

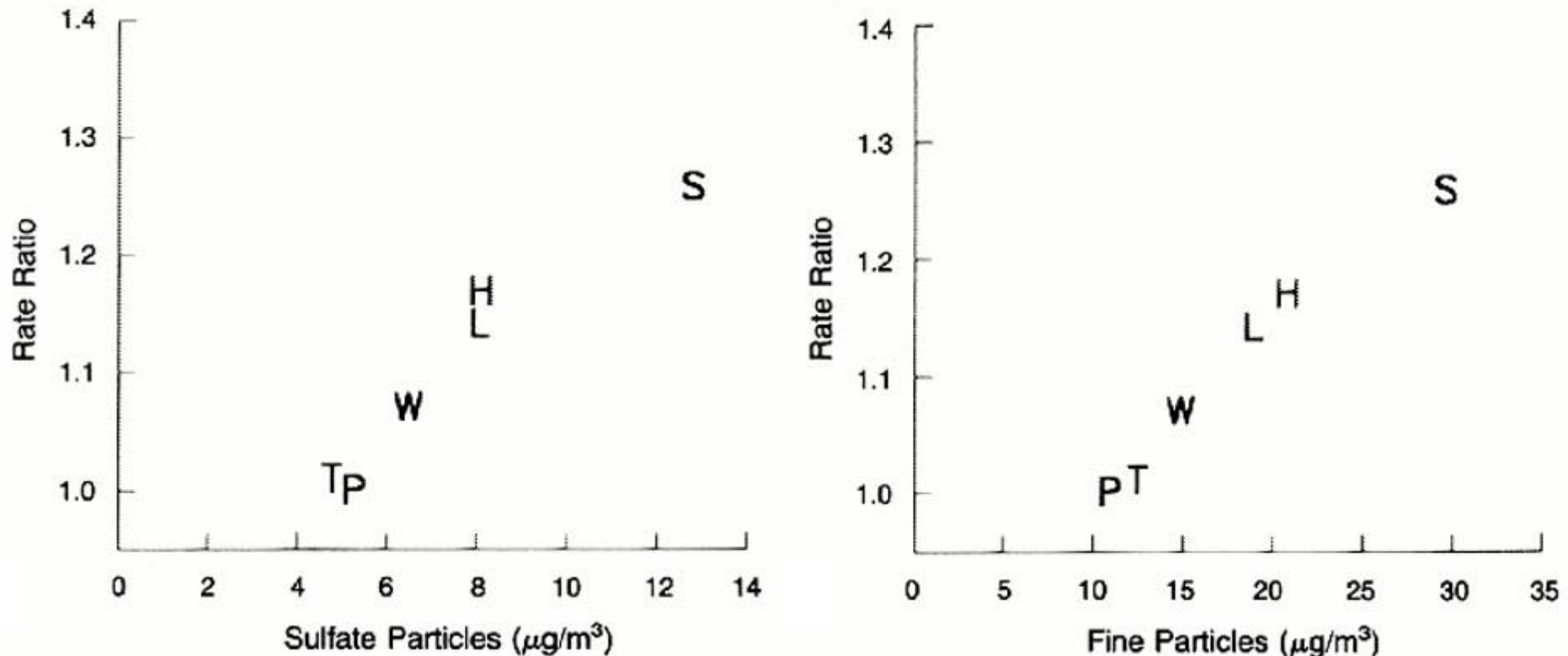
Fine Particulate Matter in the San Joaquin Valley: Introduction to Sources, Atmospheric Chemistry, and Transport

Michael Kleeman

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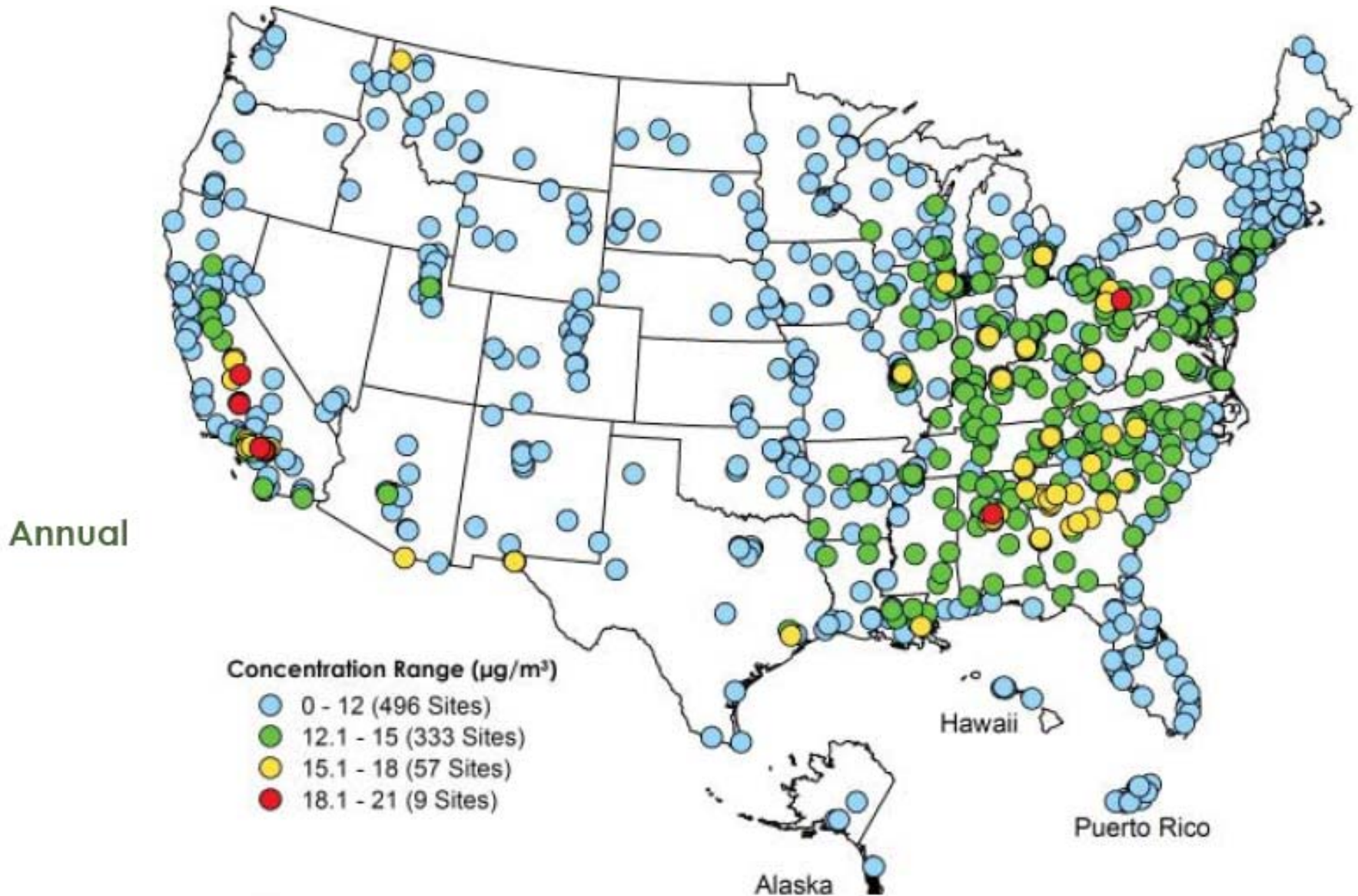


Health Effects of Airborne Particles



Source: DOCKERY DW, POPE CA, XU XP, et al. "AN ASSOCIATION BETWEEN AIR-POLLUTION AND MORTALITY IN 6 UNITED-STATES CITIES", NEW ENGLAND JOURNAL OF MEDICINE 329 (24): 1753-1759 DEC 9 1993.

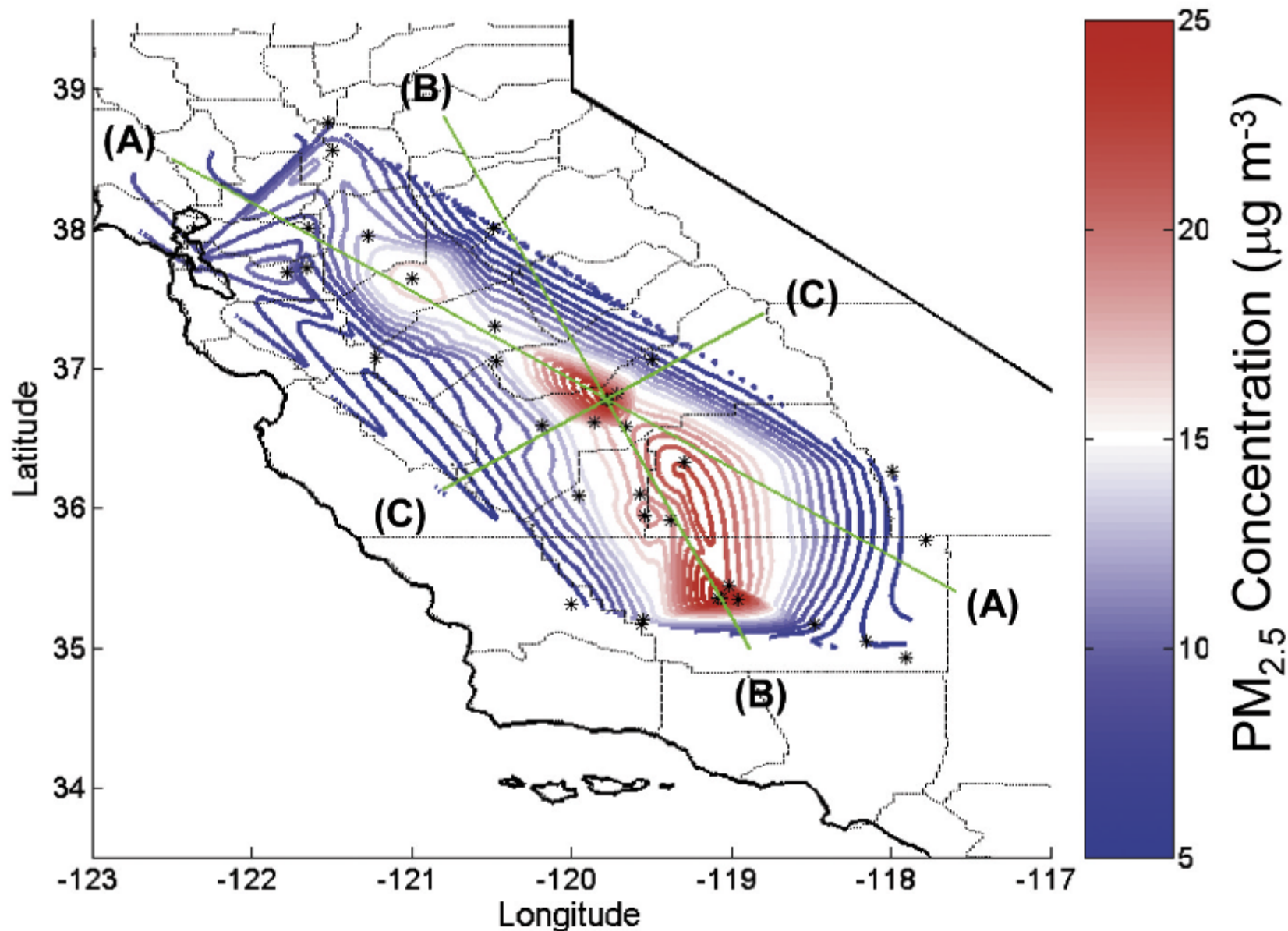
PM2.5 Concentrations in the US



Annual average and daily (98th percentile 24-hour concentrations) $\text{PM}_{2.5}$ concentrations in $\mu\text{g}/\text{m}^3$, 2006.

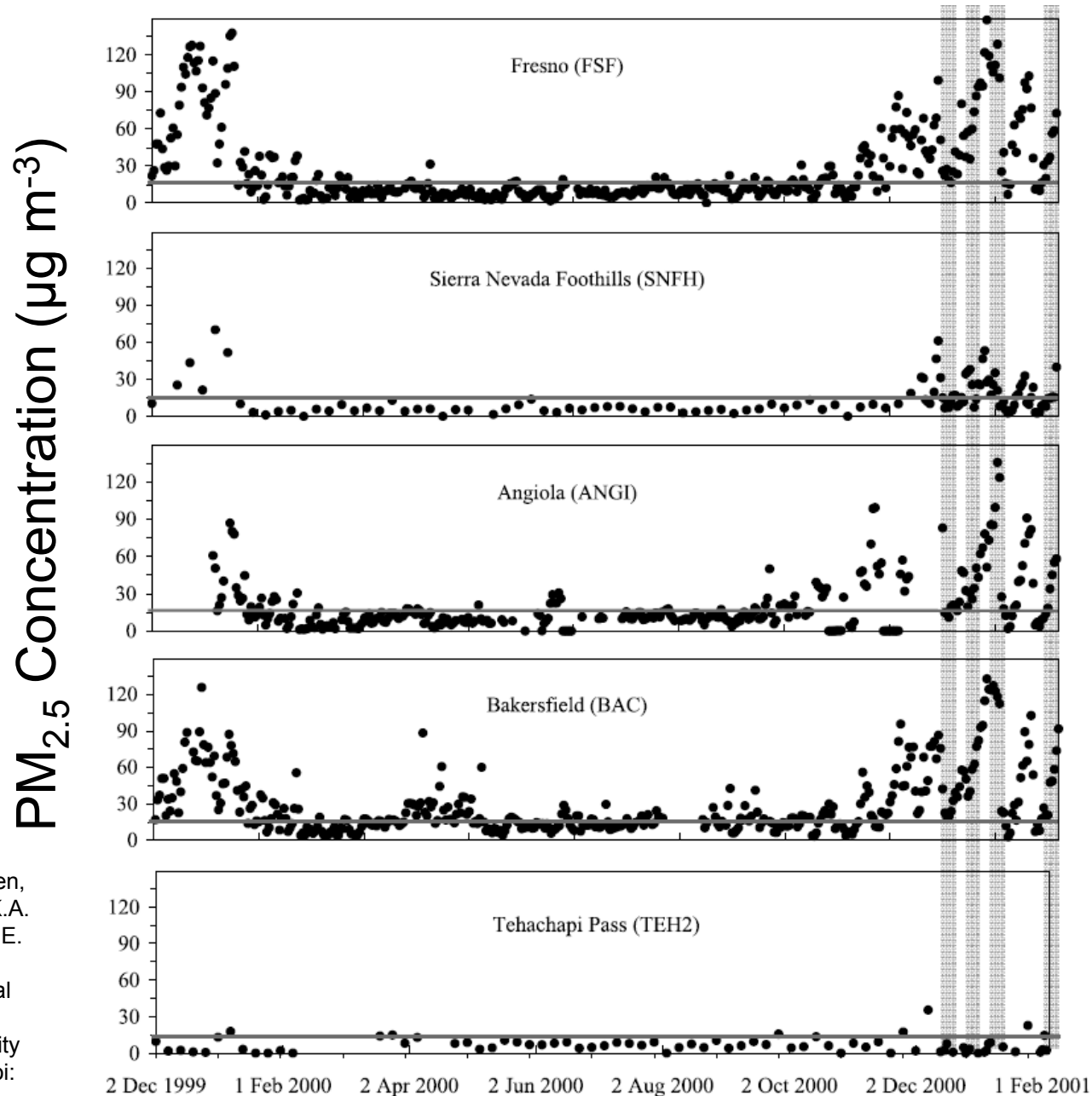
Source: US EPA (<http://www.epa.gov/air/airtrends/2007/report/particlepollution.pdf>).

PM_{2.5} Concentrations in the SJV



Feb 1, 2000 – Jan 31, 2001

PM_{2.5} Seasonal Variation in the SJV



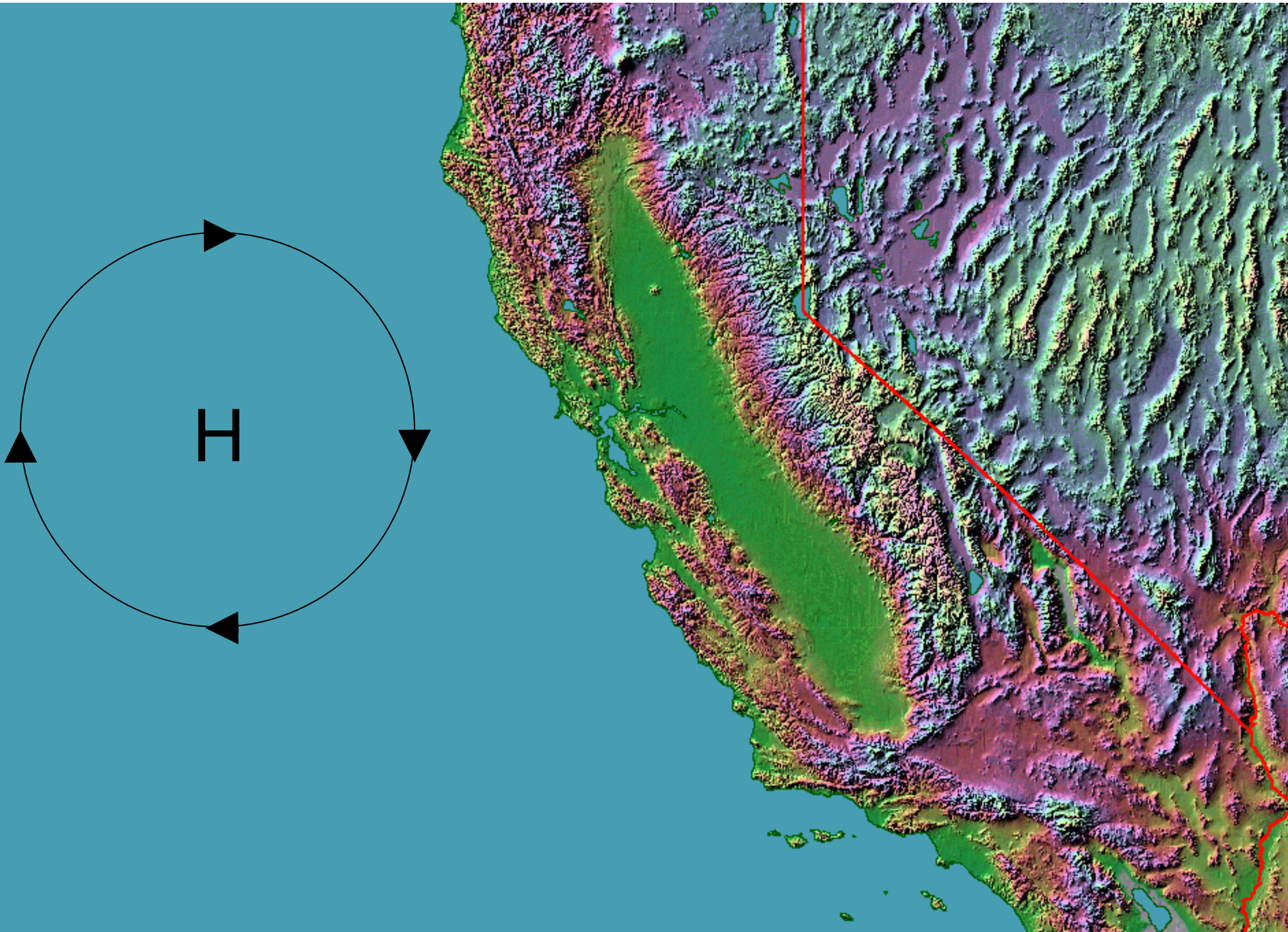
Source: J.C. Chow, L.W. A. Chen, J.G. Watson, D.H. Lowenthal, K.A. Magliano, K. Turkiewicz, and D.E. Lehrman, "PM_{2.5} Chemical Composition and Spatiotemporal Variability During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS), JGR, 111, doi: 10.1029/2005JD006457, 2006.

Questions

- *What are the sources of PM 2.5 in the region and why do they concentrate in winter?*
- *Primary vs. secondary PM 2.5 species;*
- *Where and when do PM 2.5 concentrations vary in the Valley?*
- *What types of control measures have been most successful?*

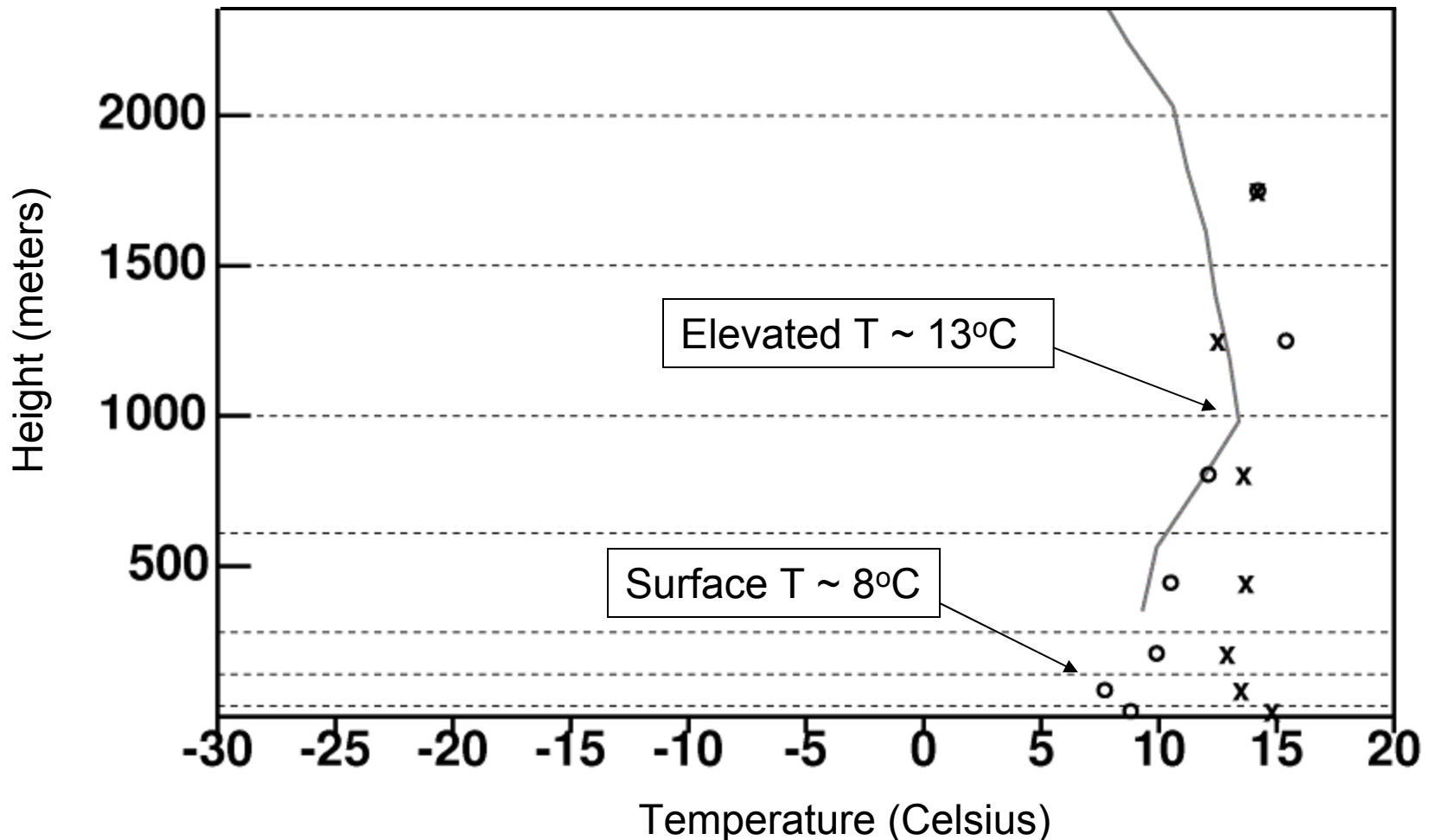
Overview of San Joaquin Valley (SJV)

- Includes Fresno, Kings, Madera, Merced, San Joaquin, Stanislaus, Tulare, and Kern counties
- Approximately 25,000 square miles
- 10% of California's population and growing!
- Days exceeding 8-hr O₃ standard in 2002:
 - LA = 100; SJV = 101
- Peak 24-hr PM_{2.5} concentration in 1999-2000:
 - LA = 121 $\mu\text{g m}^{-3}$; SJV = 160 $\mu\text{g m}^{-3}$

