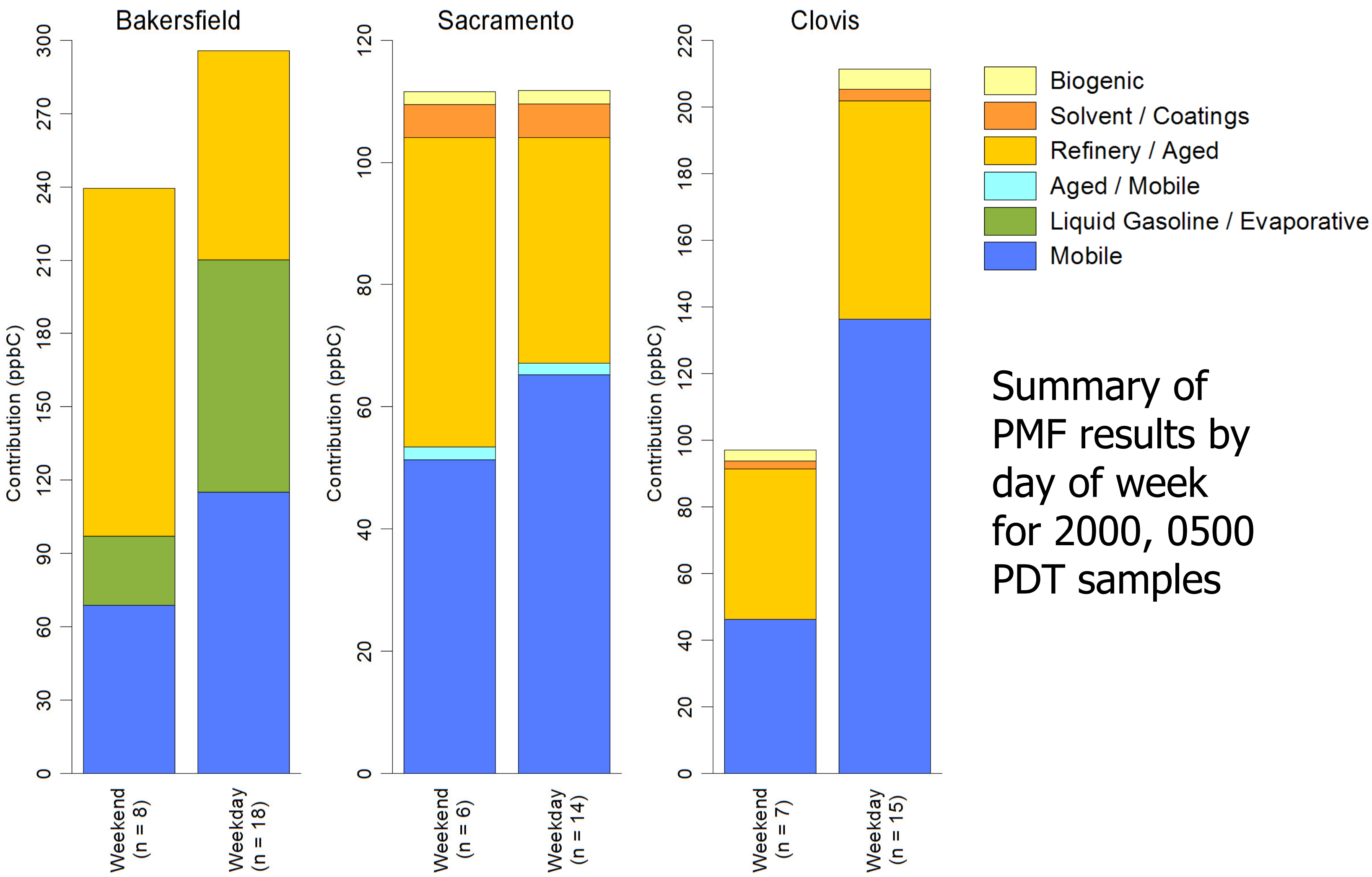


Summary of Results (7 of 8)



Summary of CMB results by day of week for 2000, 0500 PDT samples

Summary of Results (8 of 8)



Summary of PMF results by day of week for 2000, 0500 PDT samples

Conclusions

- The consistent results between the receptor modeling and EI at Sacramento, coupled with good photochemical modeling suggest the mix of mobile and industrial sources is about right.
- At Clovis and Bakersfield, photochemical modeling did not perform as well, and receptor modeling results did not compare as well with EI estimates in both mix of sources and total emissions. Mobile sources appear to be under-predicted at both sites.
- Use of additional years of ambient data could allow for the usage of data with better precision and provide information on trends over a longer time period.

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