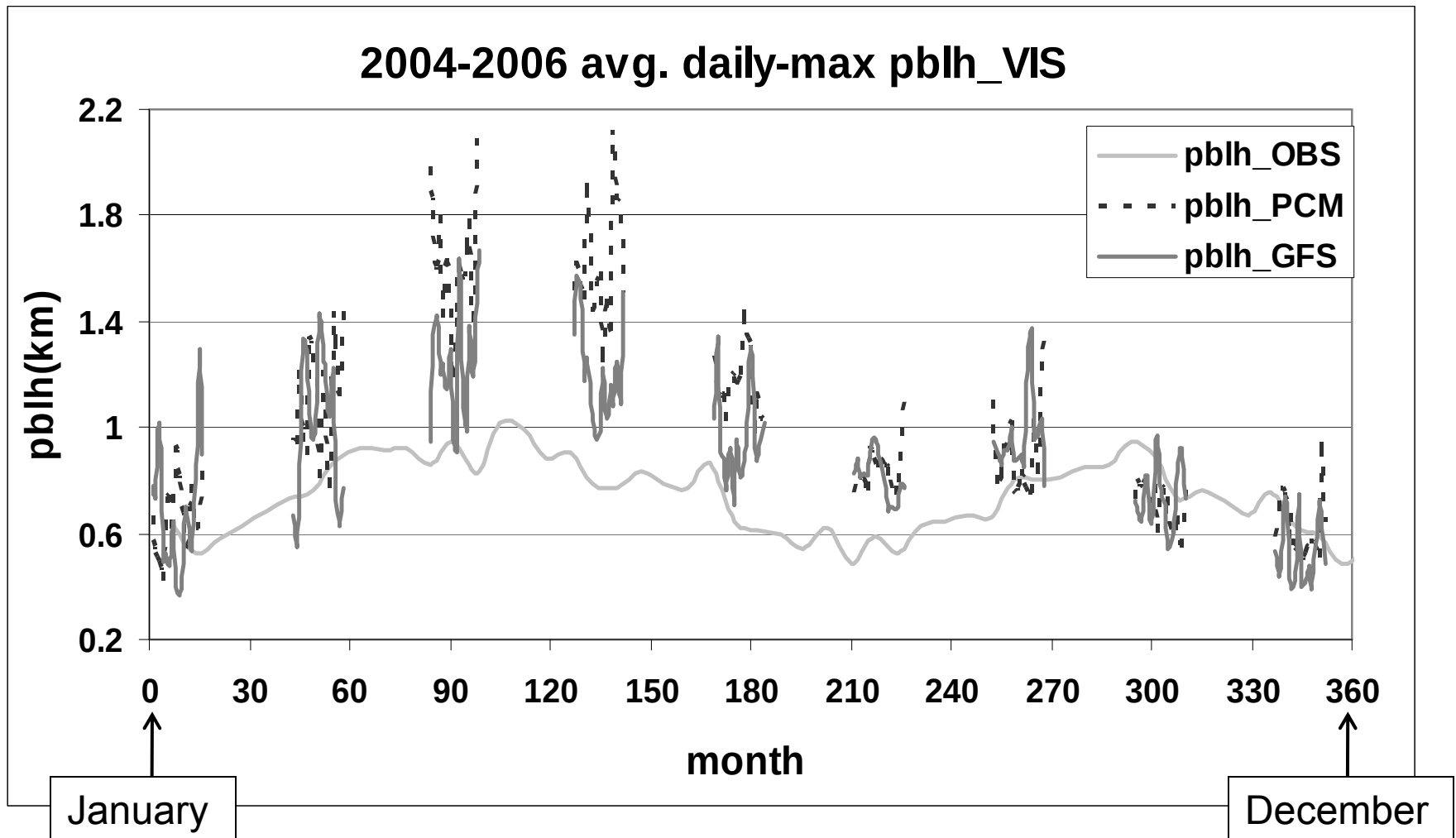


Vertical Temperature Profile

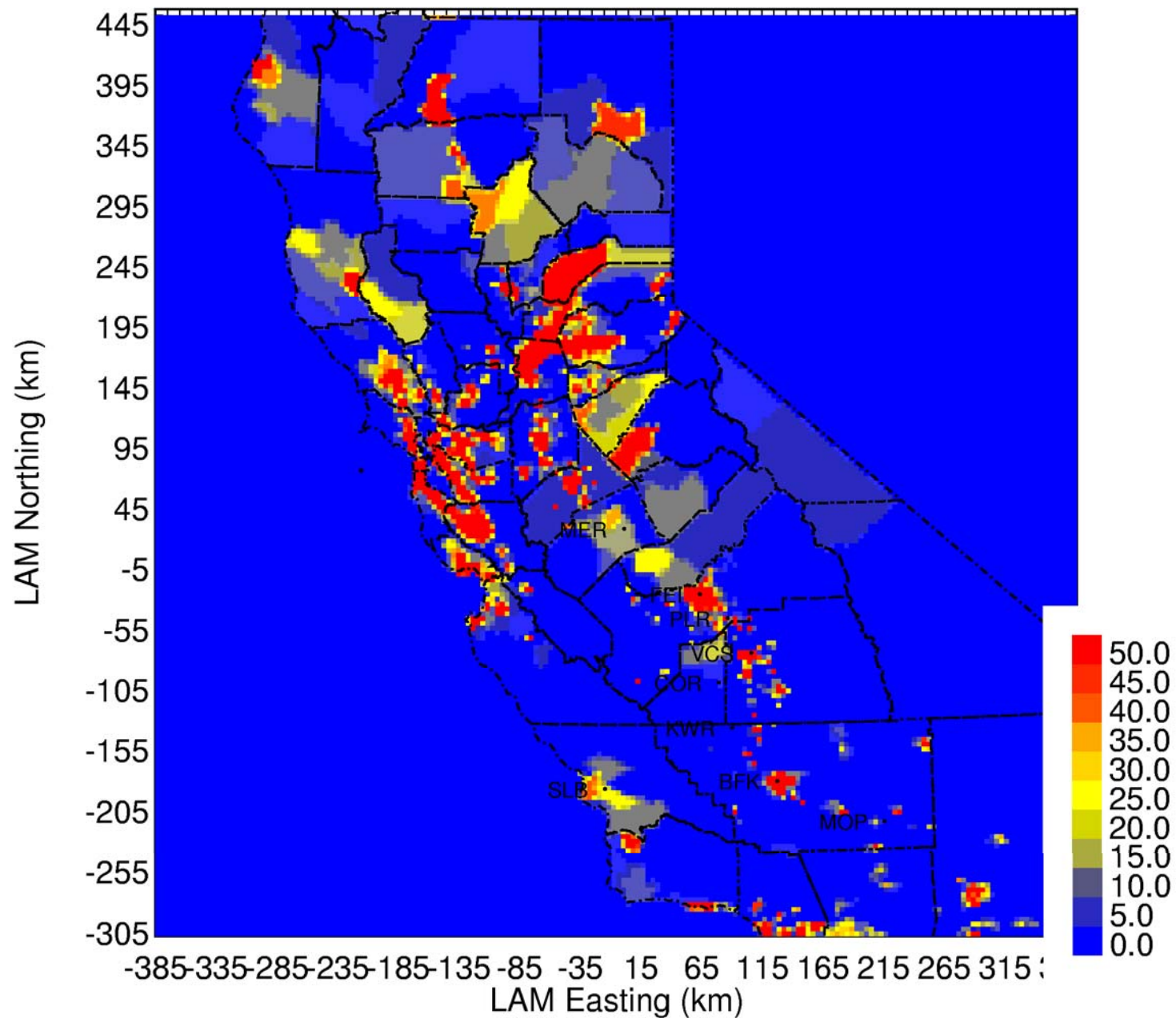
Fresno December 31 2000, 12PST



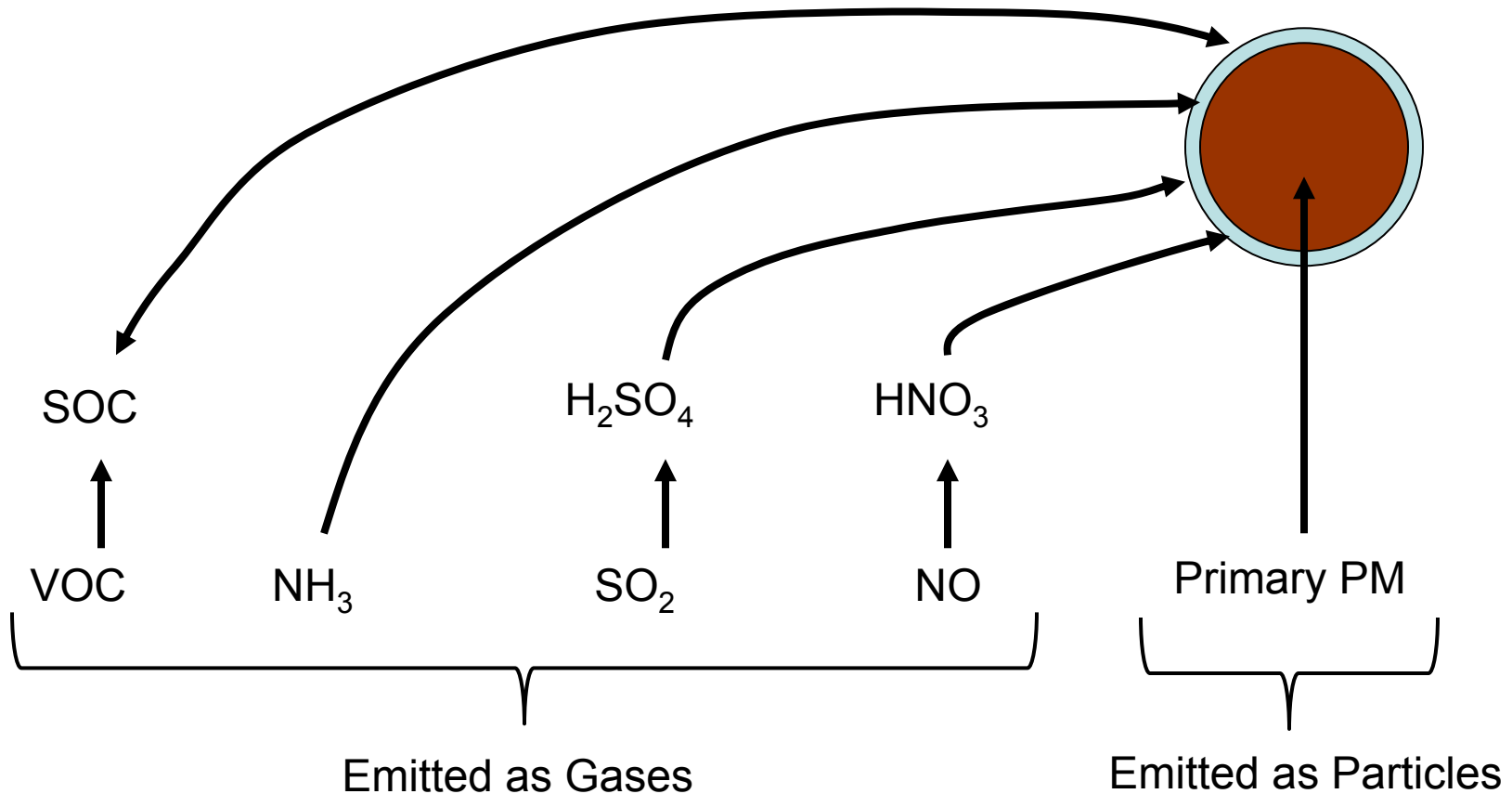
Mixing Depth Annual Cycle



Wood Smoke MASS



Basic Particle Chemistry

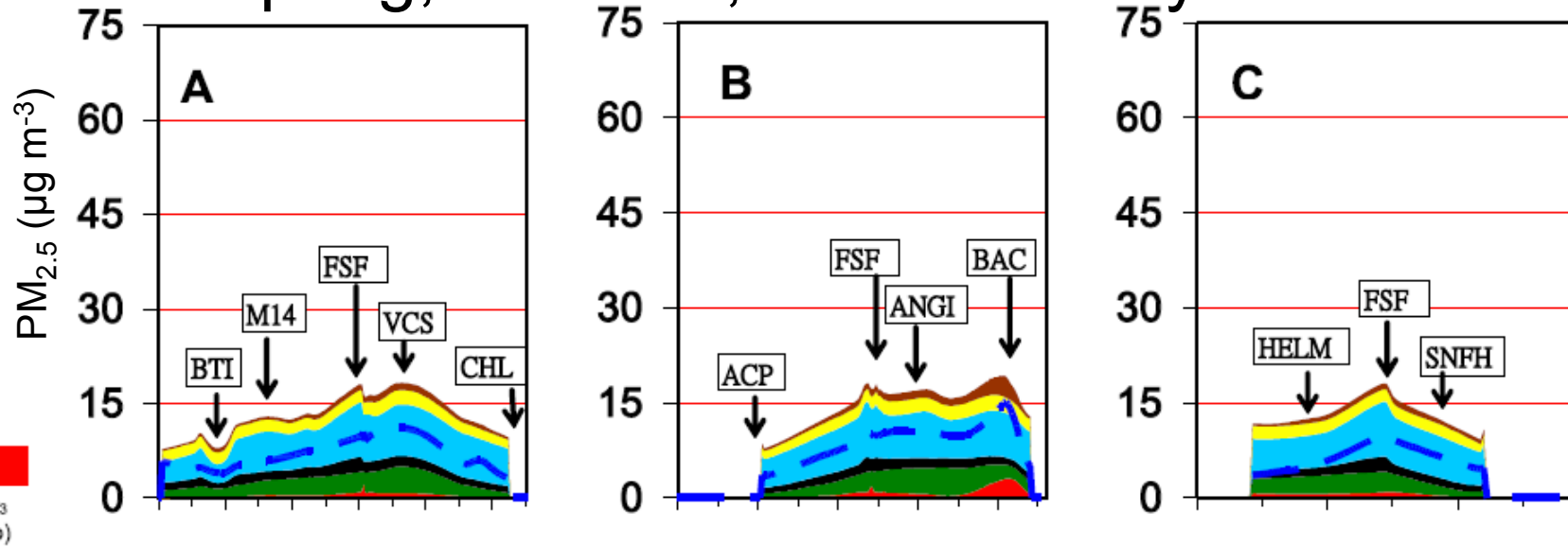


VOC = Volatile Organic Compounds (benzene, ethanol, formaldehyde, ...)

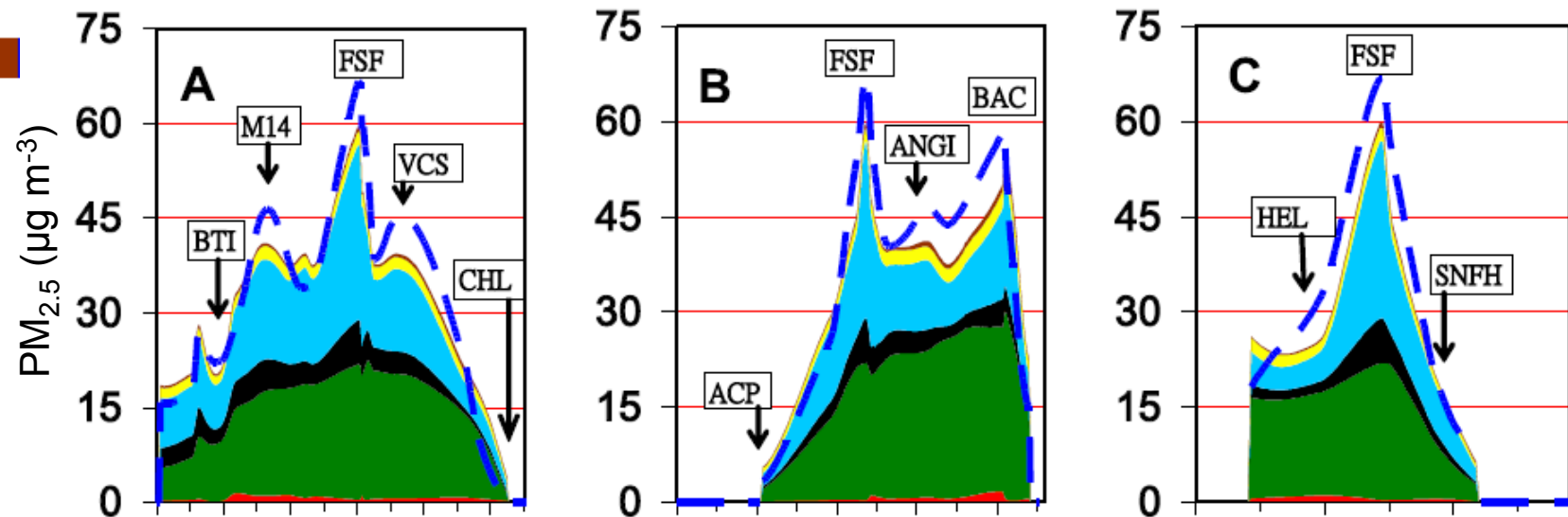
SOC = semi-volatile organic compounds (mostly unknown)

Primary PM = particulate matter emitted directly from sources (trace metals – aluminum, silicon, iron, nickel, etc, elemental carbon, organic carbon)

Spring, Summer, Fall: February - October



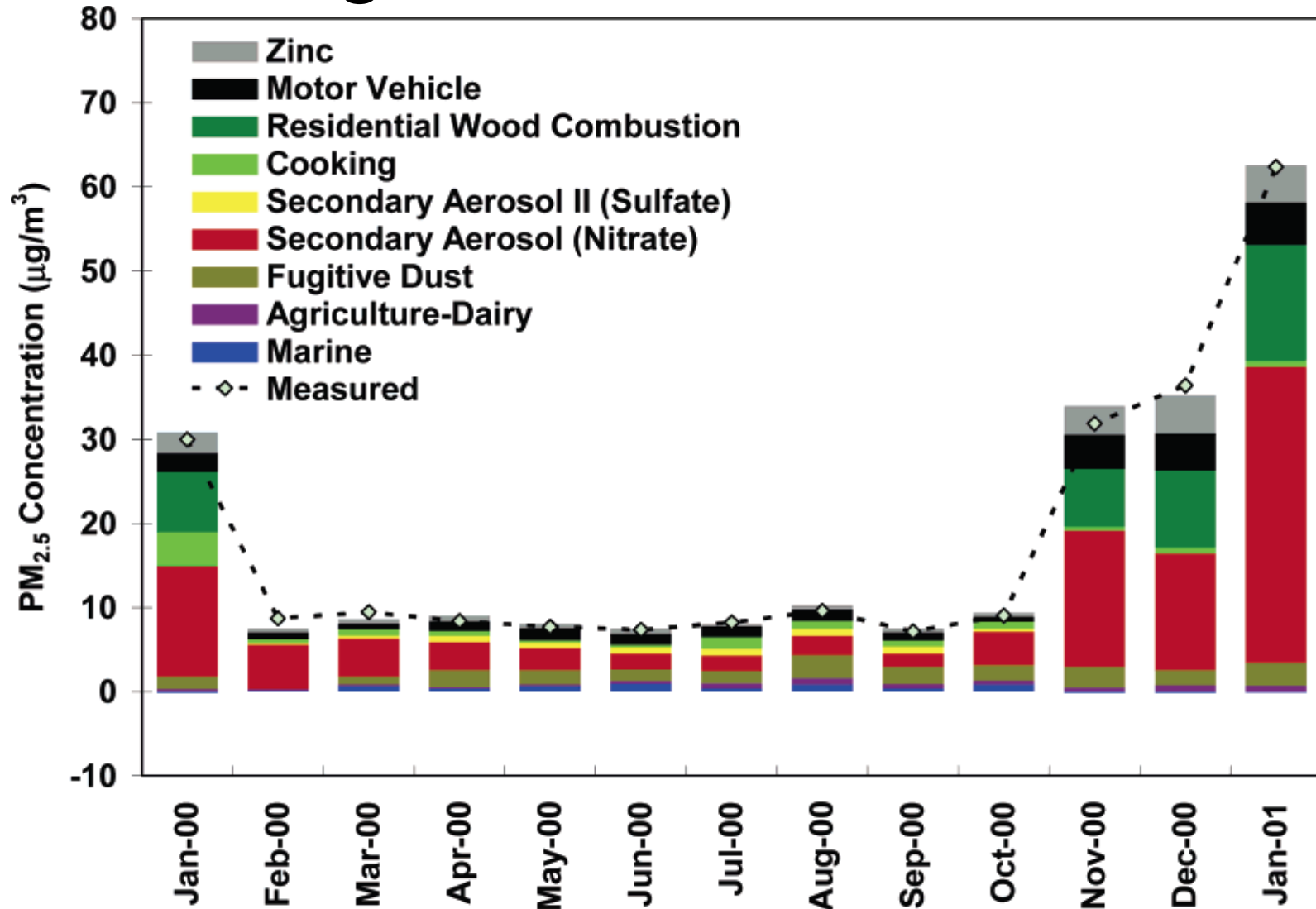
Winter: November - January



Statistical Source-Receptor Models

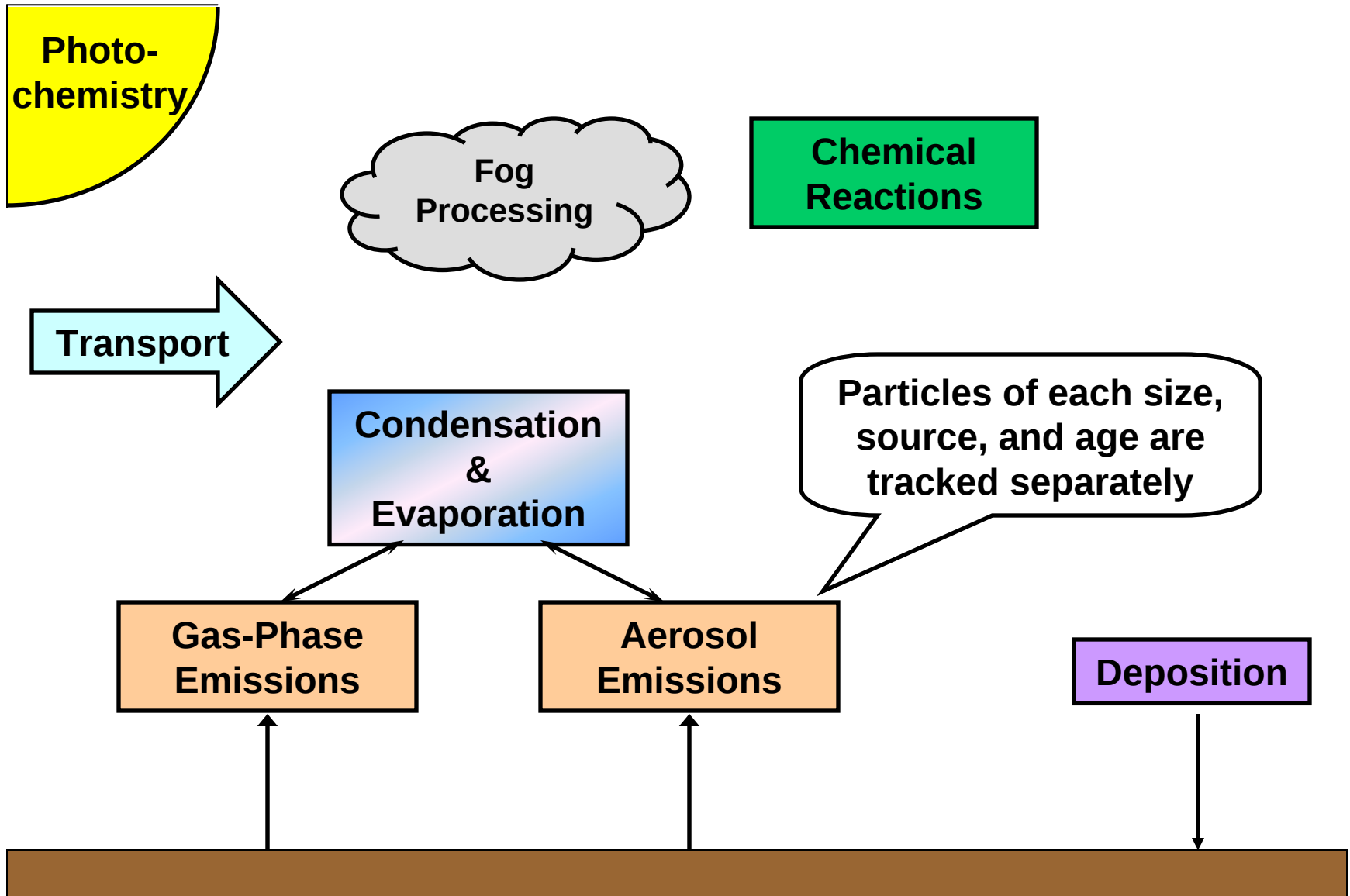
- Measure the composition of the PM at a receptor site
- Calculate source contributions to PM
 - Chemical Mass Balance (CMB)
 - Use source profiles (chemical “fingerprints”)
 - Factor Analysis, PMF, UNMIX, ...
 - Use patterns of variation in the measured signal at the receptor site
 - identifies factors that are “interpreted” as sources

PM_{2.5} Source Contributions Averaged Over CRPAQS Sites

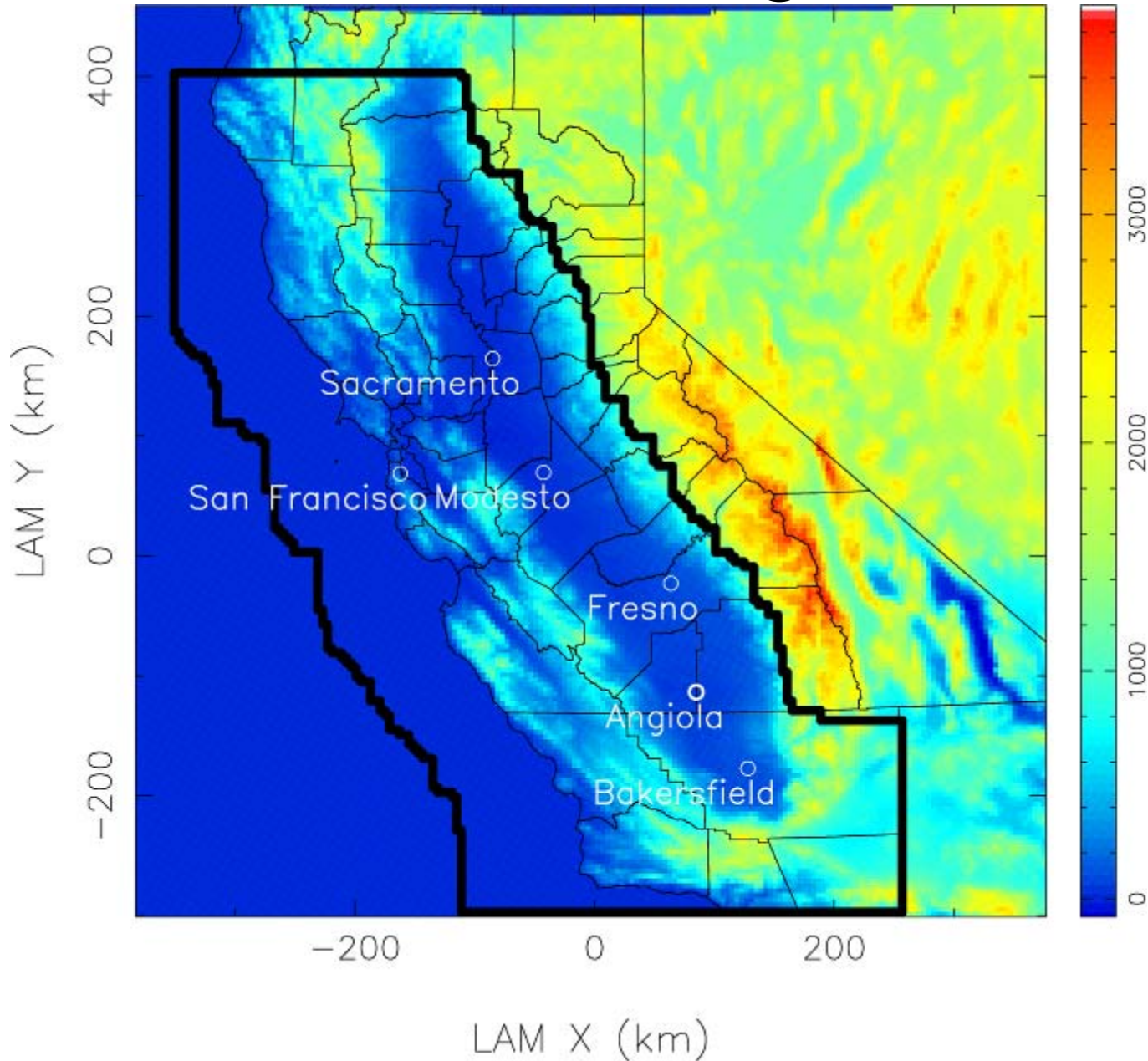


Source: L.W. A. Chen, J.G. Watson, J.C. Chow, and K.A. Magliano, "Quantifying PM_{2.5} Source Contributions for the San Joaquin Valley with Multivariate Receptor Models", ES&T, 41, pg2818-2826, 2007.

Mechanistic Air Quality Models



CRPAQS Modeling Domain



CRPAQS PM2.5 Mass

Black Line – measurements

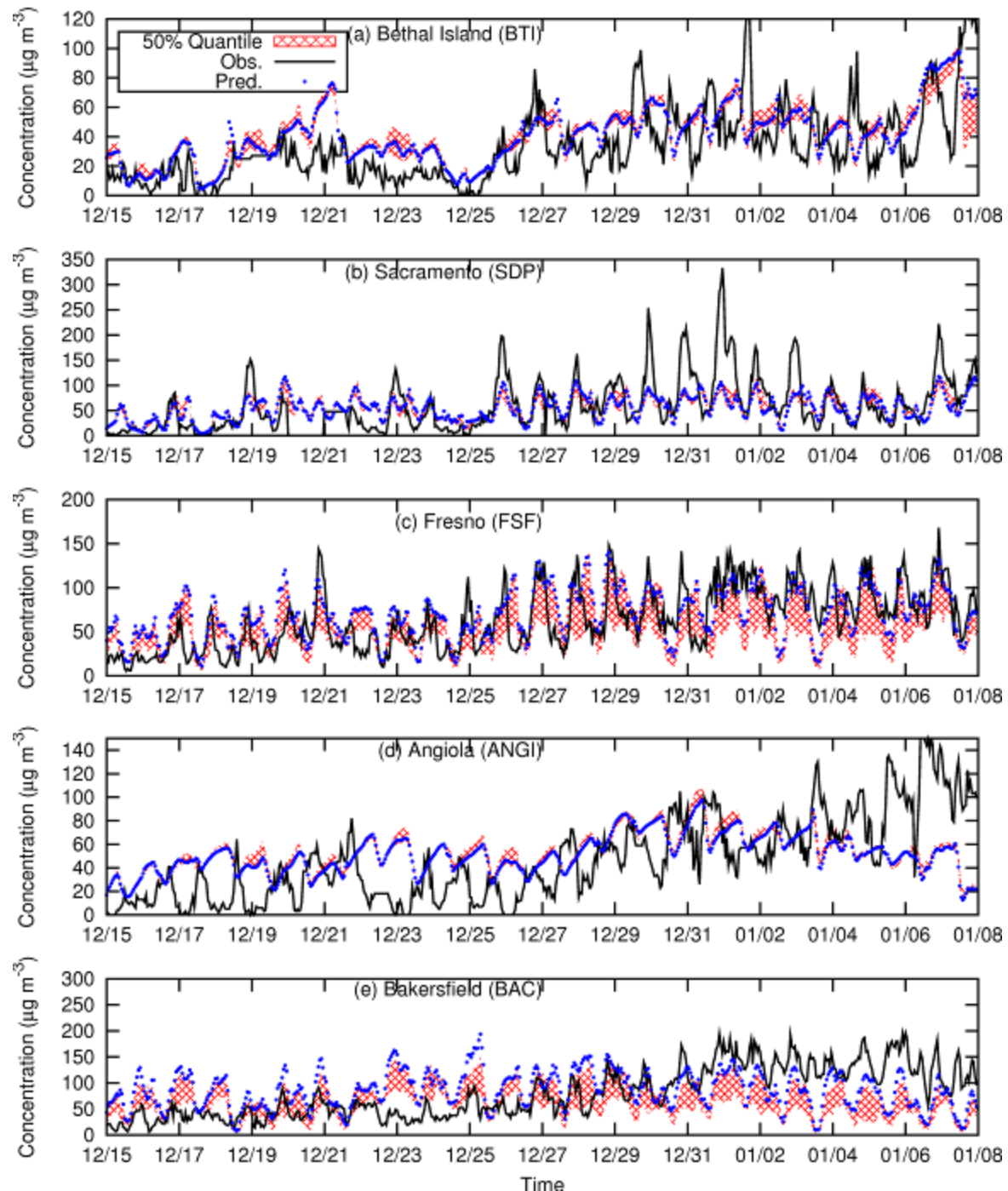
Blue Line – predictions

Red Shading – Mid 50%
Quantile within 10km of
monitor

Major trends are captured at
most stations

Under-prediction of mass at
Angiolo and Bakersfield near
the end of the episode

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., 42, pg8954-8966, 2008.



Relative Component Contributions to PM

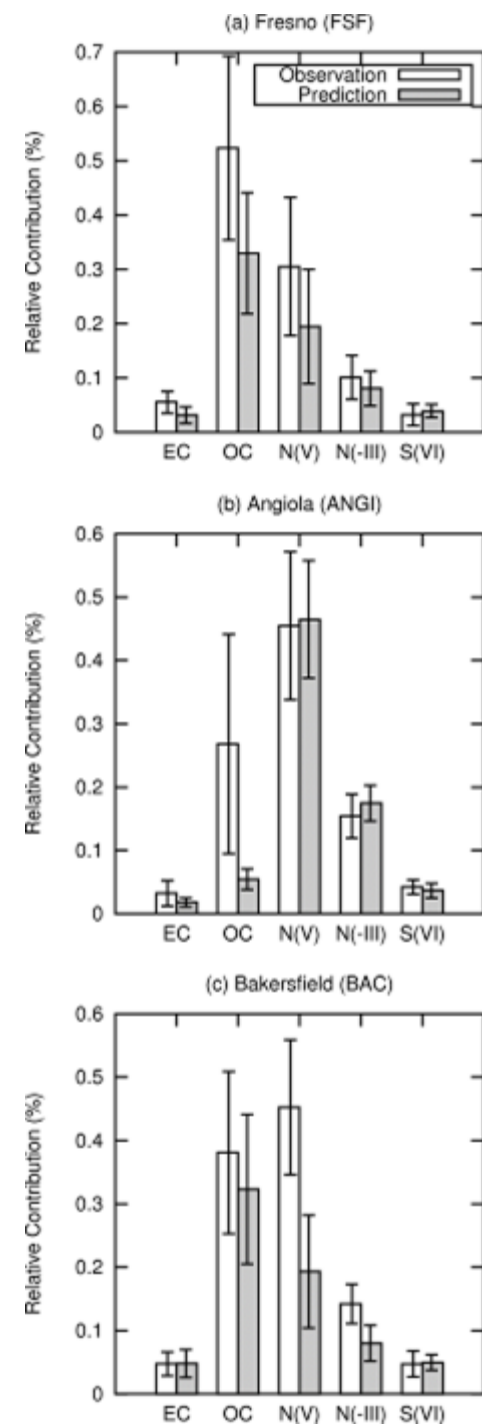
Average and standard deviation of predictions and observations is based on 55 samples

Urban locations (Fresno and Bakersfield)

Predictions and observations match except for nitrate under-prediction at Bakersfield

Rural location (Angiola)

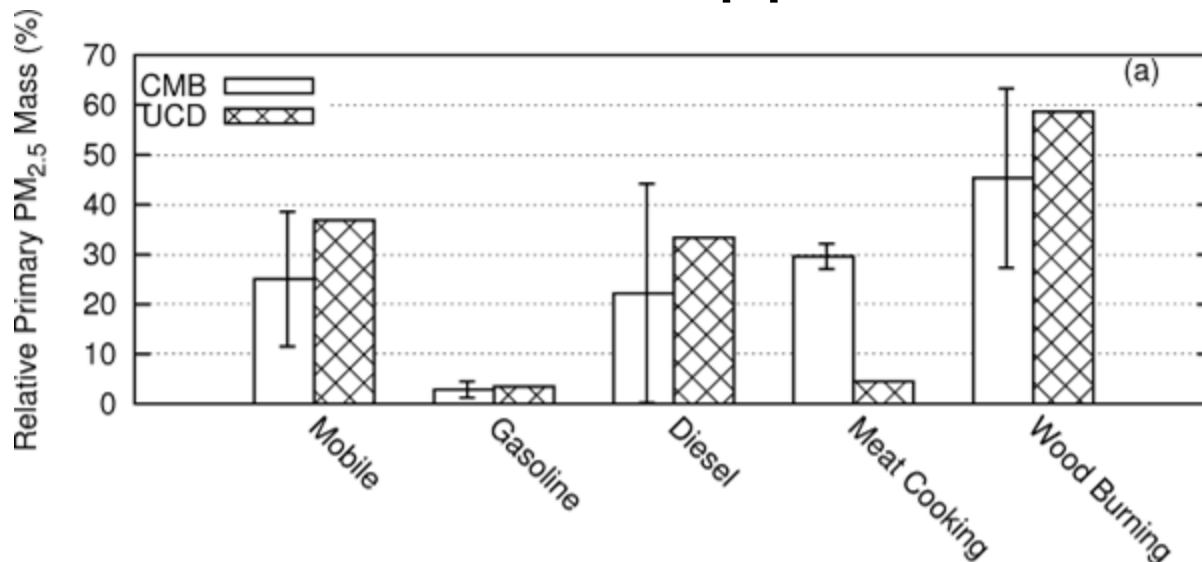
OC under-prediction. What primary sources are we missing? What SOA formation mechanisms are we missing?



Grid Model vs. CMB Source Apportionment

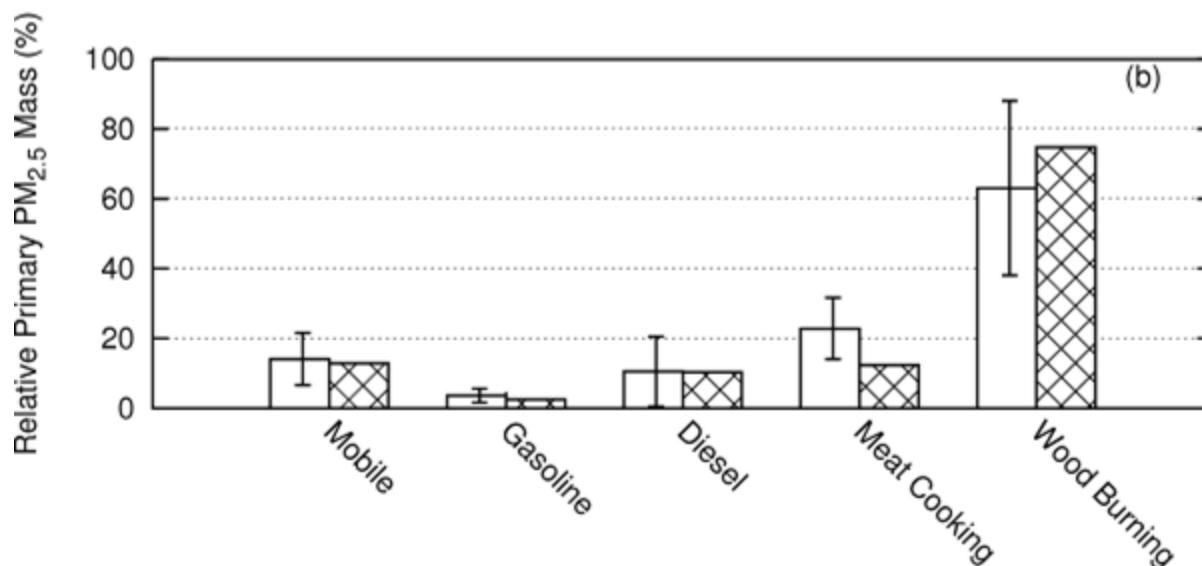
Angiola

**Dust sources removed from grid model



Fresno

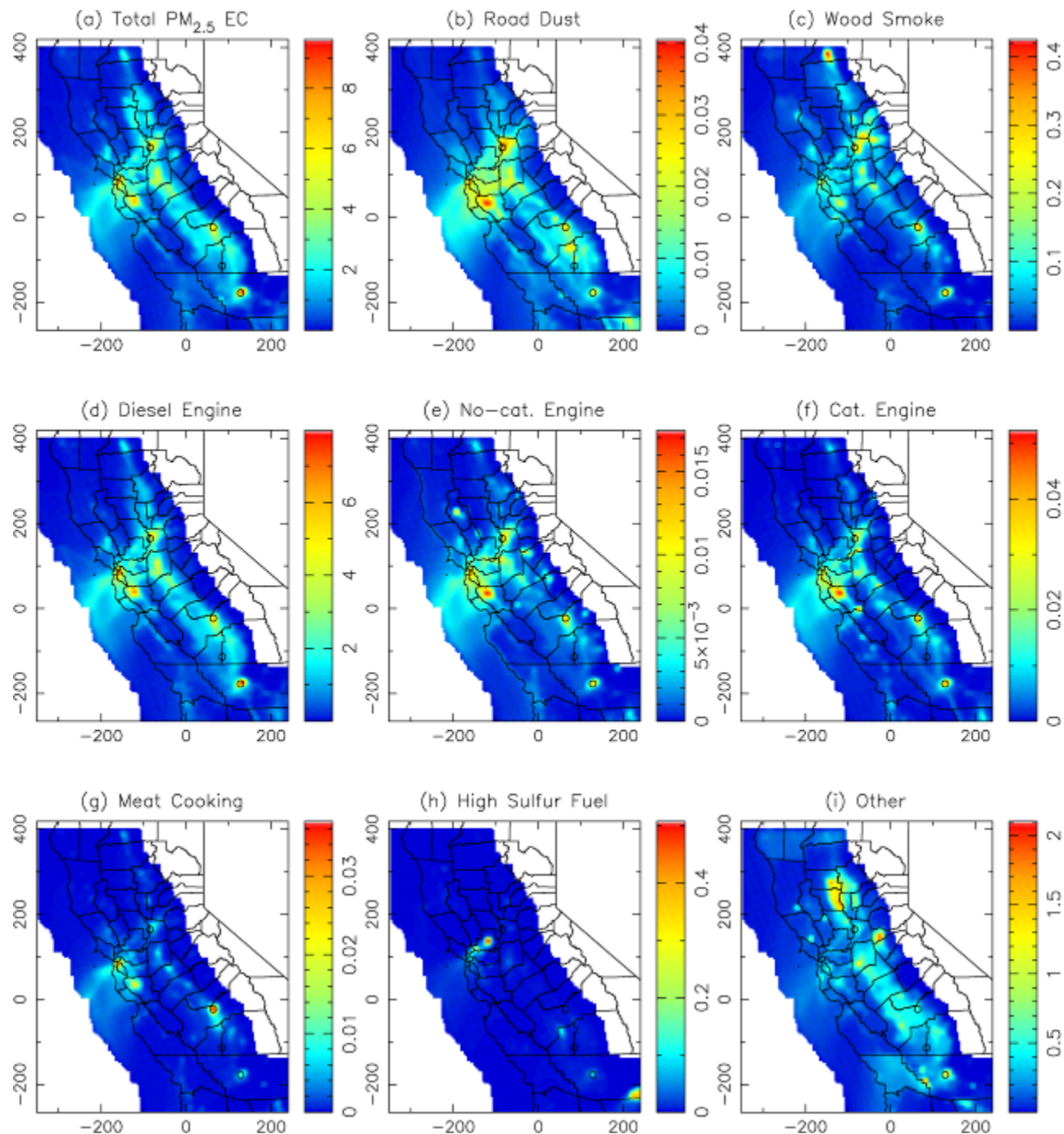
**Dust sources removed from grid model



Regional EC Source Contributions

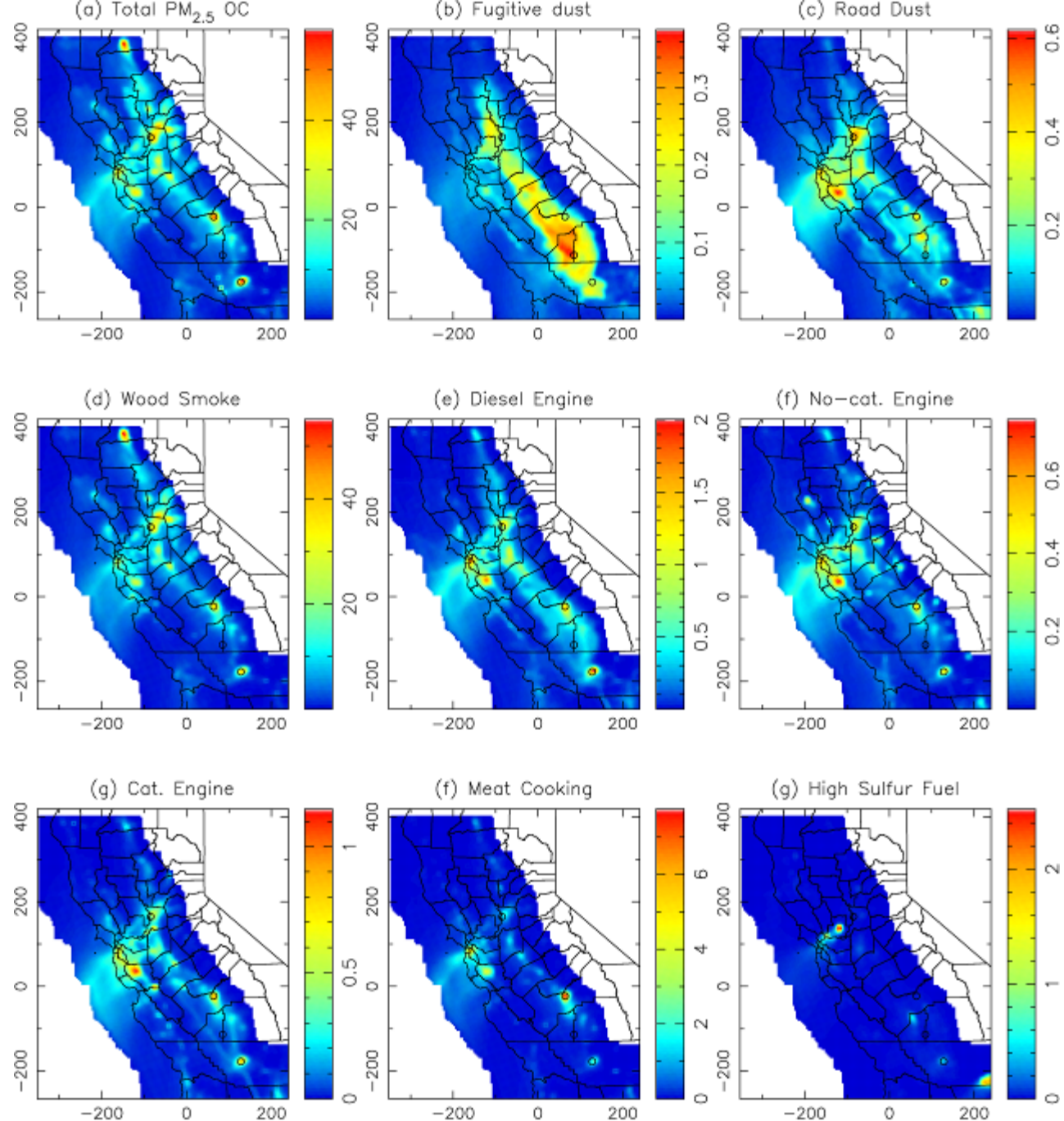
Urban hotspots

Diesel dominates



Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", *Atmos. Env.*, 42, pp8967-8978, 2008.

Regional OC Source Contributions

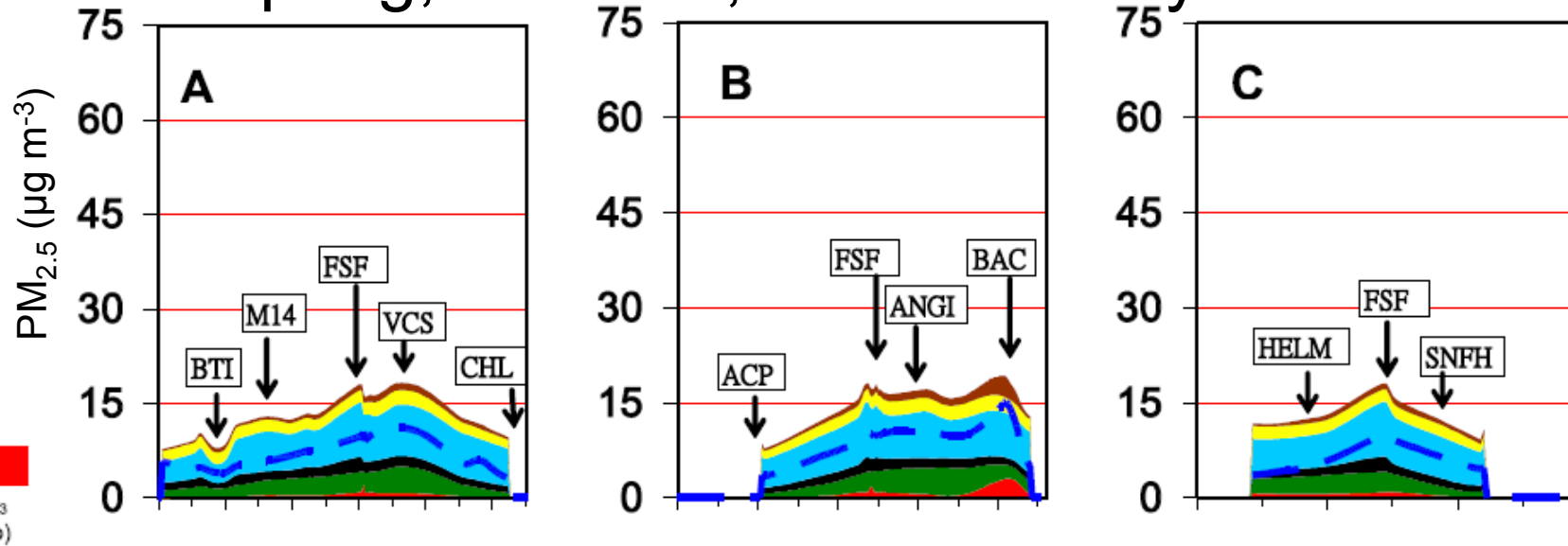


Urban hotspots

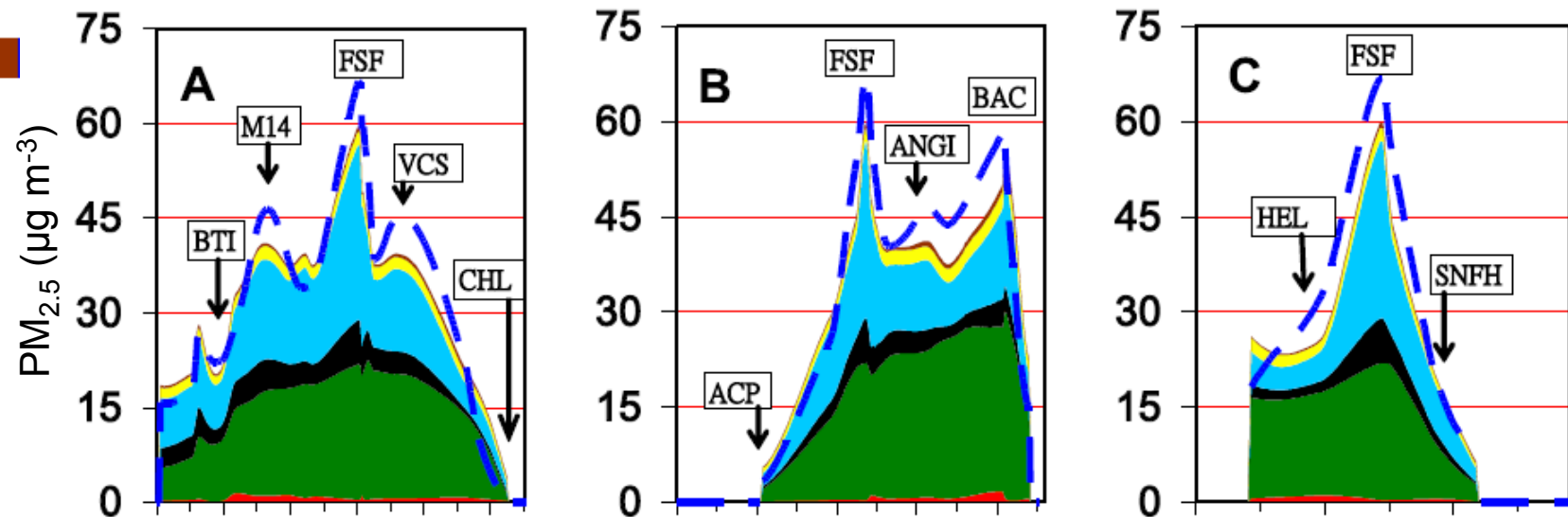
Wood smoke dominates

Source: Q. Ying, J. Lu, A. Kaduvela, and M. Kleeman "Modeling Air Quality During the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", *Atmos. Env.*, 42, pp8967-8978, 2008.

Spring, Summer, Fall: February - October

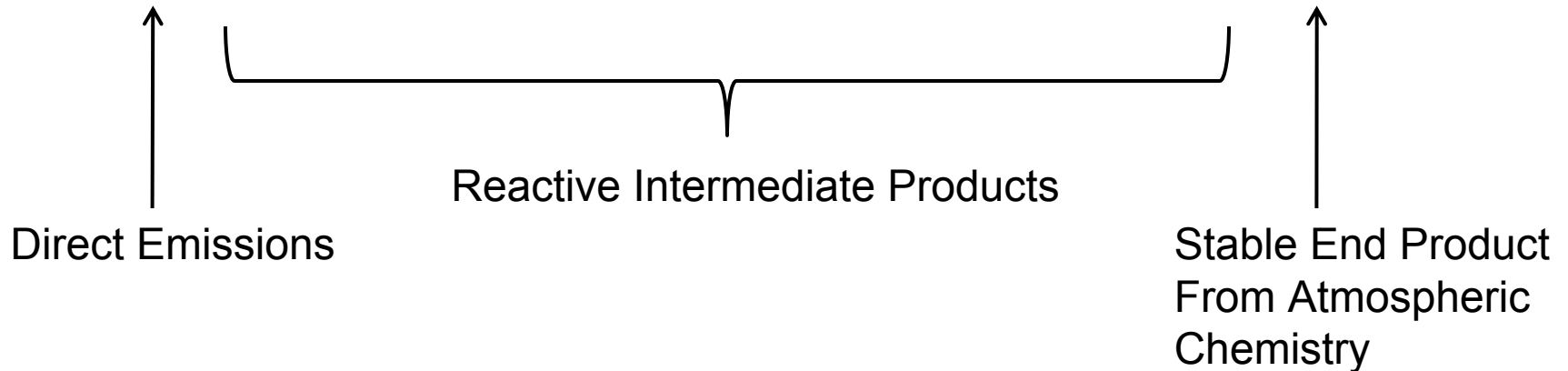


Winter: November - January



Spectrum of Reactive Nitrogen Compounds

- NO, NO₂, NO₃, N₂O₅, HONO, PAN, HNO₃



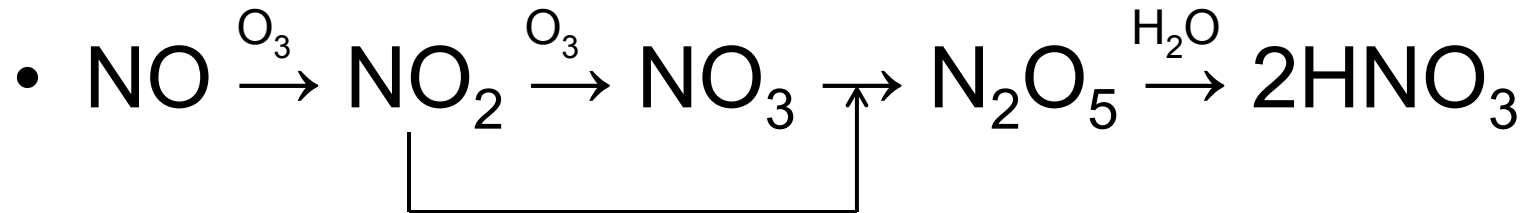
Direct Emissions

Particle Phase Nitrate

Daytime/Summer Nitrate Formation

- $\text{NO} \xrightarrow{\text{O}_3} \text{NO}_2 \xrightarrow{\text{OH}} \text{HNO}_3$
- Main oxidant is OH – requires high sunlight, VOC rich environment

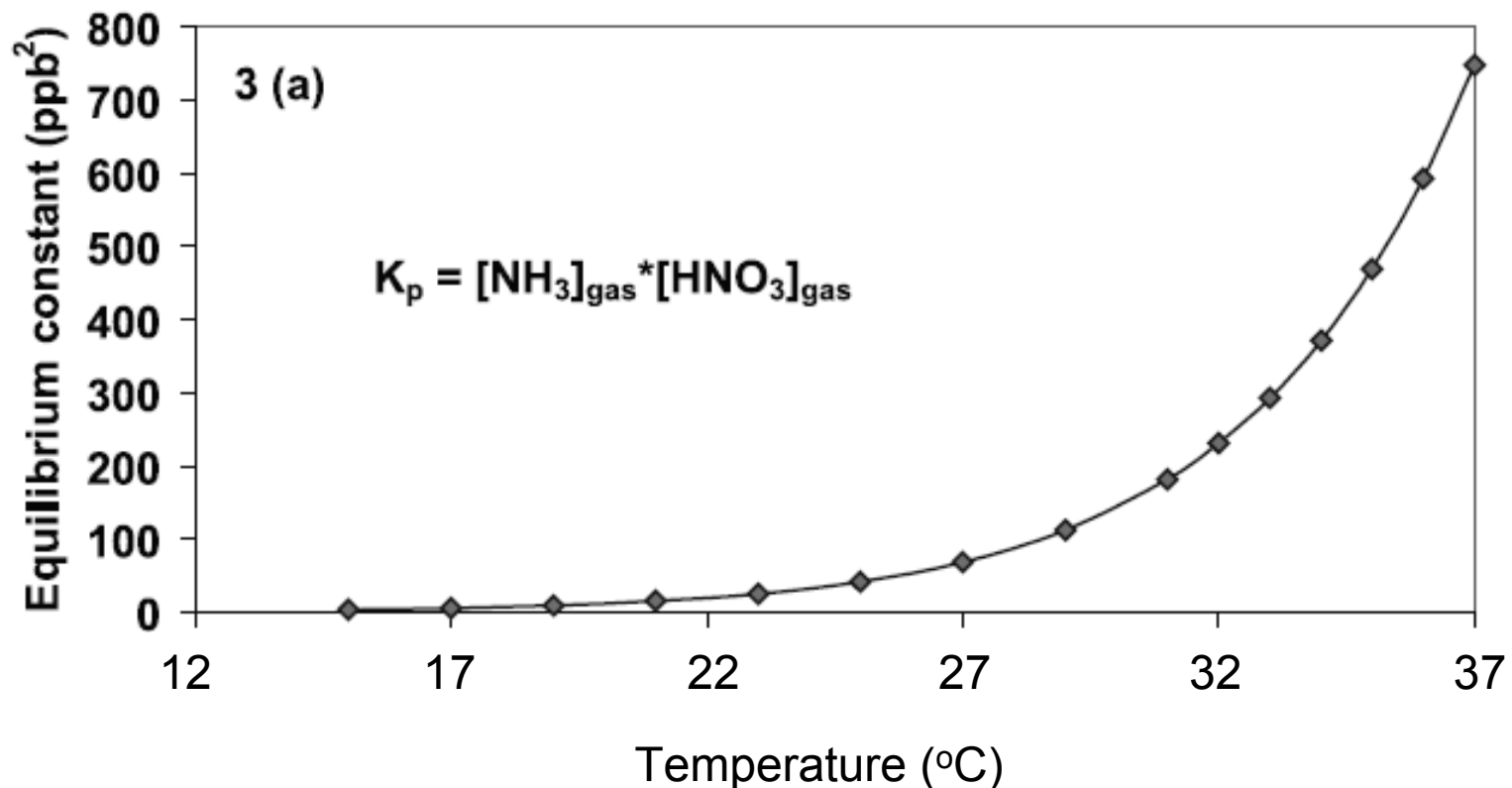
Nighttime/Winter Nitrate Formation



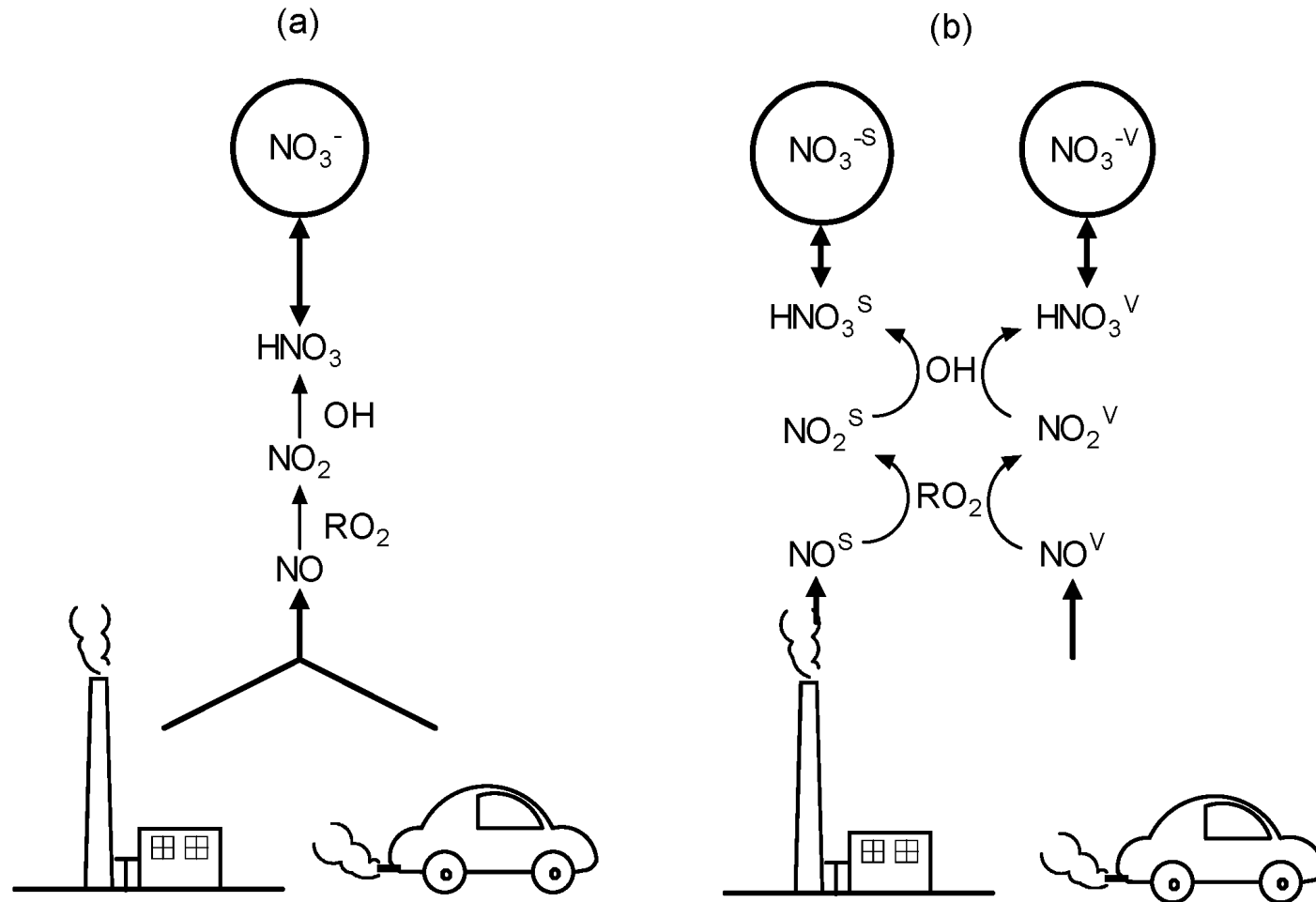
- Main oxidant is O_3 – favors low sunlight intensity, wet conditions

Equilibrium Dissociation Constant for Ammonium Nitrate

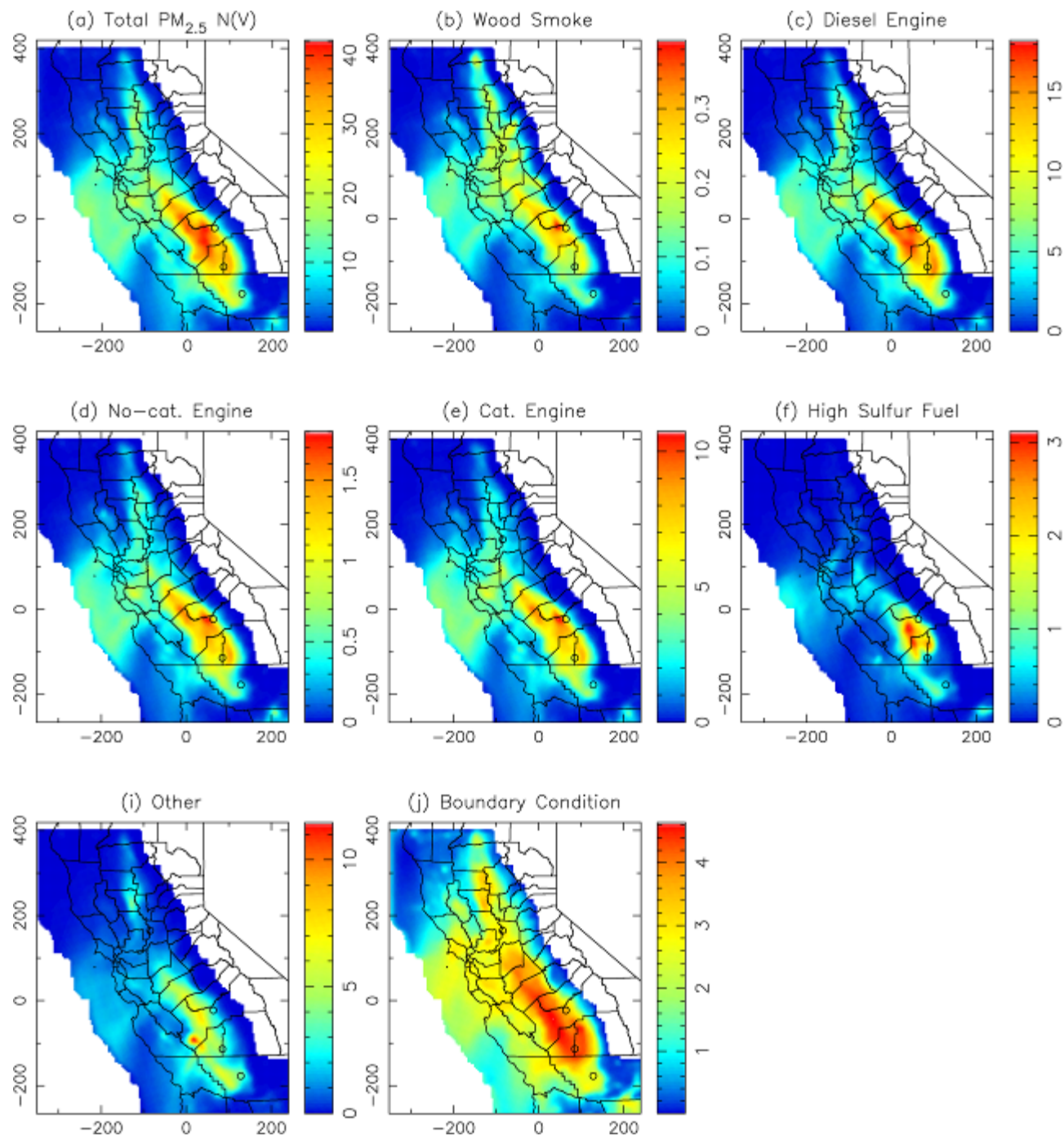
Ammonium nitrate will not form when $[\text{NH}_3] \cdot [\text{HNO}_3] < K_p$



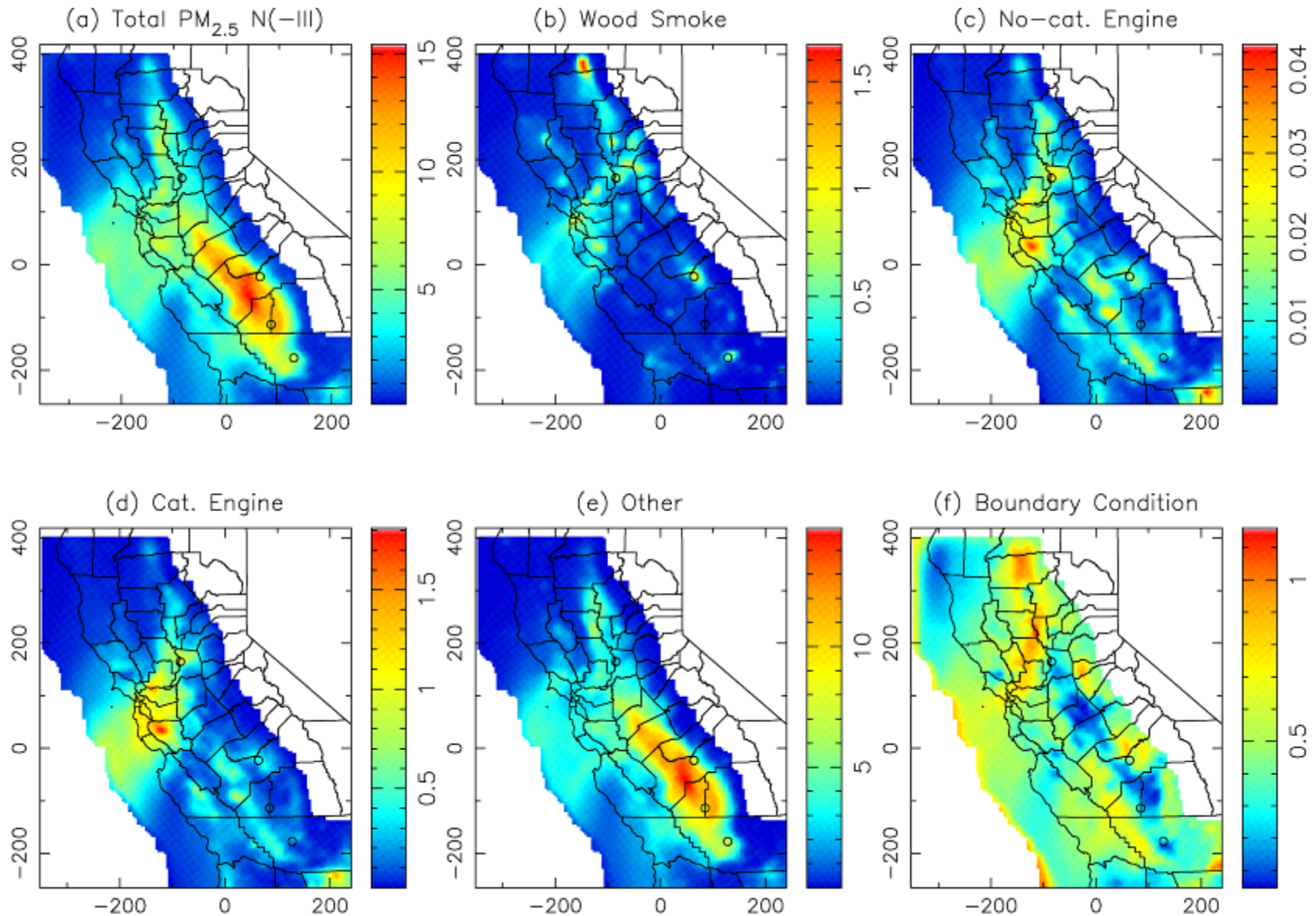
Source Apportionment of Secondary PM



Regional Nitrate Source Contributions

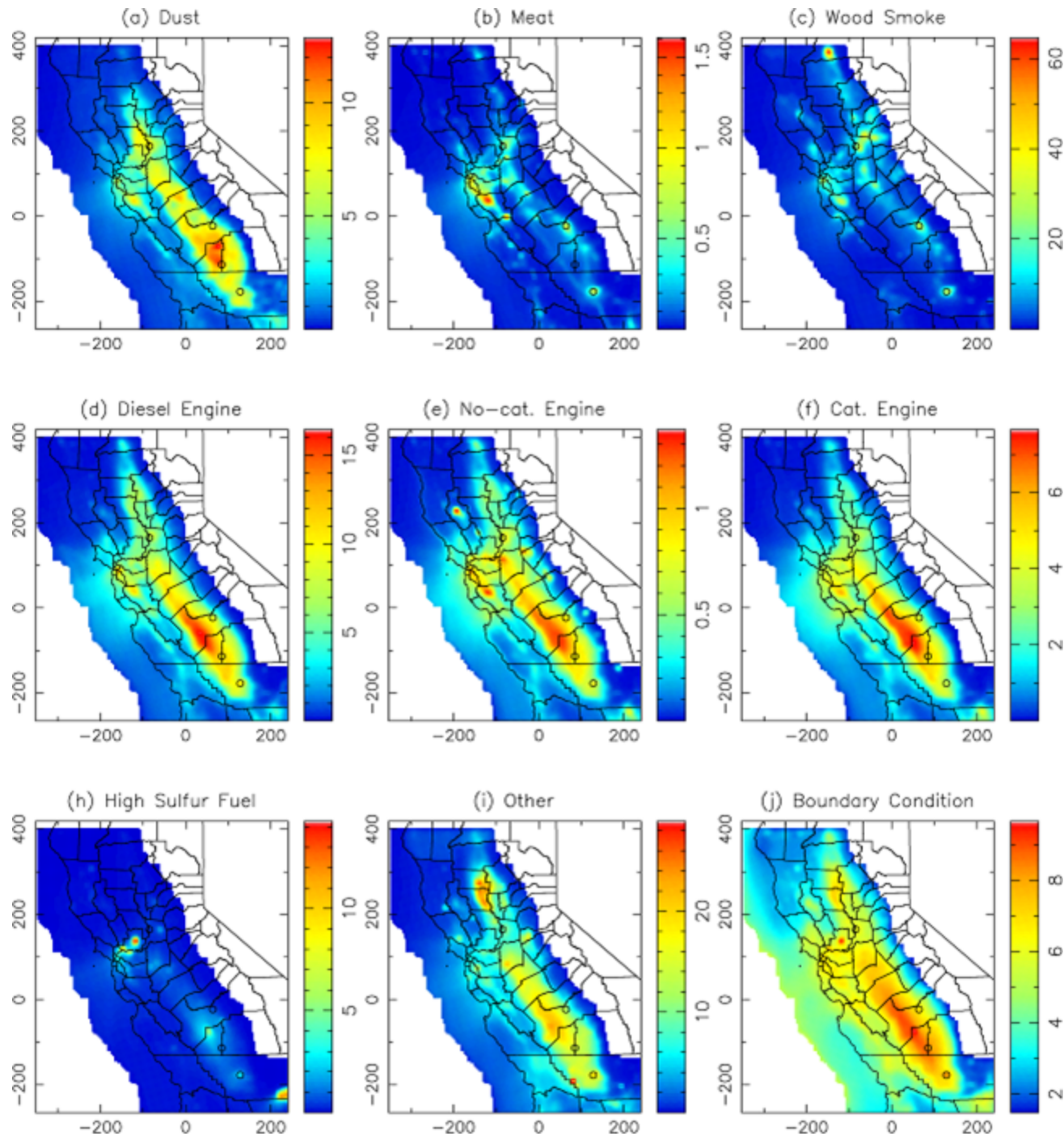


Regional NH₄⁺ Source Contributions



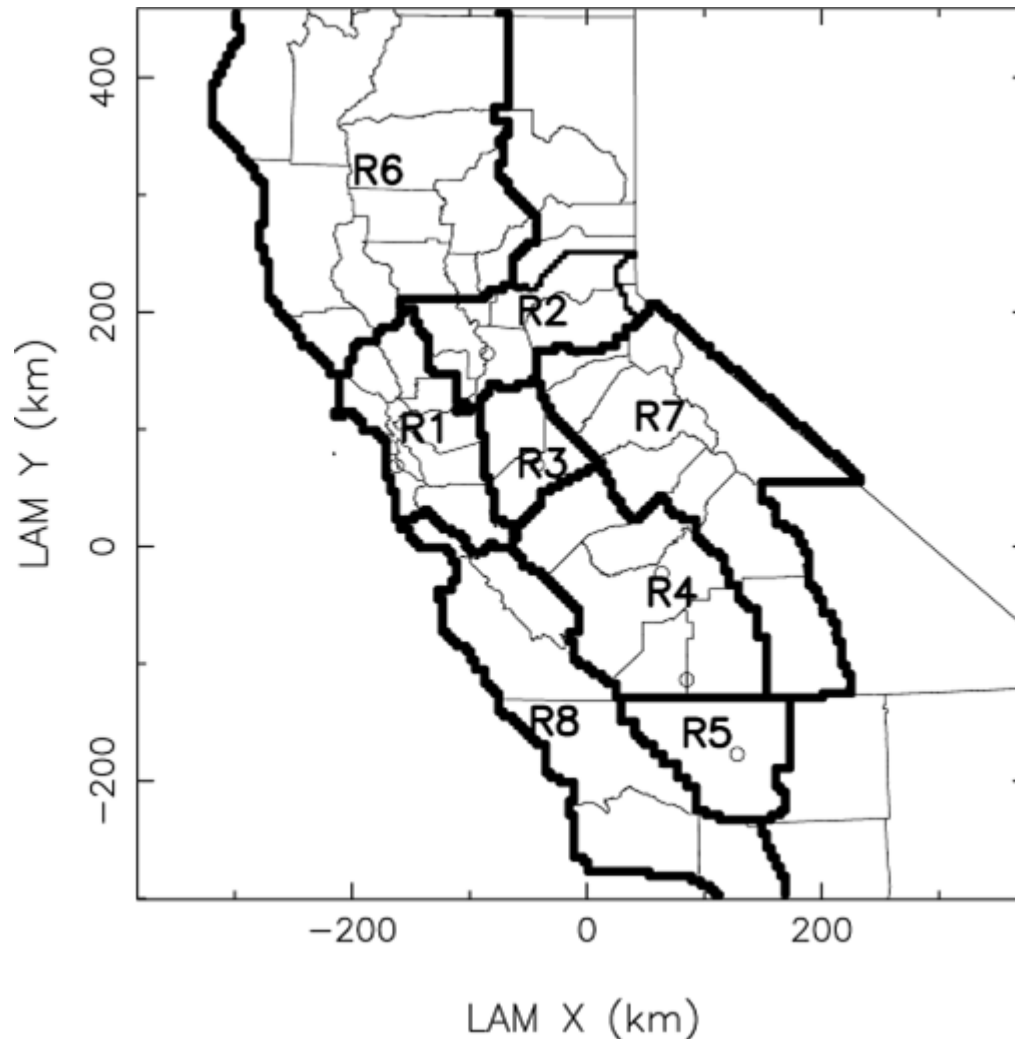
Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM_{2.5} and PM_{0.1}.", *Atmos. Env.*, 42, pp8967-8978, 2008.

Regional PM_{2.5} (primary + secondary) Source Contributions

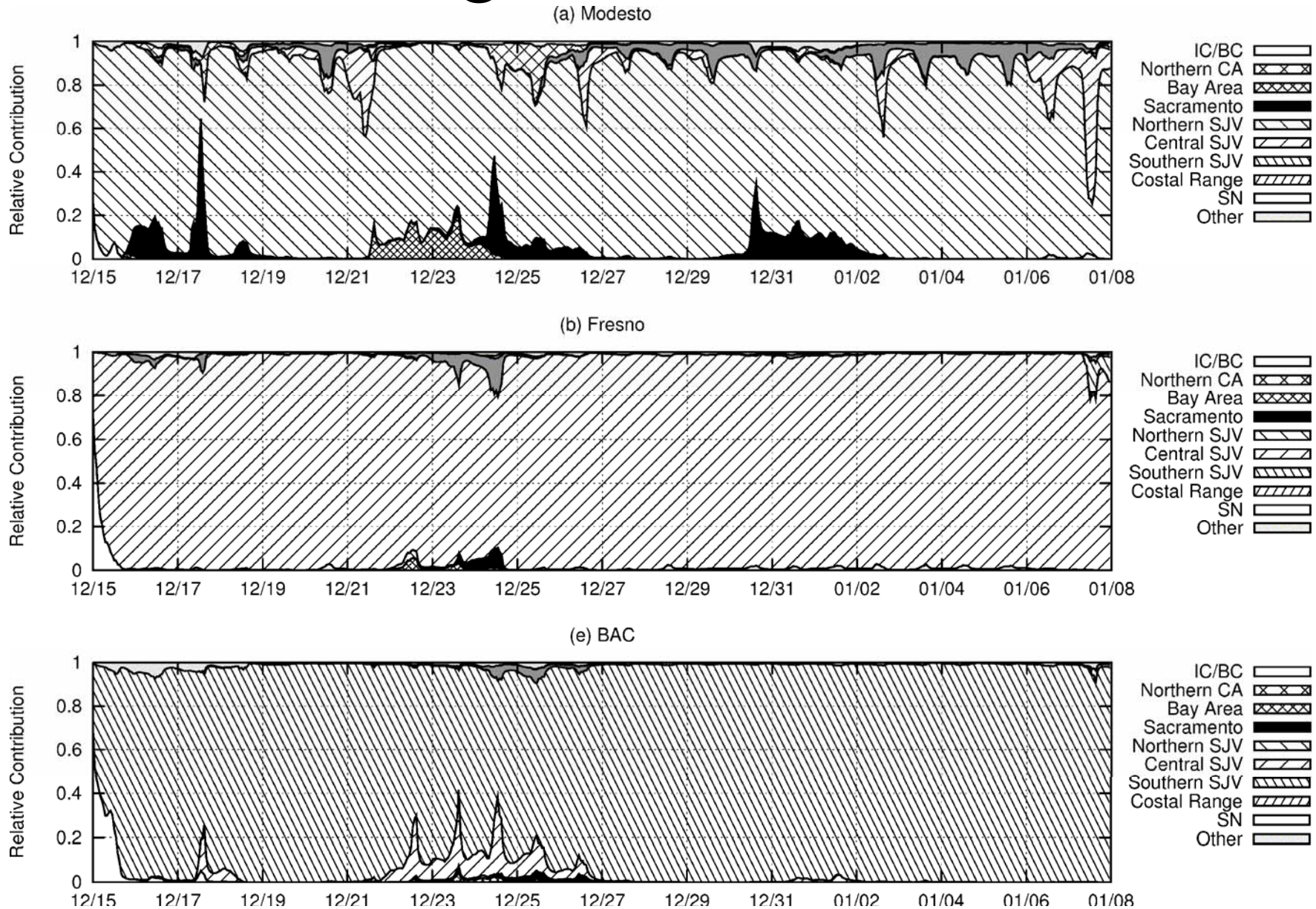


Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM_{2.5} and PM_{0.1}.", Atmos. Env., 43, pp419-430, 2009.

How Much PM Does Each Region Contribute to Other Regions?

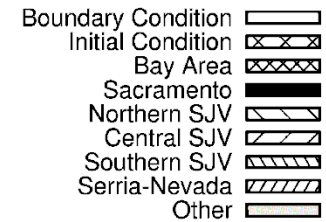
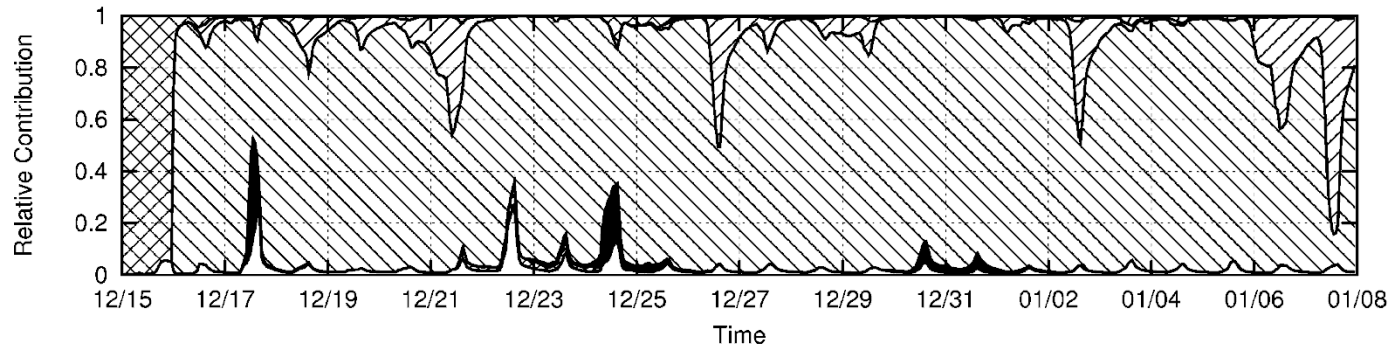


OC Region Contributions

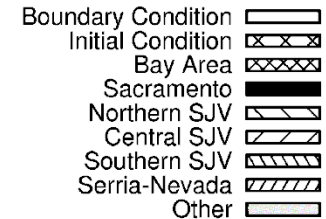
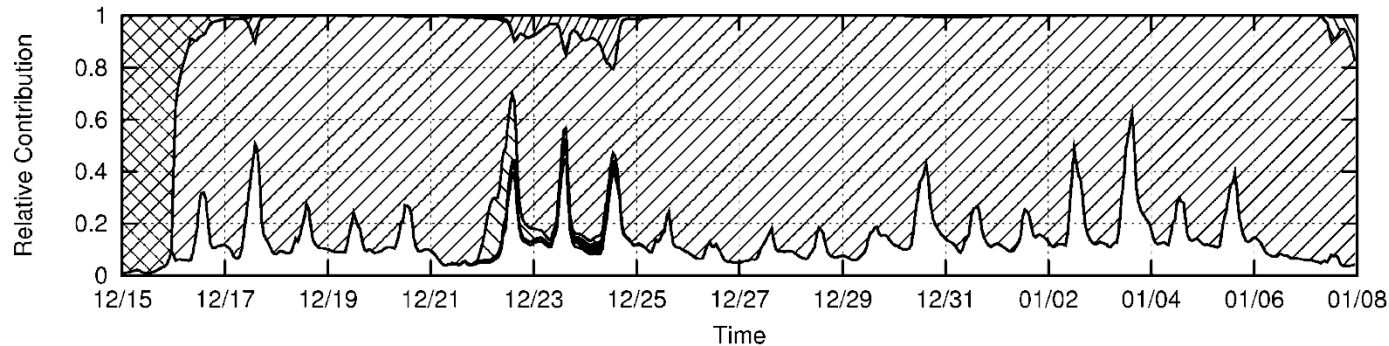


Ammonium Region Contributions

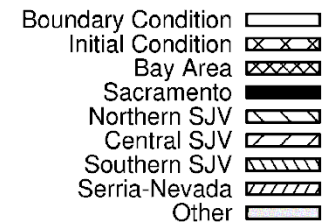
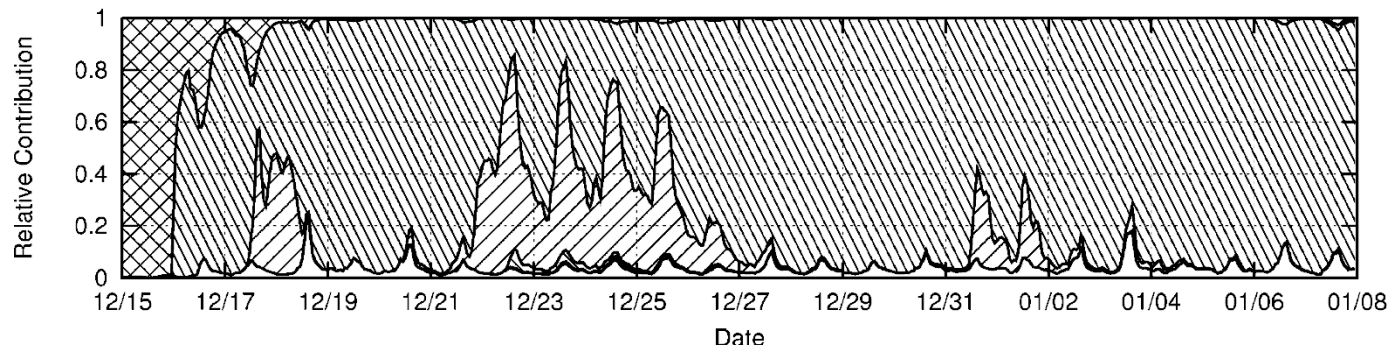
(a) Modesto



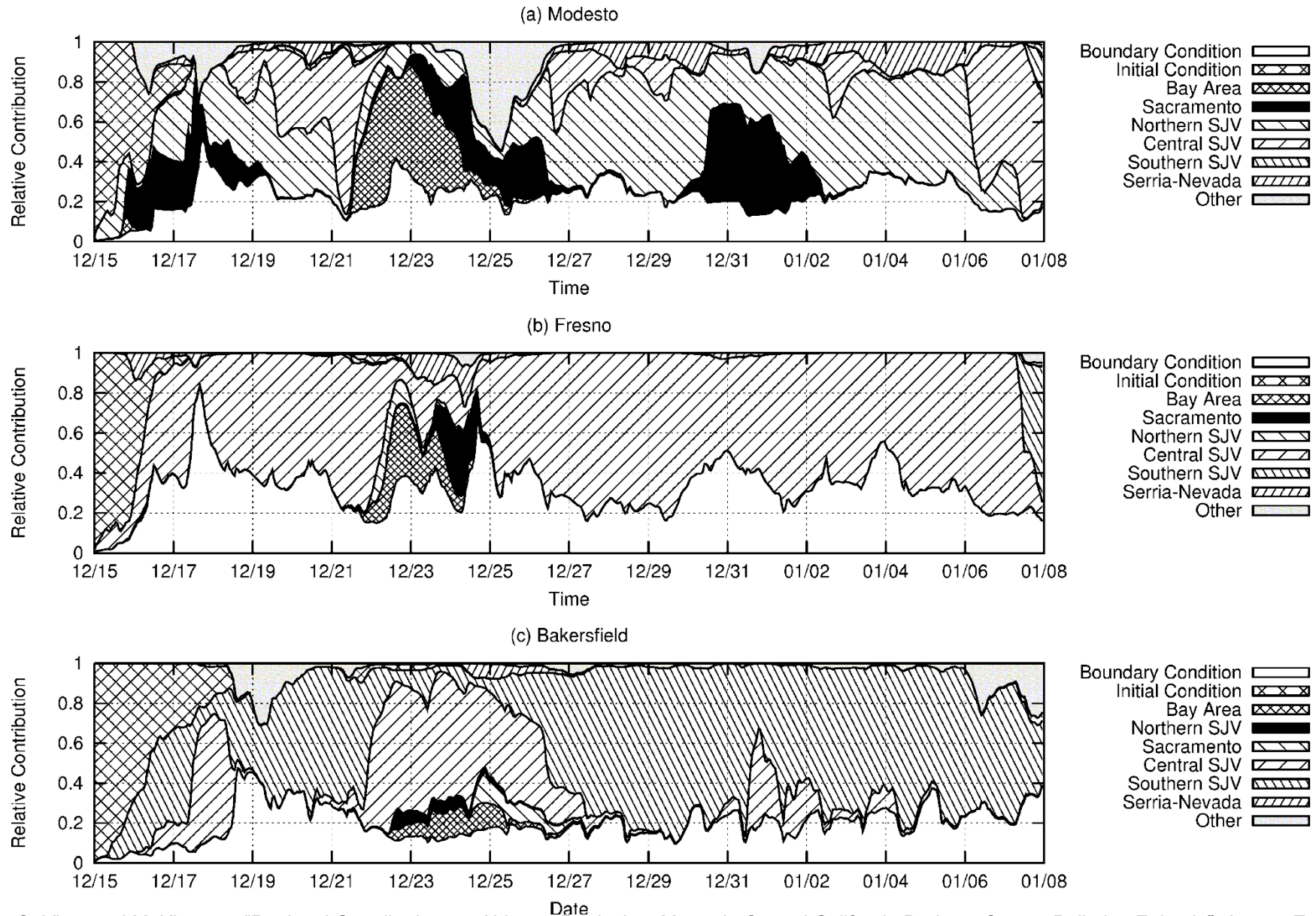
(b) Fresno



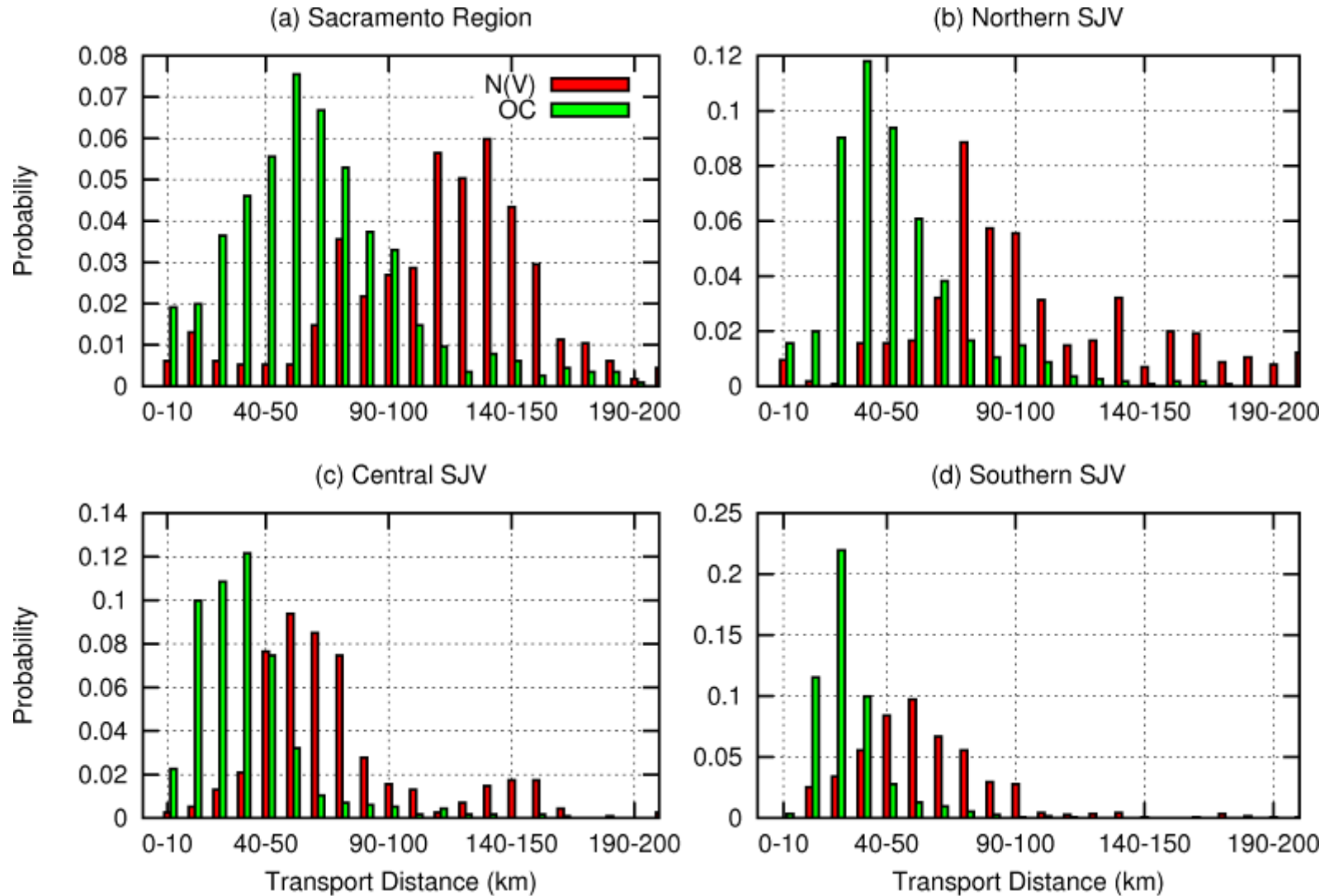
(c) Bakersfield



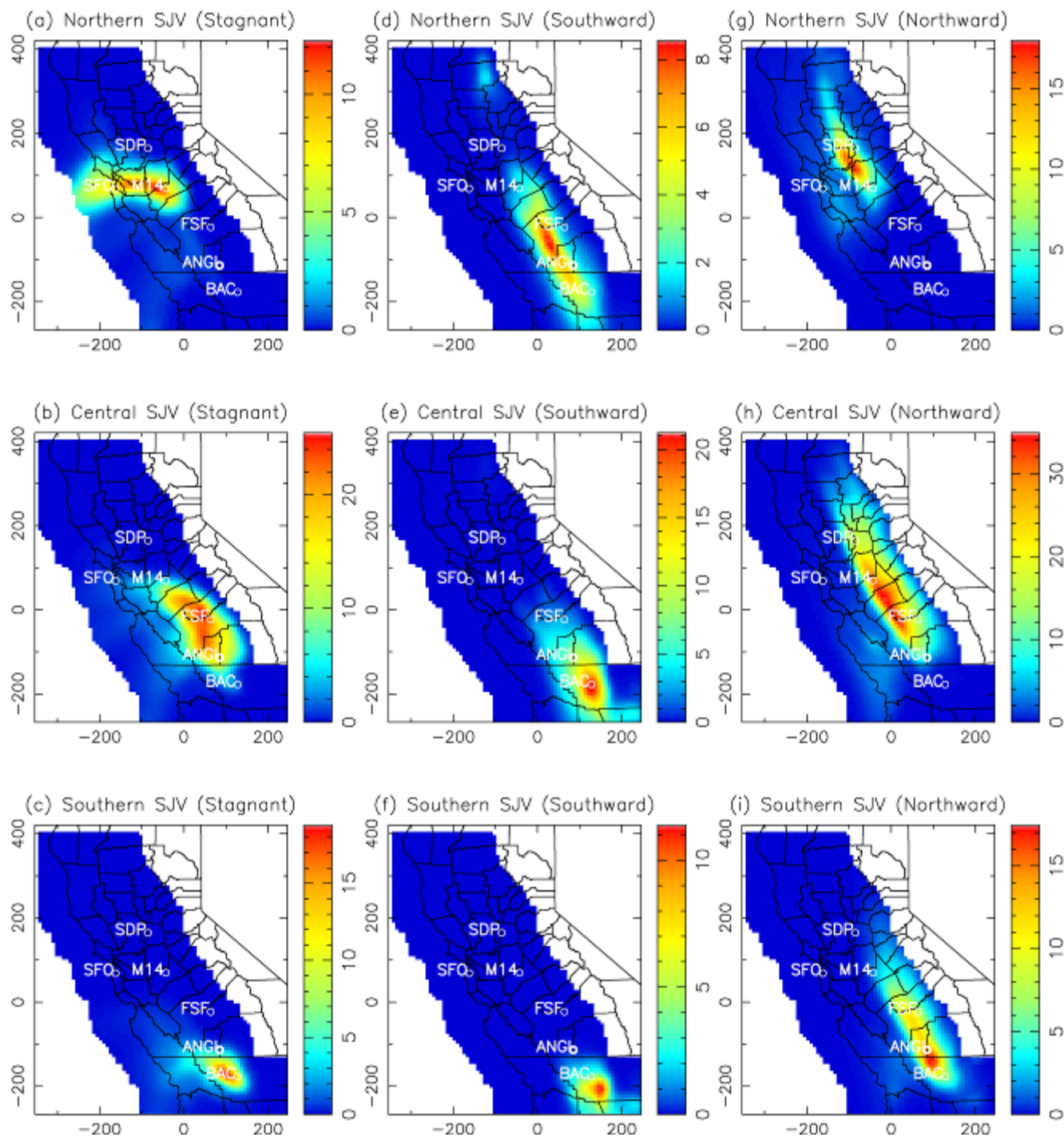
Nitrate Region Contributions



Distribution of Transport Distances

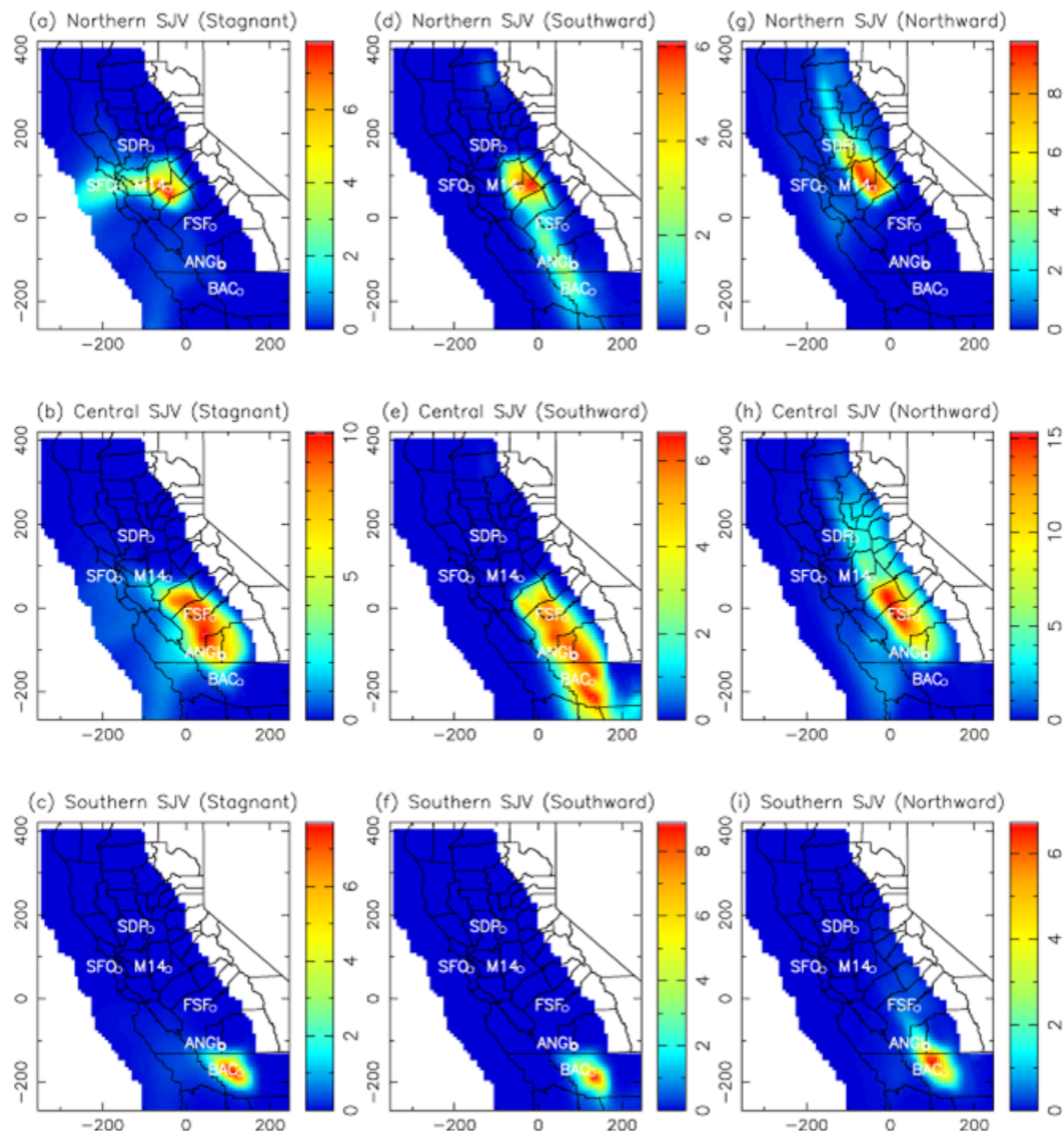


PM_{2.5} Nitrate



Source: Q. Ying, and M. Kleeman
 "Regional Contributions to Airborne
 Particulate Matter in Central California
 During a Severe Pollution Episode",
 Atmos. Env., 43, 1218-1228, 2009.

PM_{2.5} Ammonium

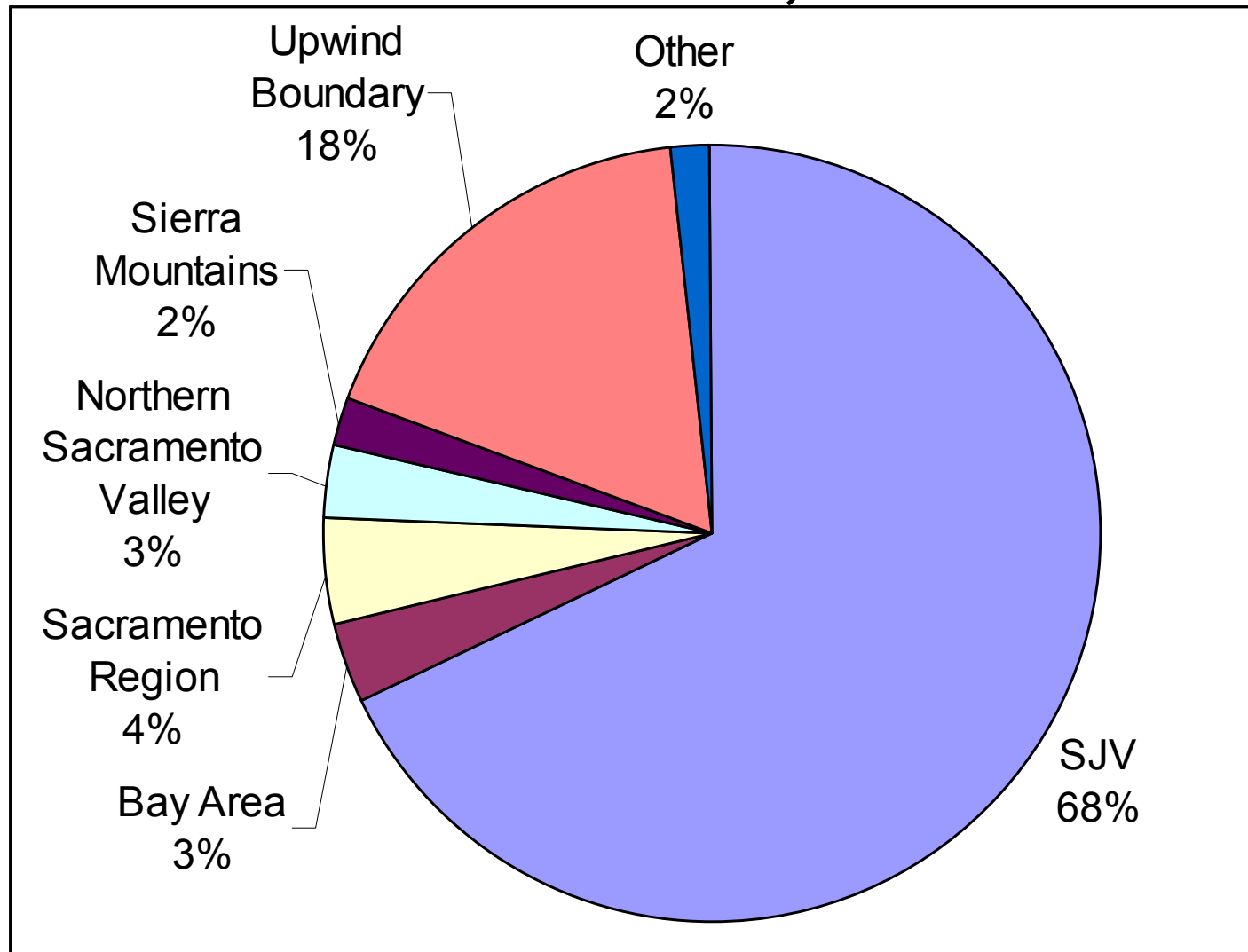


Source: Q. Ying, and M. Kleeman
 "Regional Contributions to Airborne
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 During a Severe Pollution Episode",
 Atmos. Env., 43, 1218-1228, 2009.

Nitrate Regional Contribution Summary

Source Receptor		BC	Bay Area	Sac	N SJV	C SJV	S SJV	N SacV	Sierra	Other	
		S0	S1	S2	S3	S4	S5	S6	S7	S8	SUM
Bay Area	R1	2.1%	1.5%	1.8%	1.4%	0.4%	0.0%	0.2%	0.2%	0.7%	8.2%
Sac	R2	1.1%	0.2%	1.3%	0.3%	0.3%	0.0%	0.1%	0.1%	0.8%	4.3%
N SJV	R3	1.3%	0.3%	0.8%	1.7%	1.0%	0.0%	0.1%	0.4%	0.2%	5.9%
C SJV	R4	5.0%	0.8%	0.9%	1.7%	17.7%	0.7%	0.8%	0.4%	0.3%	28.3%
S SJV	R5	1.4%	0.3%	0.2%	0.2%	3.1%	3.1%	0.4%	0.0%	0.2%	9.0%
N SacV	R6	3.4%	1.1%	0.6%	1.1%	4.0%	1.4%	2.0%	0.1%	0.7%	14.5%
Sierra	R7	0.5%	0.1%	0.1%	0.1%	0.3%	0.0%	0.1%	0.2%	0.0%	1.5%
Other	R8	8.4%	3.9%	2.3%	1.7%	2.4%	0.6%	2.3%	0.2%	6.5%	28.4%
SUM		23.2%	8.2%	8.1%	8.2%	29.3%	6.0%	6.0%	1.6%	9.4%	100.0%

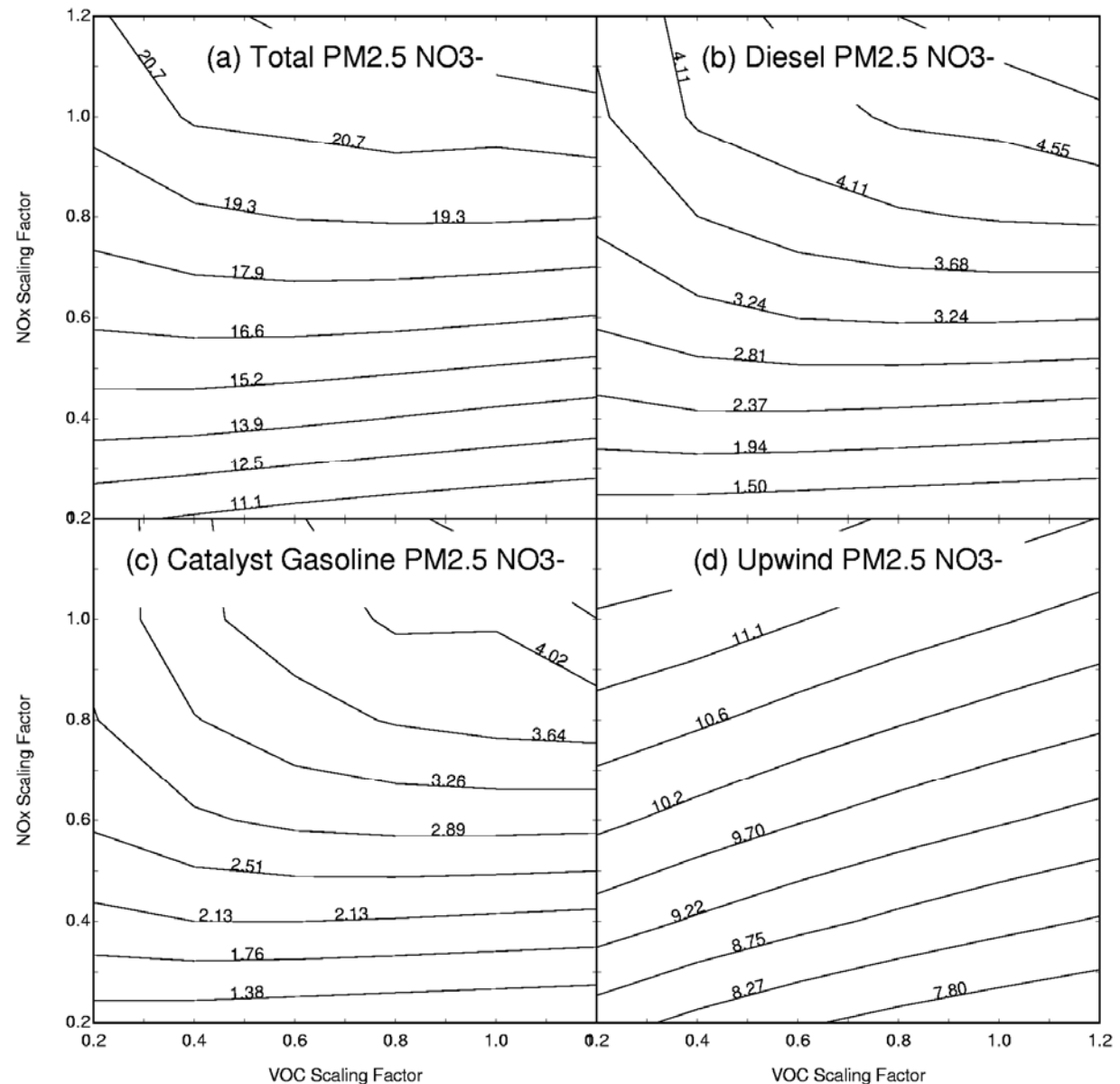
Regional Contributions to SJV PM_{2.5} Nitrate Between Dec 15, 2000 – Jan 7, 2001



Fresno January 6, 1996

Basecase NH3 Emissions

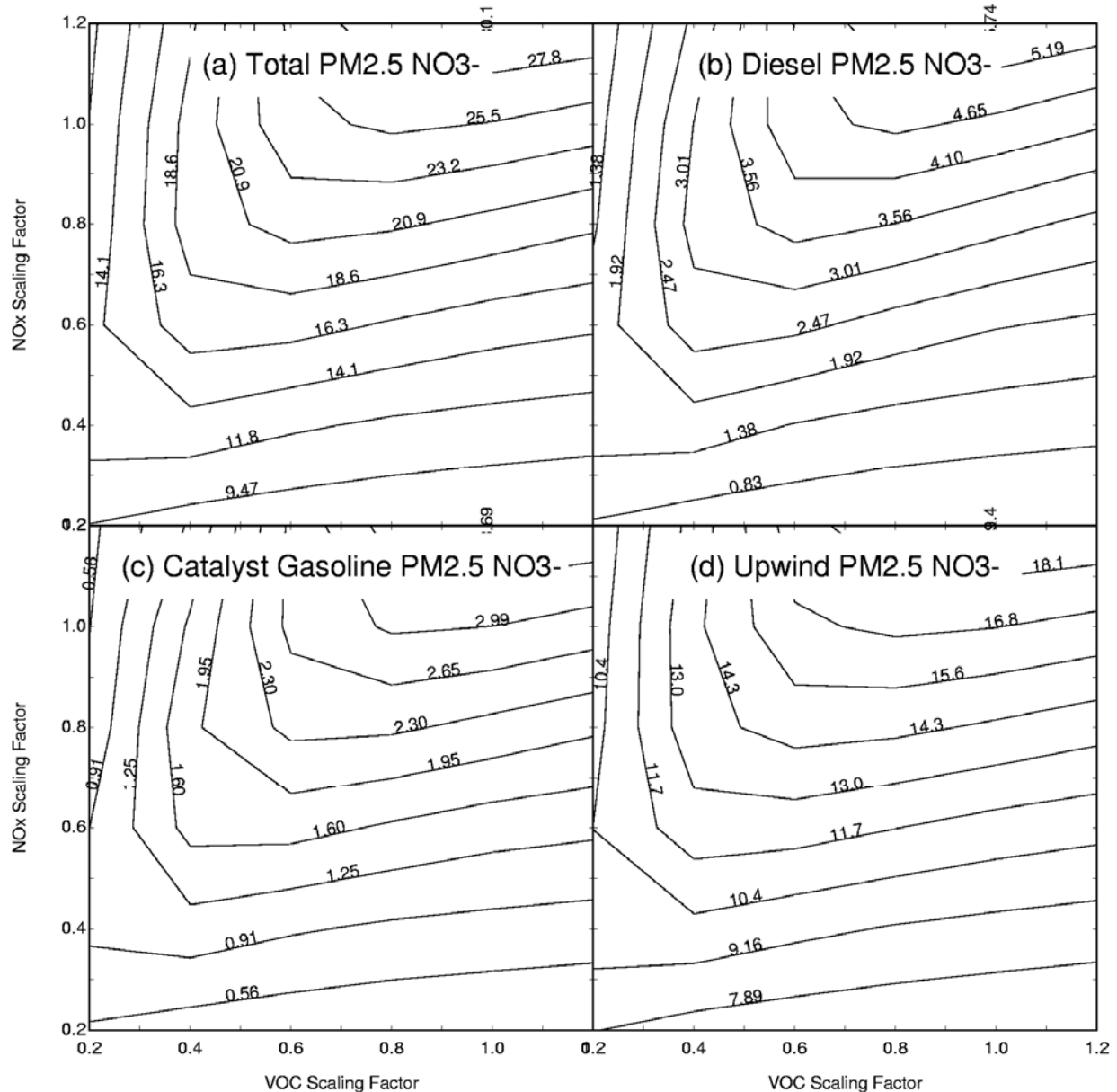
Nitrate Control Options



Kern Wildlife Refuge January 6, 1996

Basecase NH3 Emissions

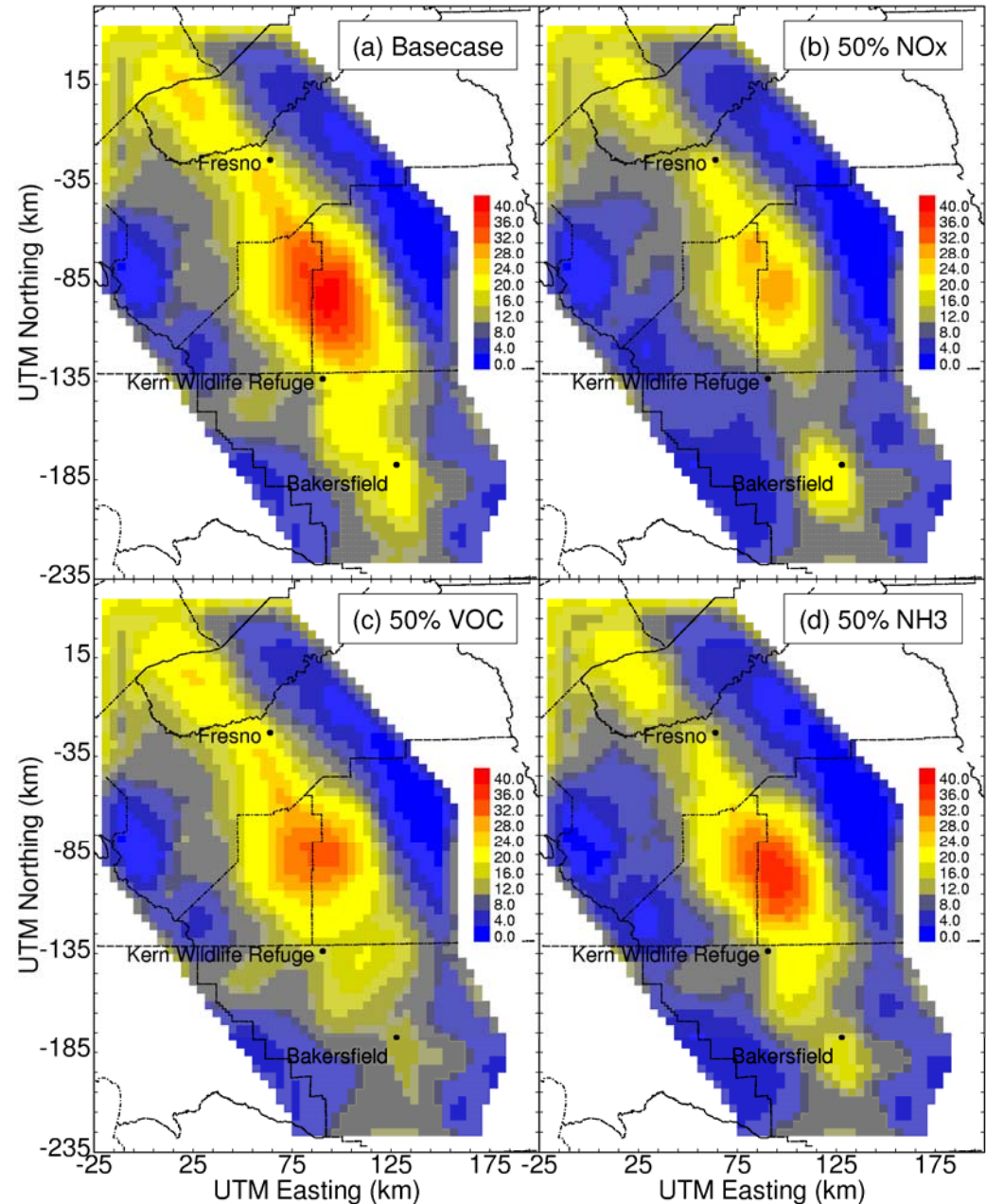
Nitrate Control Options



Control Strategy Effectiveness

Particulate Nitrate

January 6, 1996



Partial Answers

- *Primary vs. secondary PM 2.5 species*
 - *Elemental carbon (EC), organic carbon (OC), ammonium nitrate*
- *Sources of PM 2.5 in the region?*
 - *Wood smoke (OC) and diesel engines (EC) in urban areas*
 - *Diesel engines (nitrate) and gasoline engines (nitrate) contribute regionally*
 - *Agricultural activities (ammonium) contribute regionally*

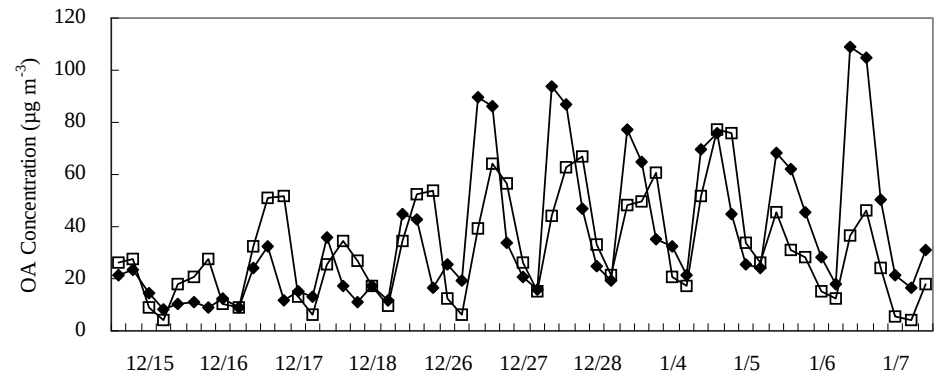
Partial Answers

- *Why do they concentrate in winter?*
 - *Lower mixing depths, colder temperature, home heating*
- *Where and when do PM 2.5 concentrations vary in the Valley?*
 - *Transport can be a factor, but mostly local emissions cause local air pollution*
- *What types of control measures have been most successful?*
 - *Restrictions on residential wood combustion*
 - *Restrictions on NO emissions*

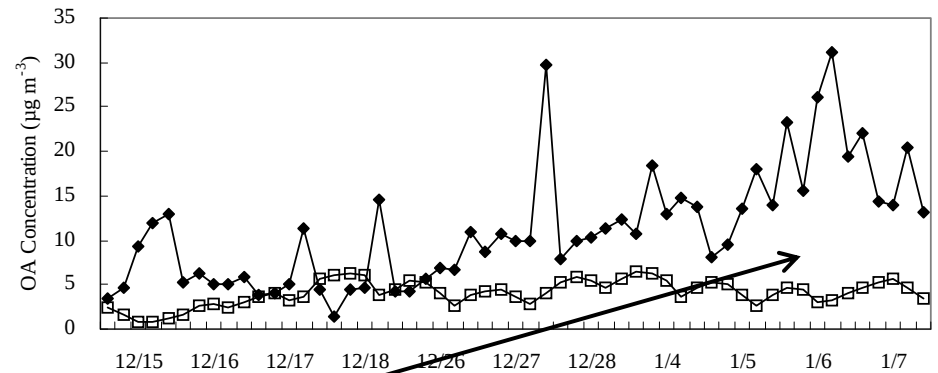
Future Challenges:

Organic Particulate Matter

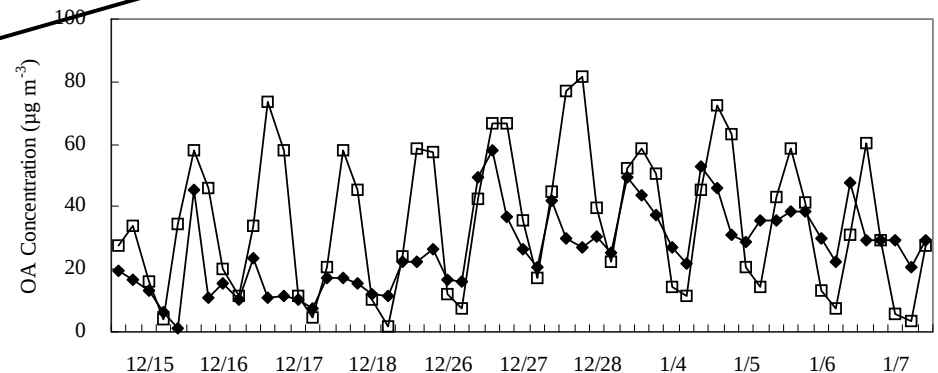
Predicted (open squares) and Observed OC (solid diamonds) using CACM



a.) Fresno



b.) Angiola



c.) Bakersfield

Large under-prediction at locations far away from urban sources

Acknowledgements

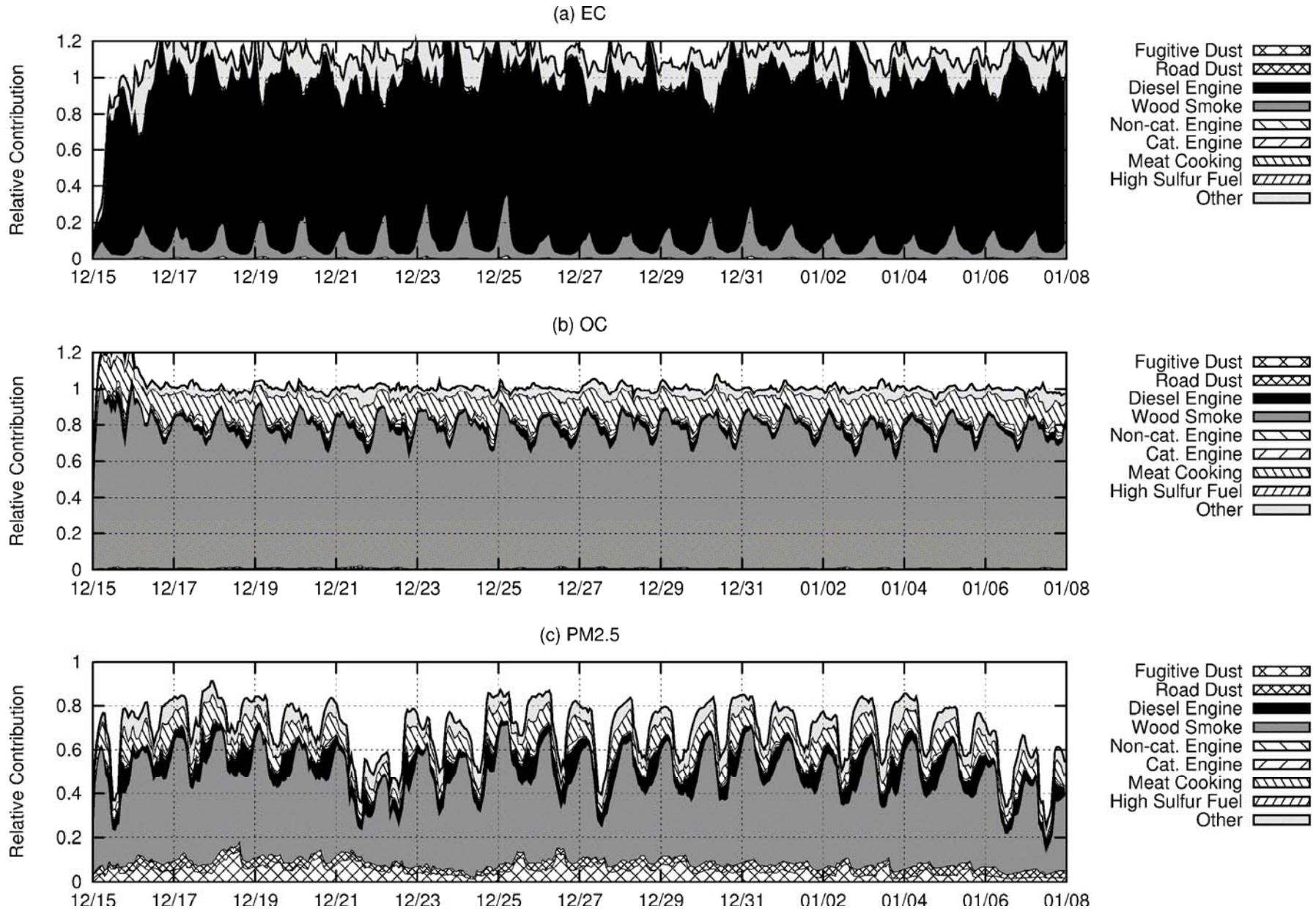
- Qi Ying, James Chen, Jianlin Hu, Jin Lu
- Karen Magliano, Ajith Kaduwela, Vernon Hughes
- Paul Allen, Paul Livingstone
- Everyone who made measurements during CRPAQS
- Zhan Zhao, Shuhua Chen
- San Joaquin Valleywide Air Pollution Study Agency
- United States Environmental Protection Agency

Supporting Slides

Atmospheric “Black Box” is Mostly Gone

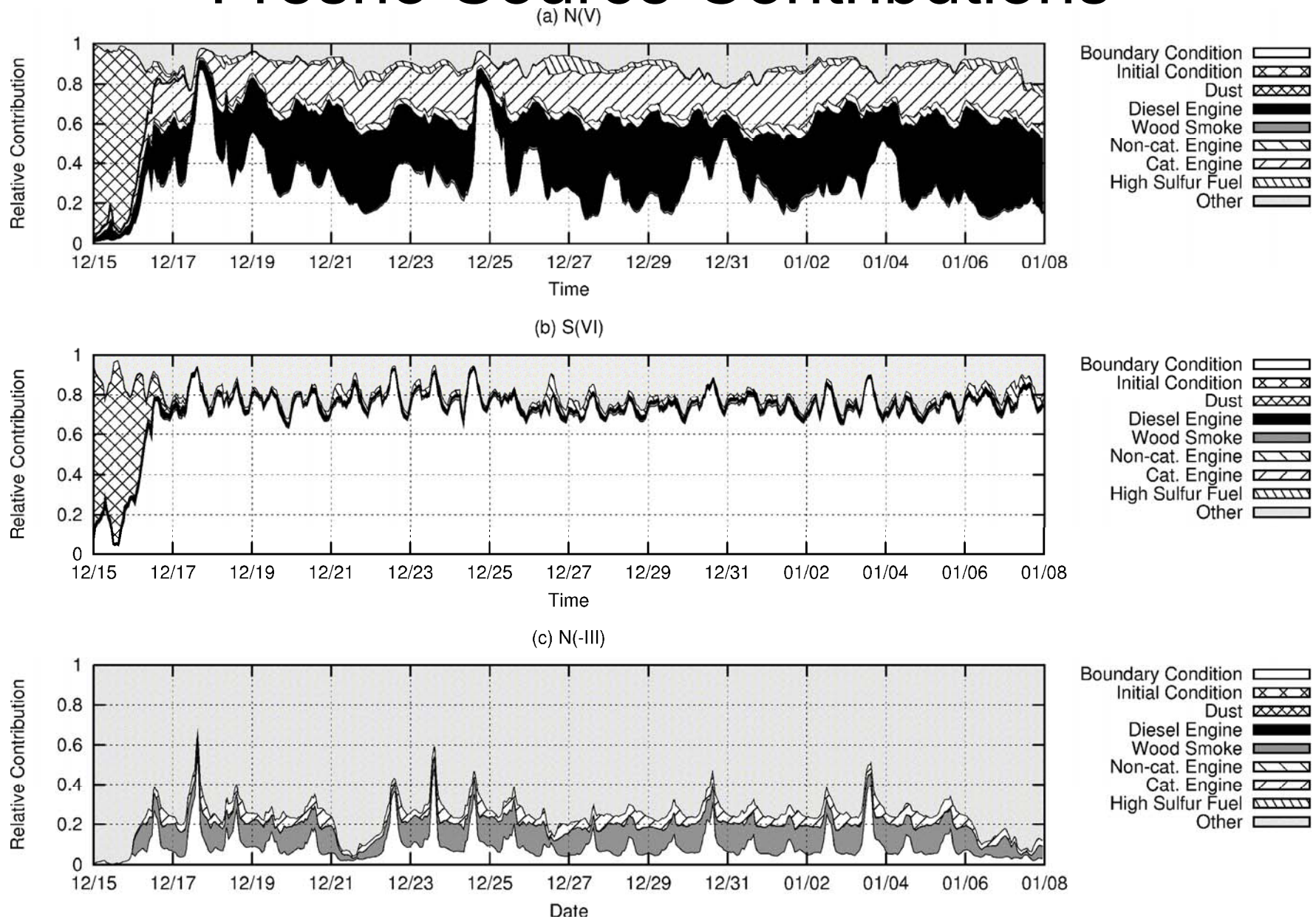
- Multiple techniques exist to identify source contributions to primary and secondary PM

Fresno PM2.5 Source Contributions



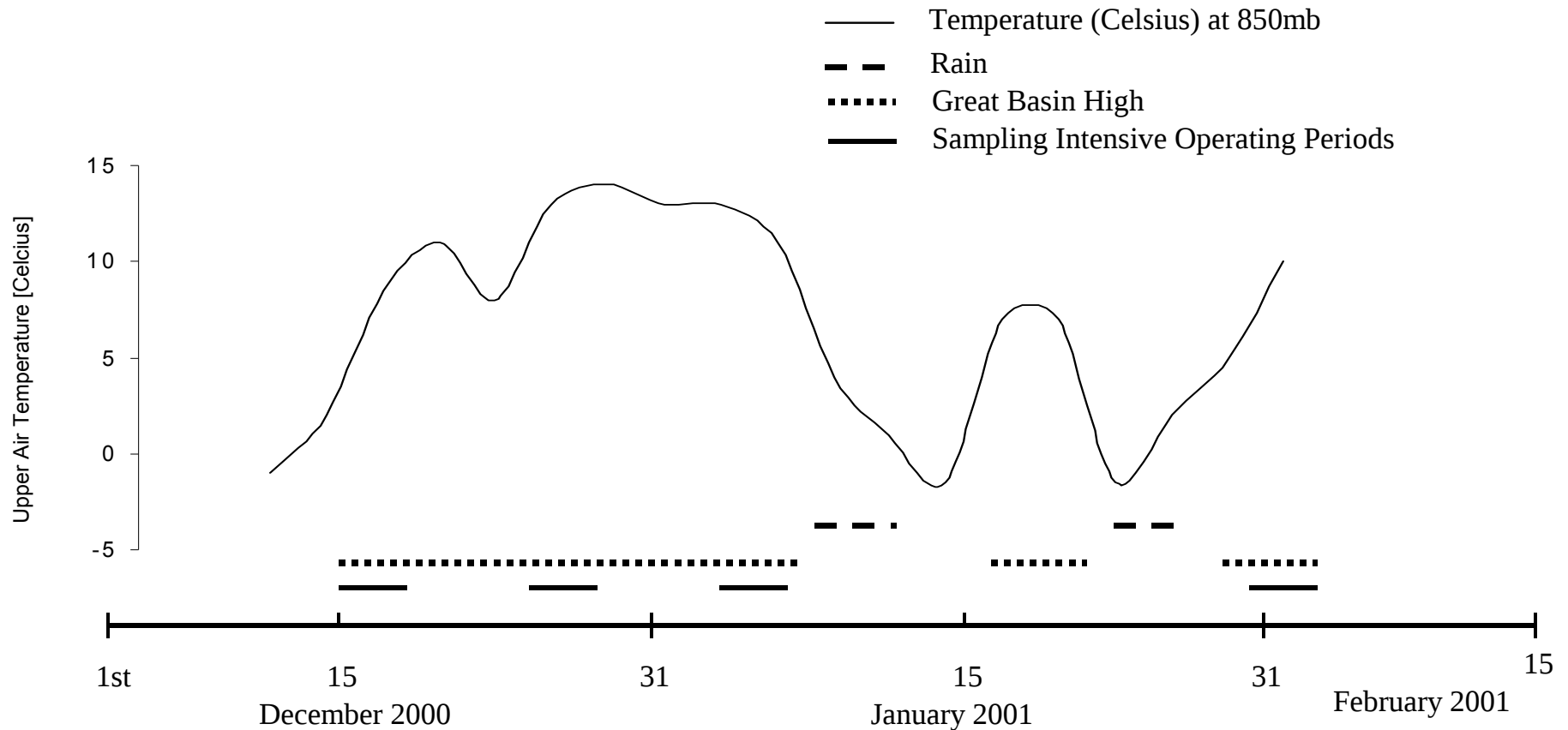
Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", Atmos. Env., in press, 2008.

Fresno Source Contributions



Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM_{2.5} and PM_{0.1}.", Atmos. Env., in press, 2008.

Meteorological Patterns During CRPAQS Winter Intensive



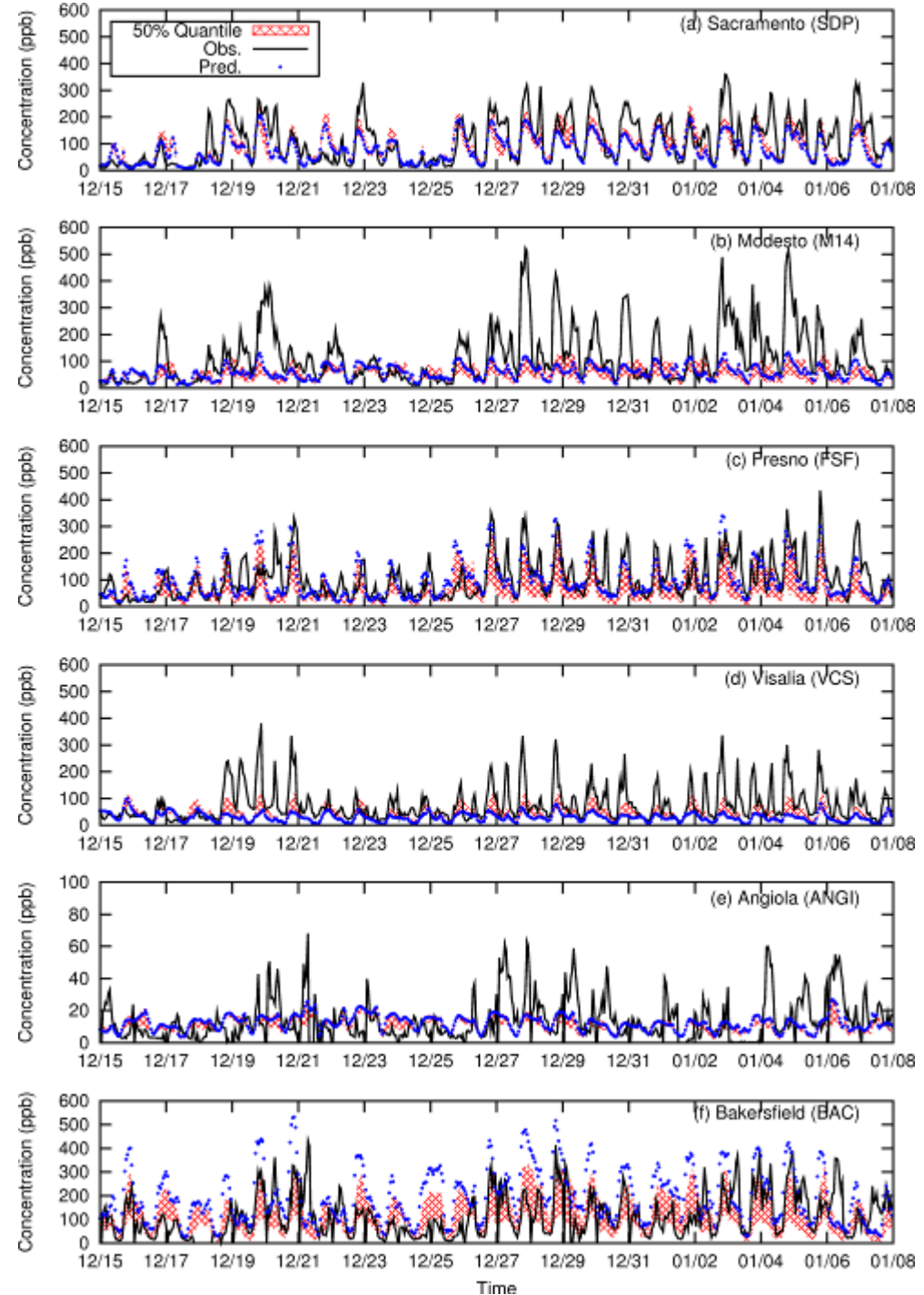
NO_x

Good agreement at Sacramento and Fresno

Slight over-prediction at Bakersfield, but spatial gradients are sharp

Miss the diurnal trend at Modesto, Visalia, and Angiola (what sources drive the observed trends?)

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.



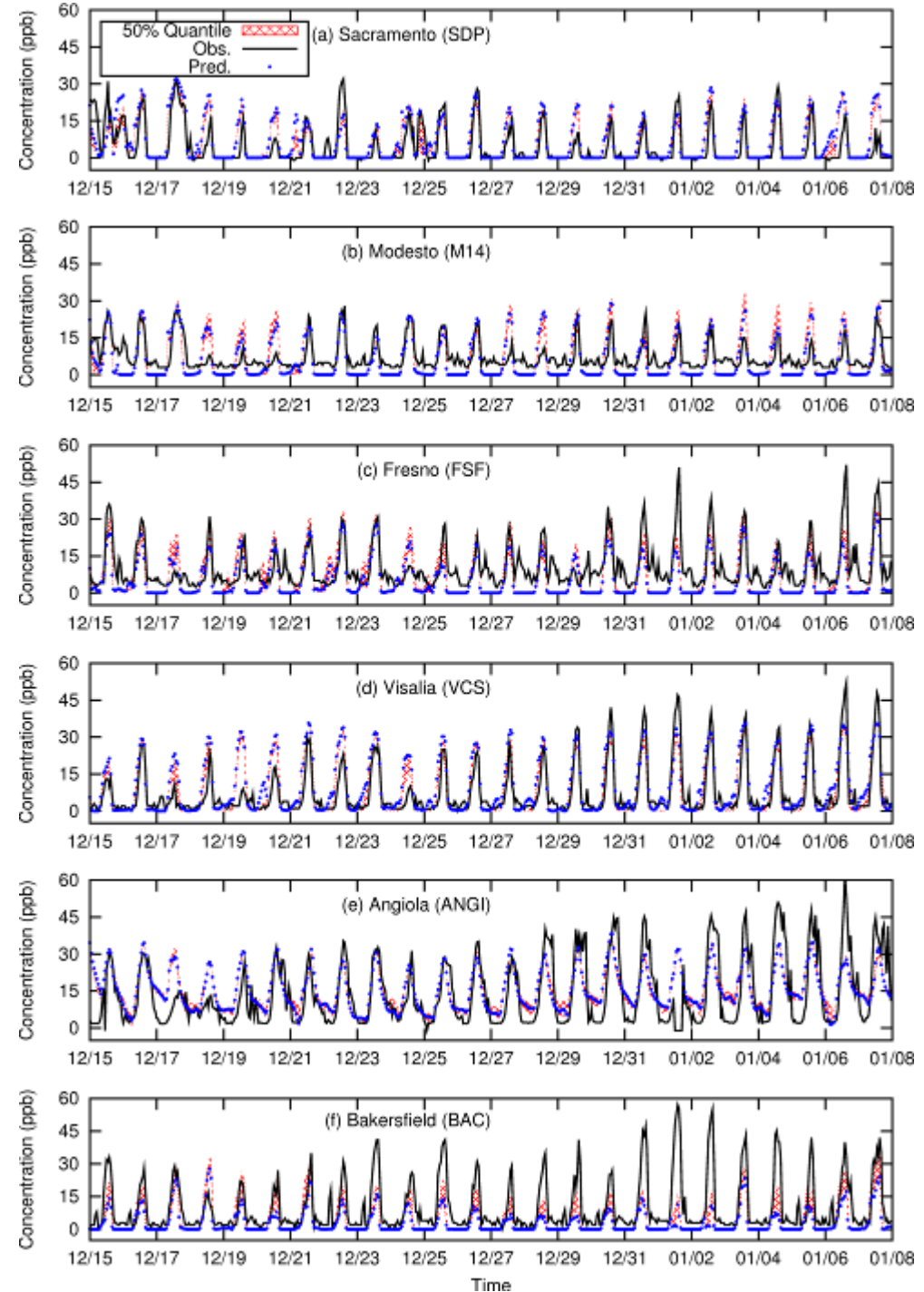
O₃

Good agreement at most stations

Majority of the ozone is background that mixes down to the surface during the middle of the day

Background O₃ is actually the dominant oxidant in the atmosphere

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.



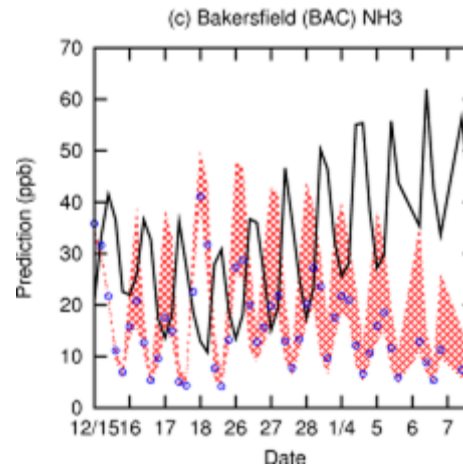
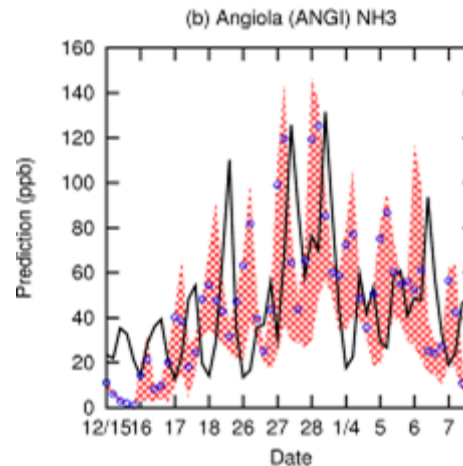
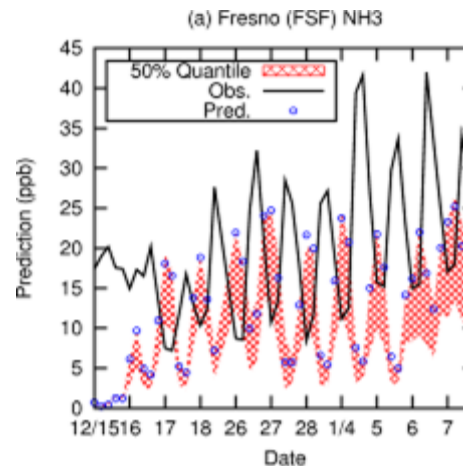
NH₃

Overall concentrations are order-of-magnitude correct

Diurnal cycle is exactly opposite measured values

Nitrate production is limited by production of nitric acid, so the details are not critical

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.



PM2.5 OC + EC

Black lines = measurements

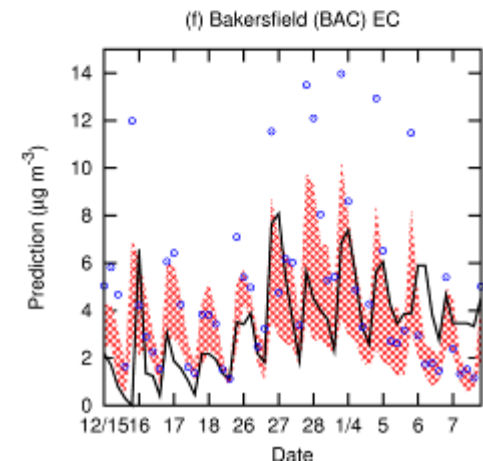
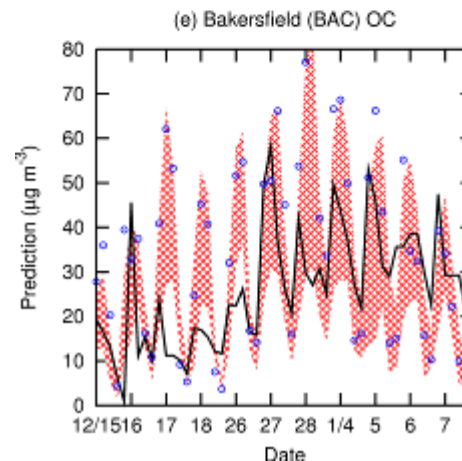
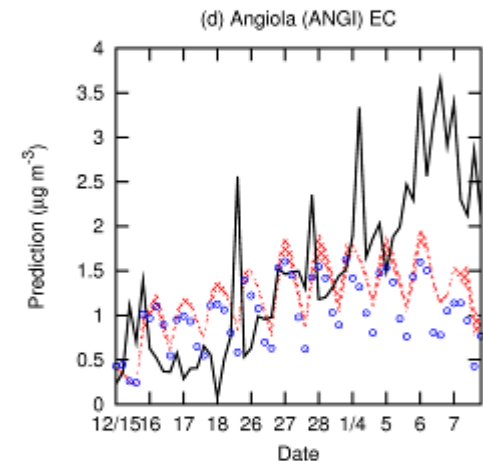
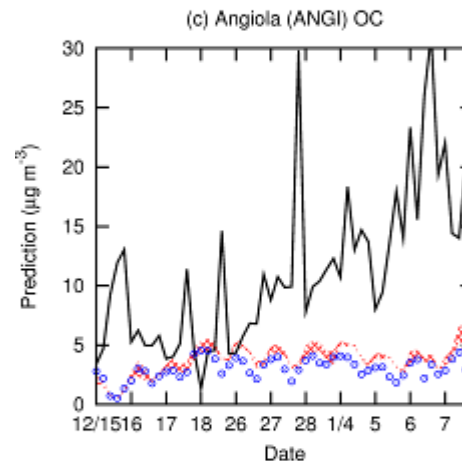
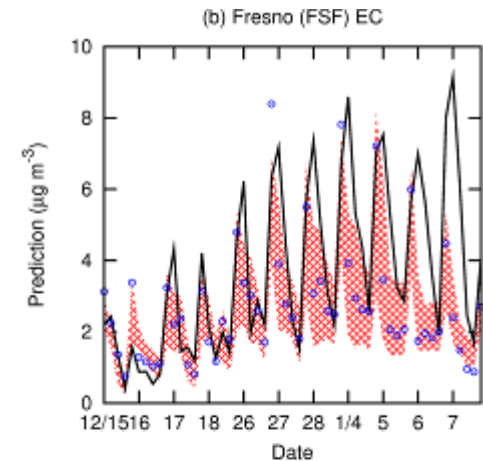
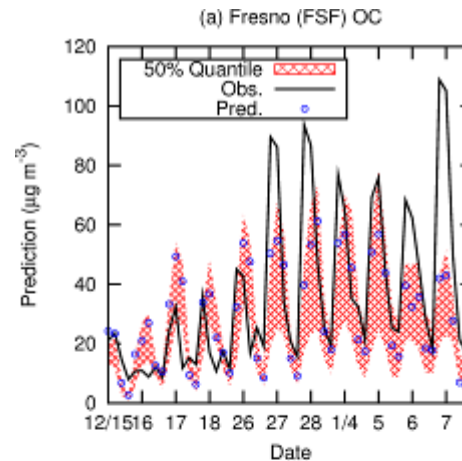
Blue circles = predictions

Red Shading – Mid 50% Quantile within 10km of monitor

Diurnal pattern predicted correctly at urban sites

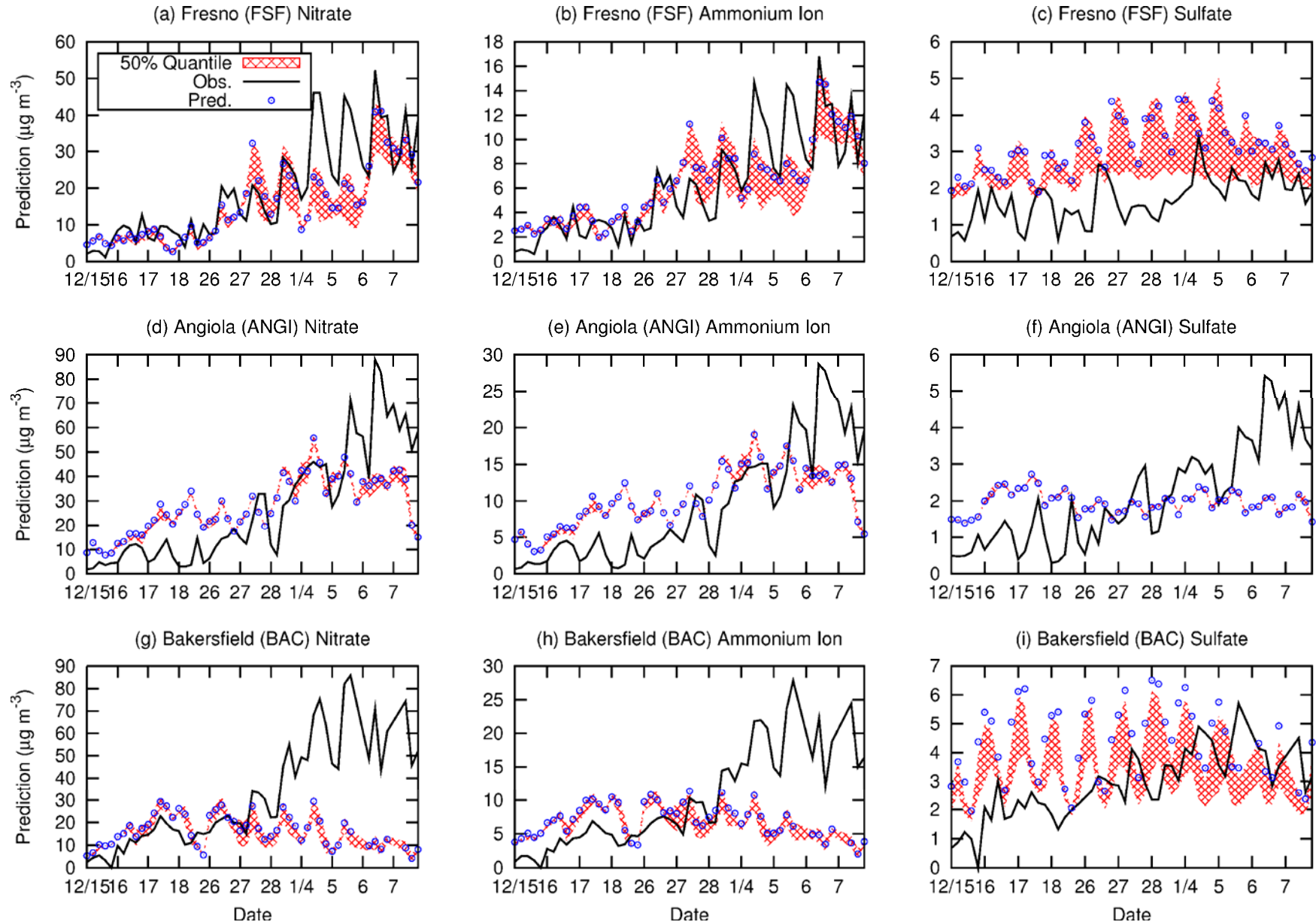
Peak values show reasonable agreement, especially considering the sharp gradients

Rural Angiola predictions are low.
Where is the EC+OC coming from?



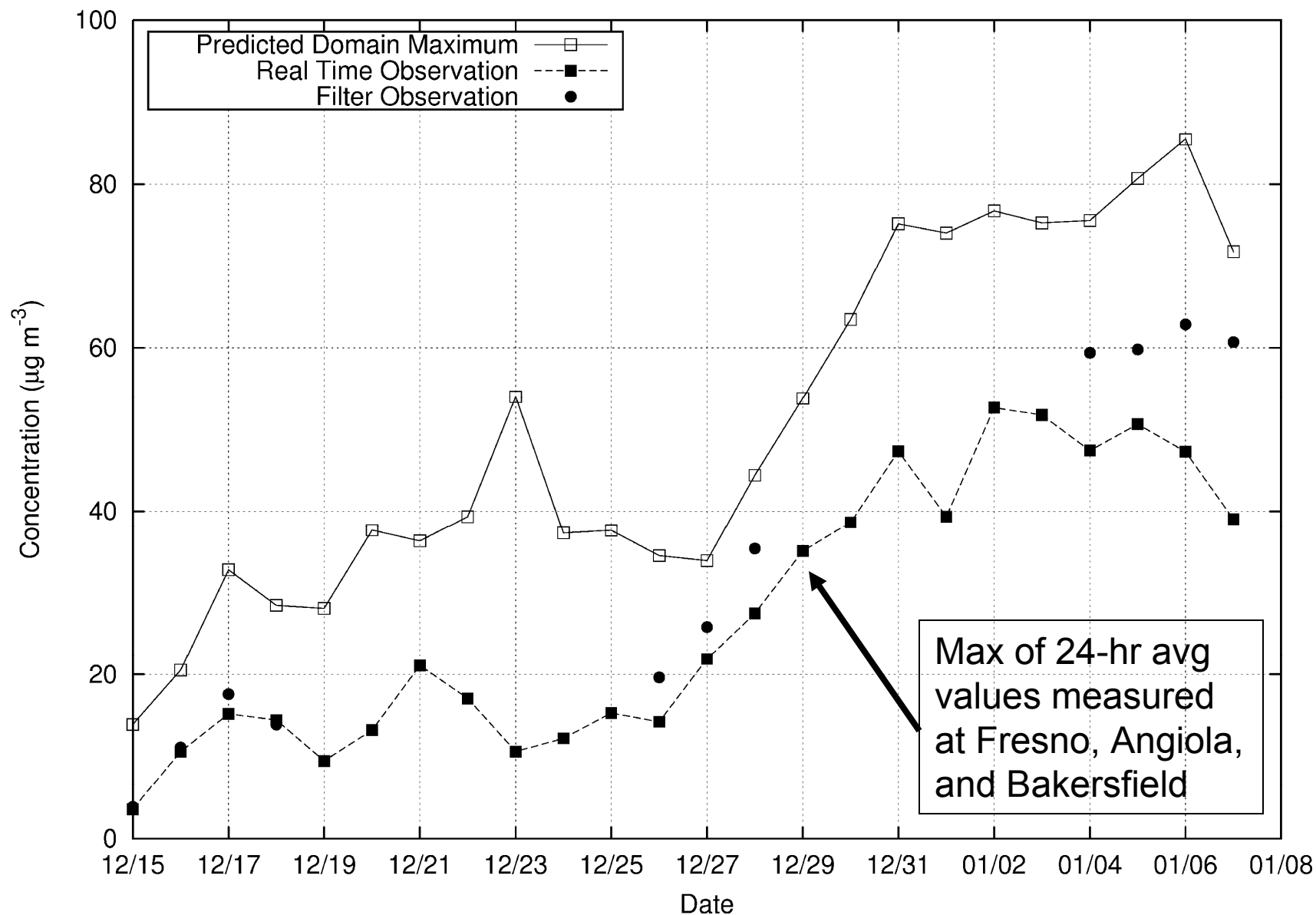
Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.

PM2.5 Nitrate, Ammonium, Sulfate



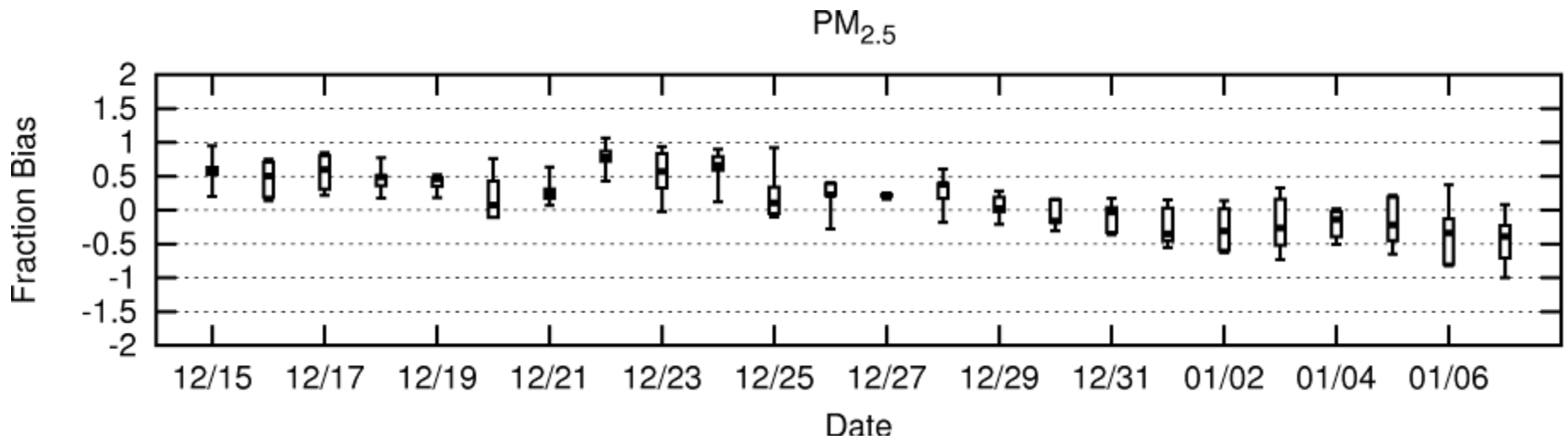
Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.

Predicted vs. Observed Nitrate Trends



Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.

PM_{2.5} Fractional Bias



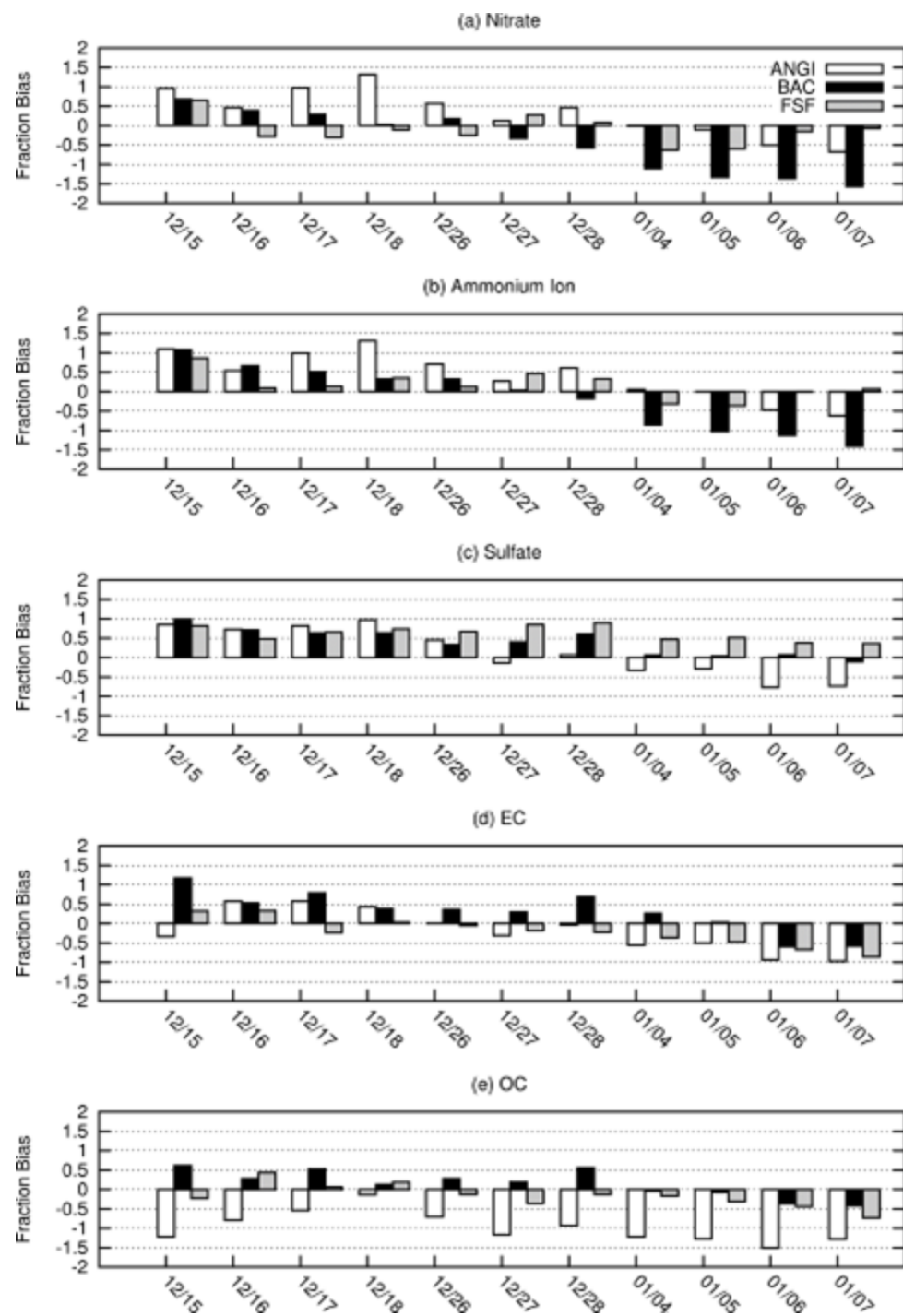
$$FB = \frac{2}{N} \times \sum \frac{C_{p,i} - C_{o,i}}{C_{p,i} + C_{o,i}}$$

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.

Fractional Bias of Individual PM2.5 Components

Most components – slight over-prediction during early portion of episode evolving to slight under-prediction later in episode

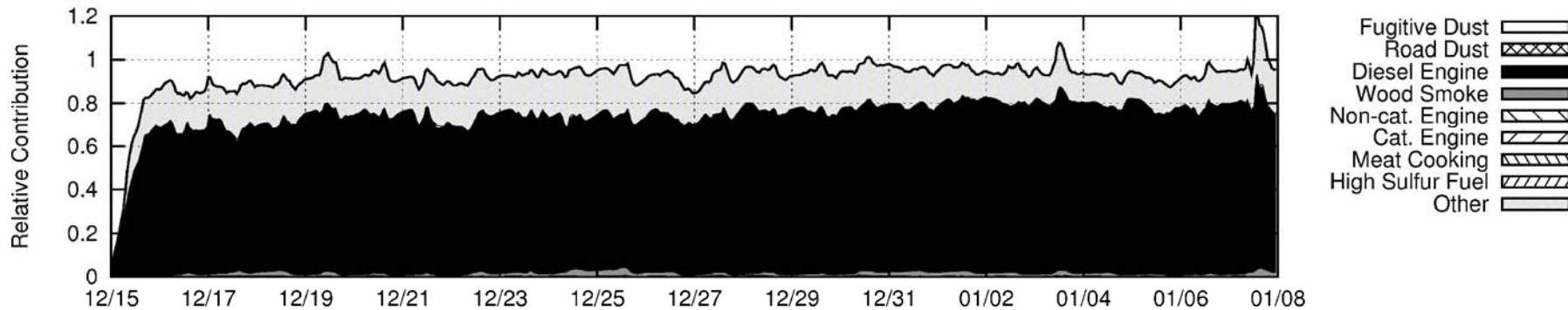
OC – always under-predicted at Angiola



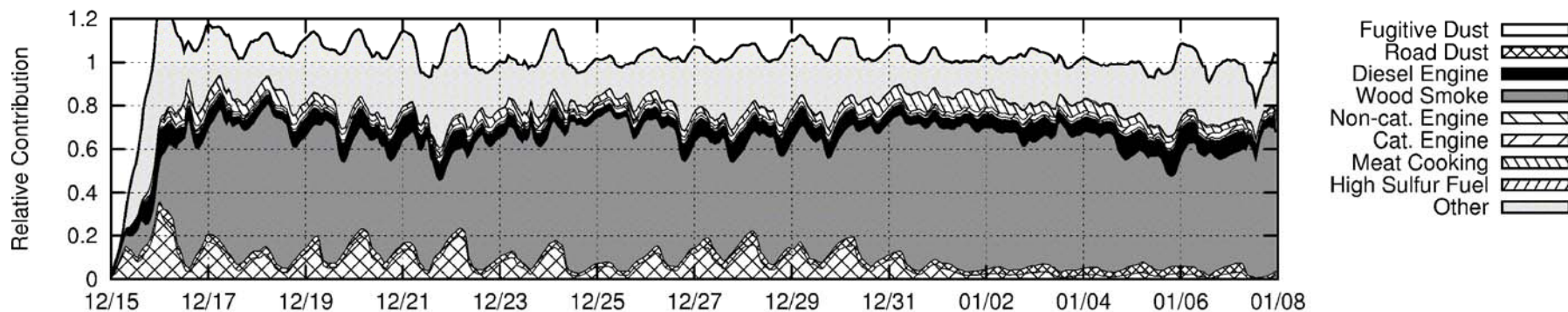
Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., in press, 2008.

Angiola PM2.5 Source Contributions

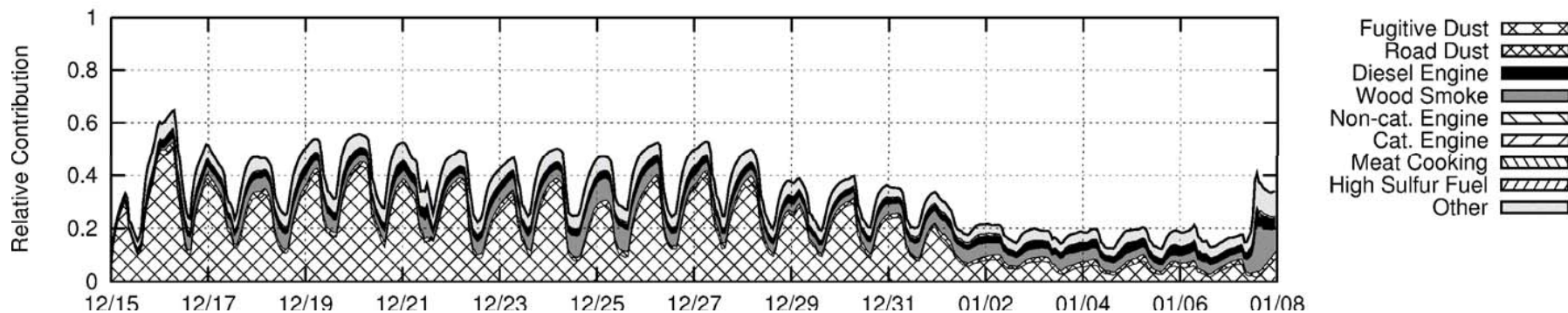
(a) EC

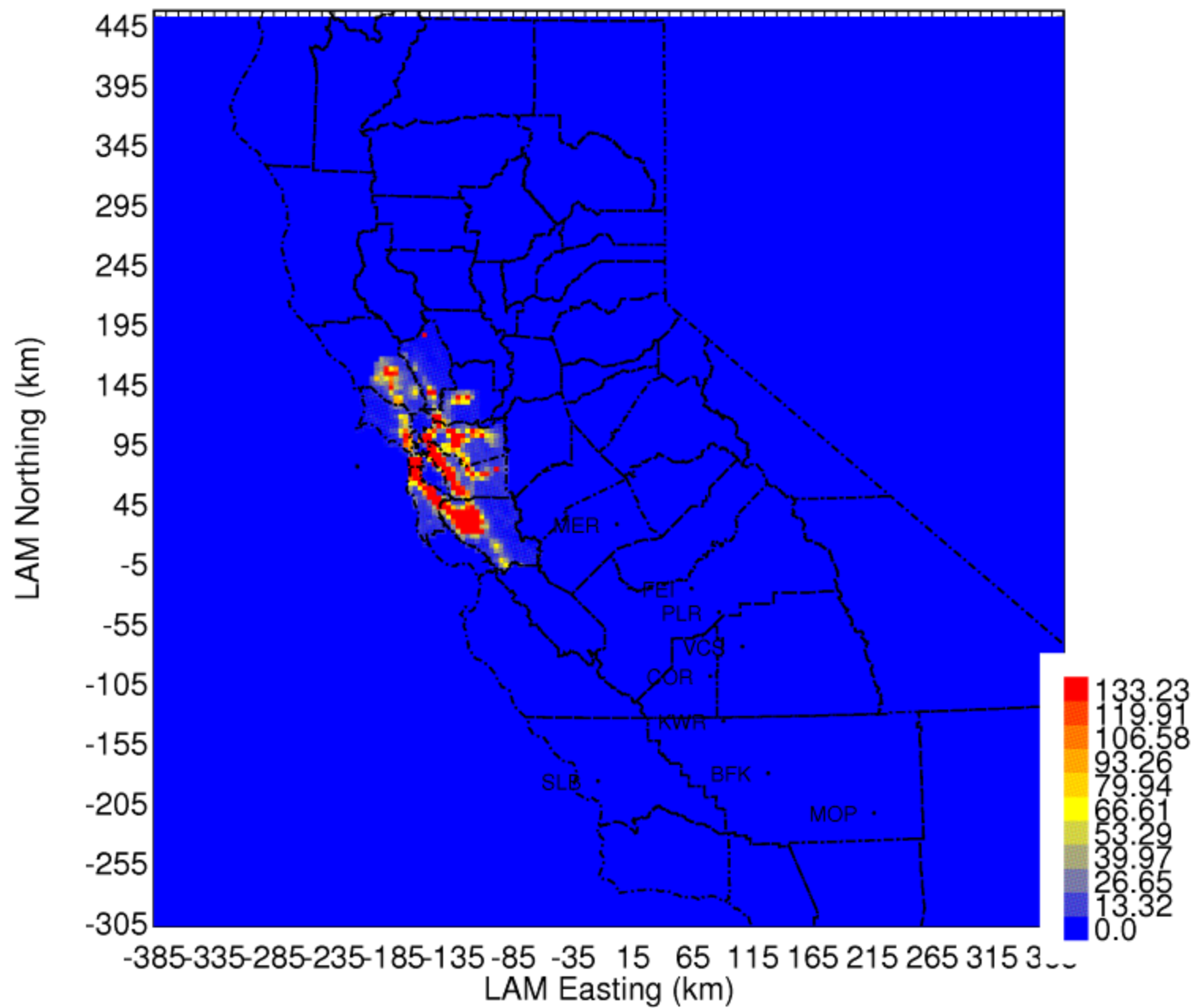


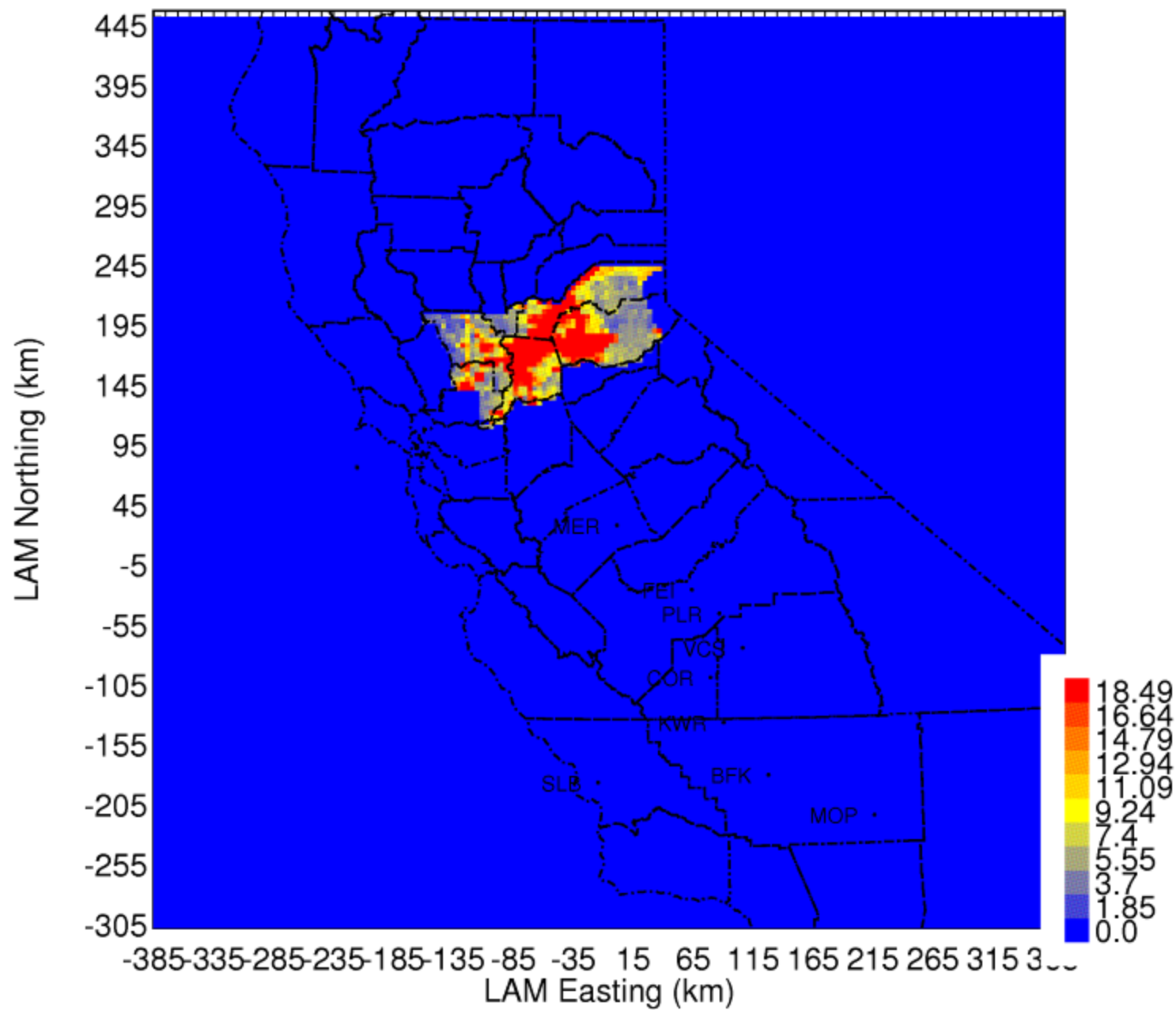
(b) OC

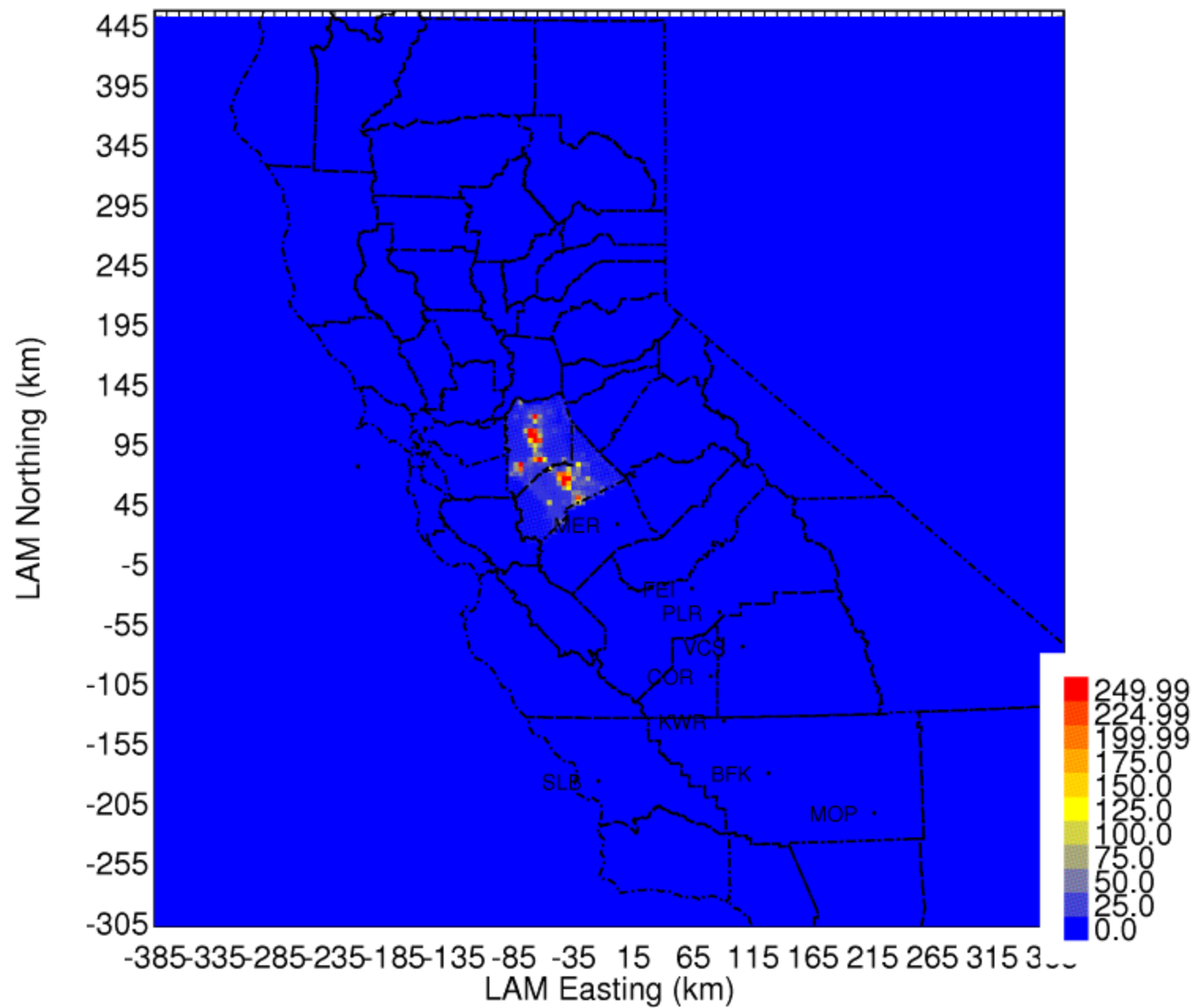


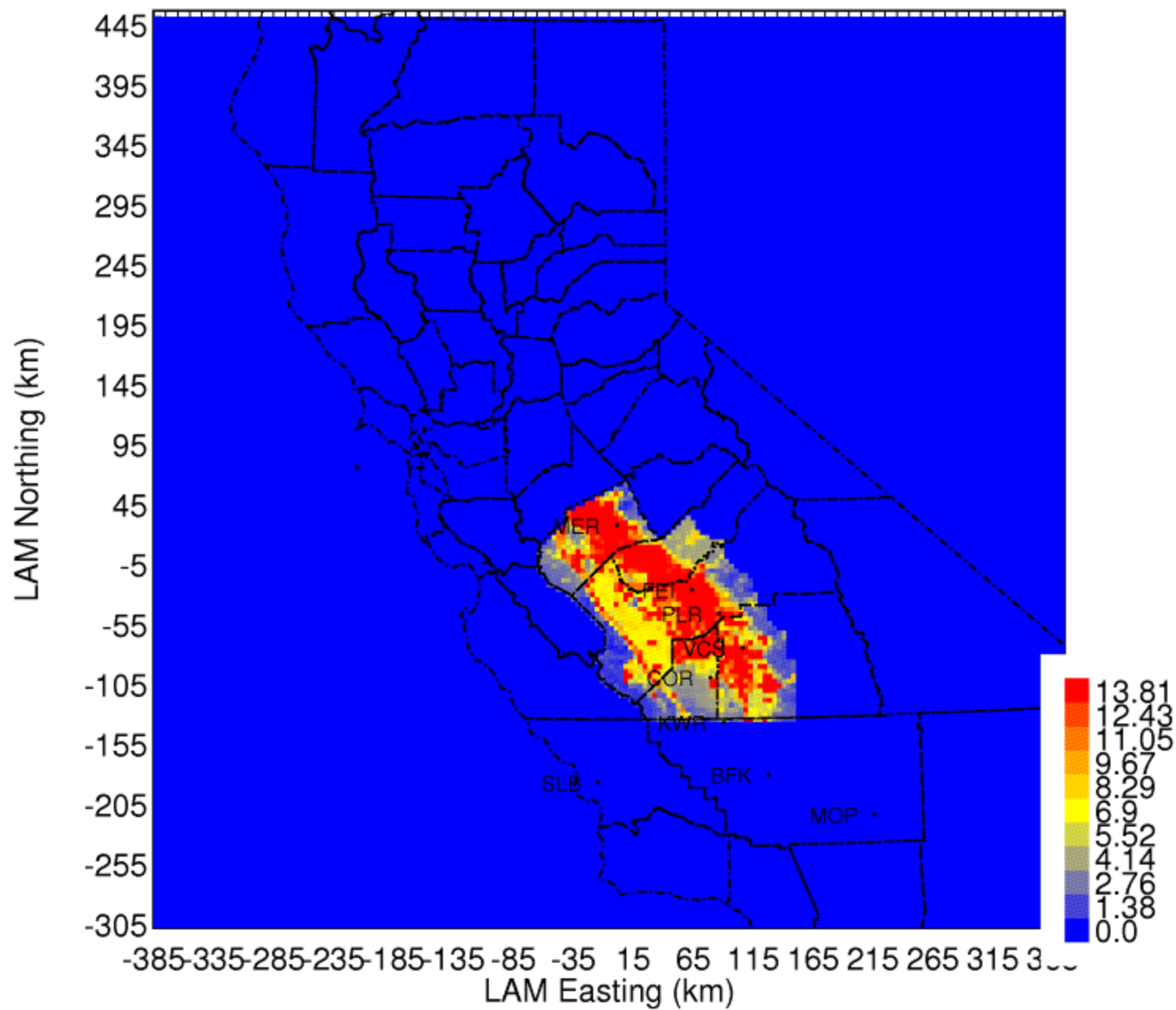
(c) PM2.5

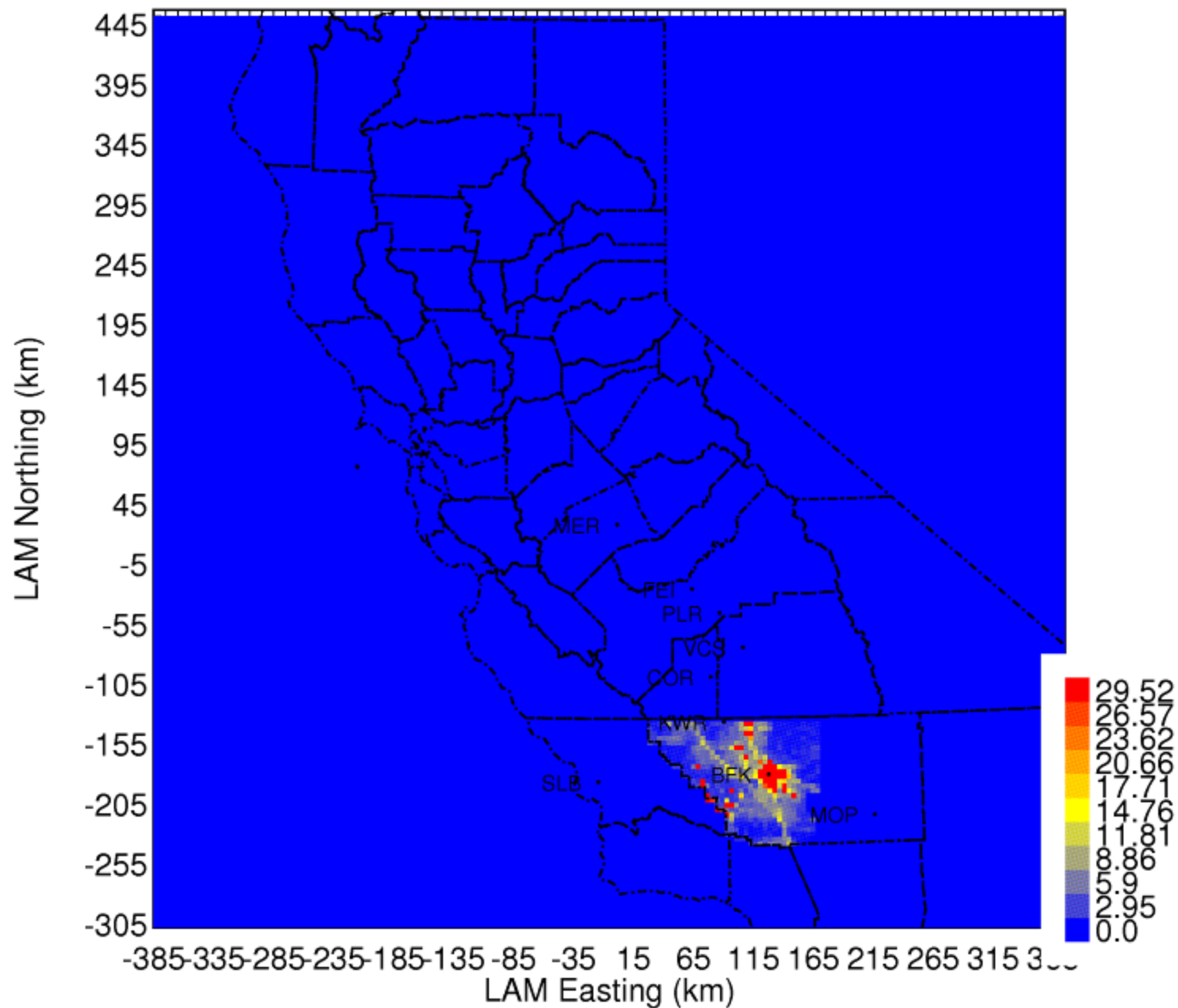


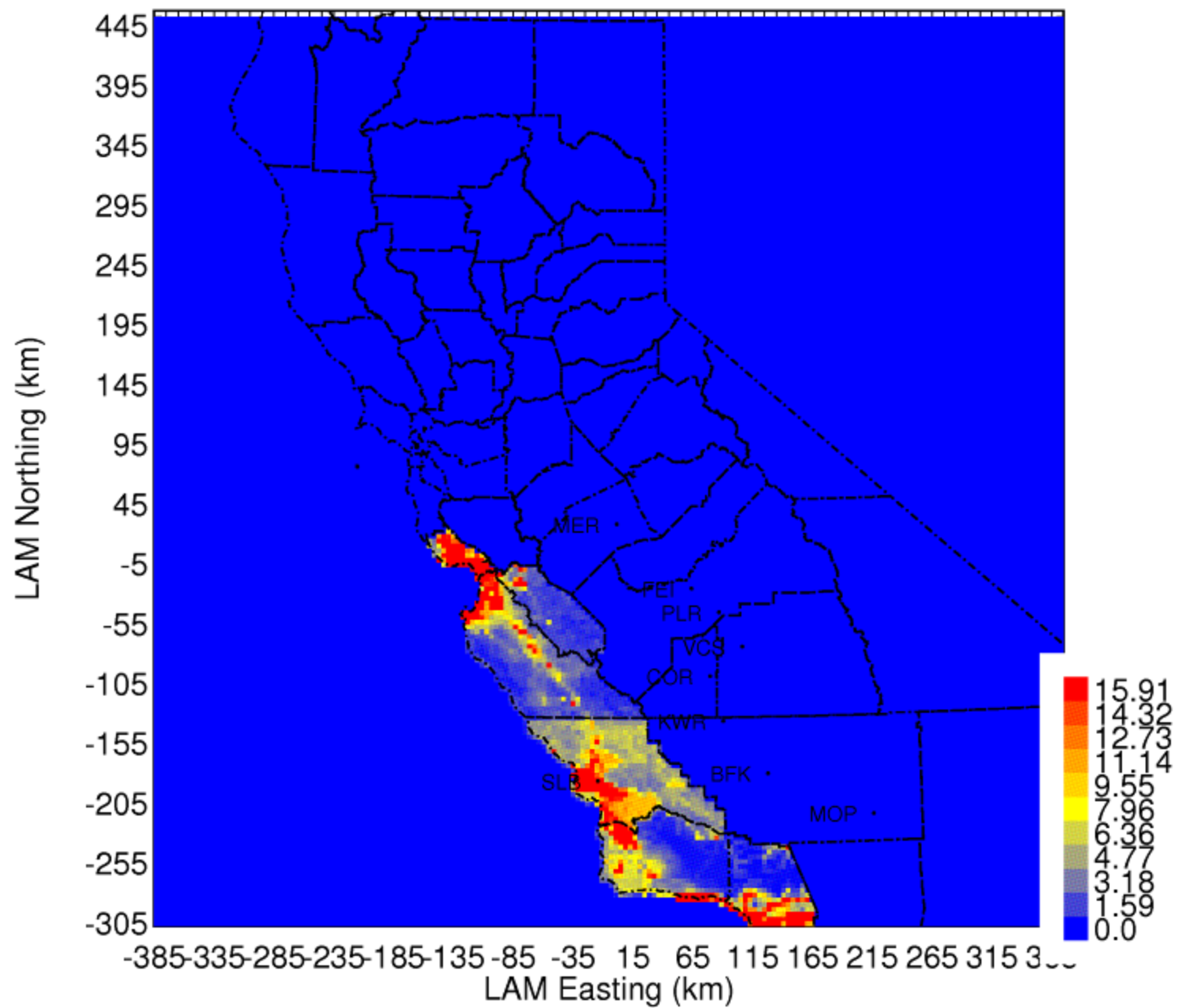


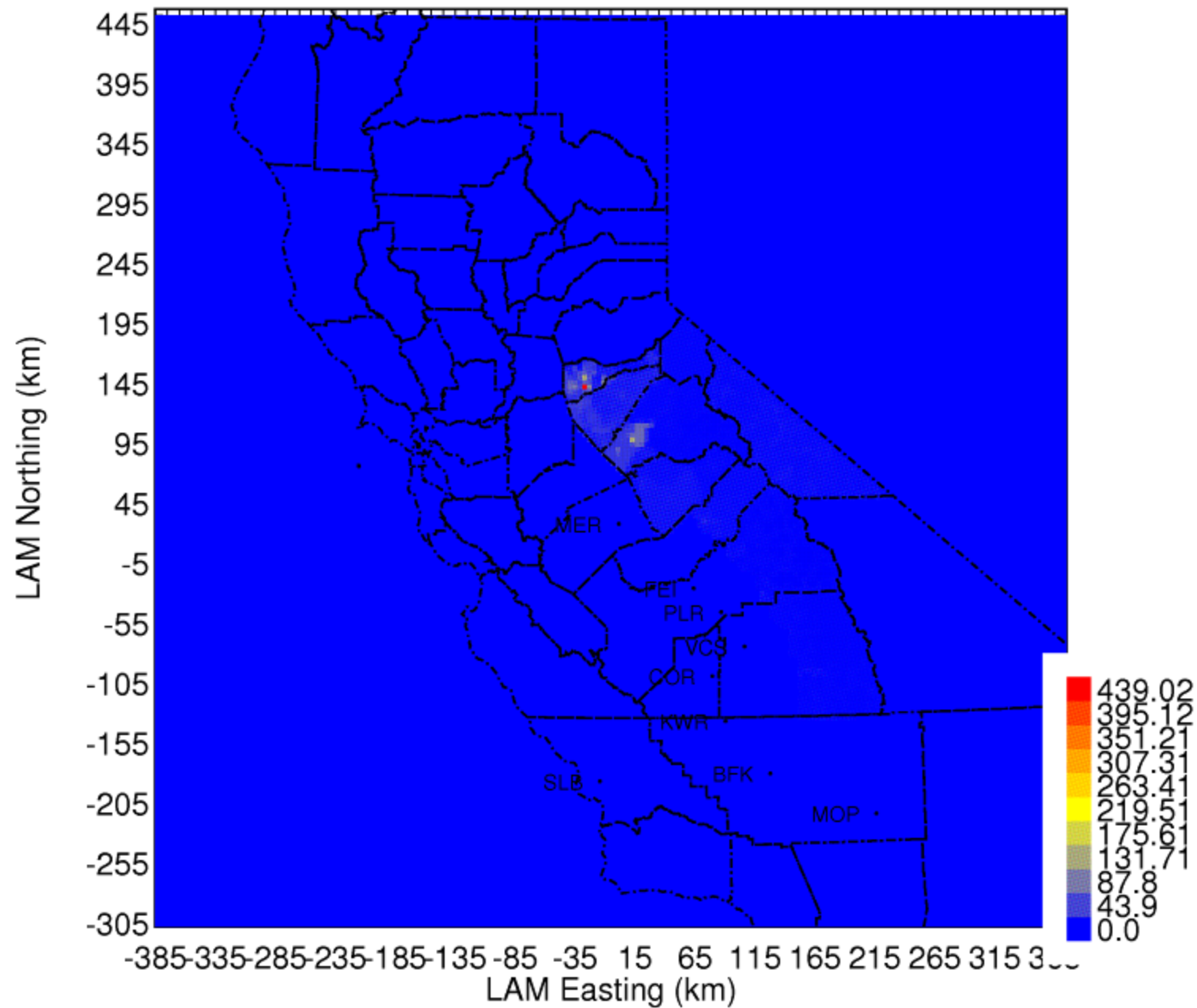


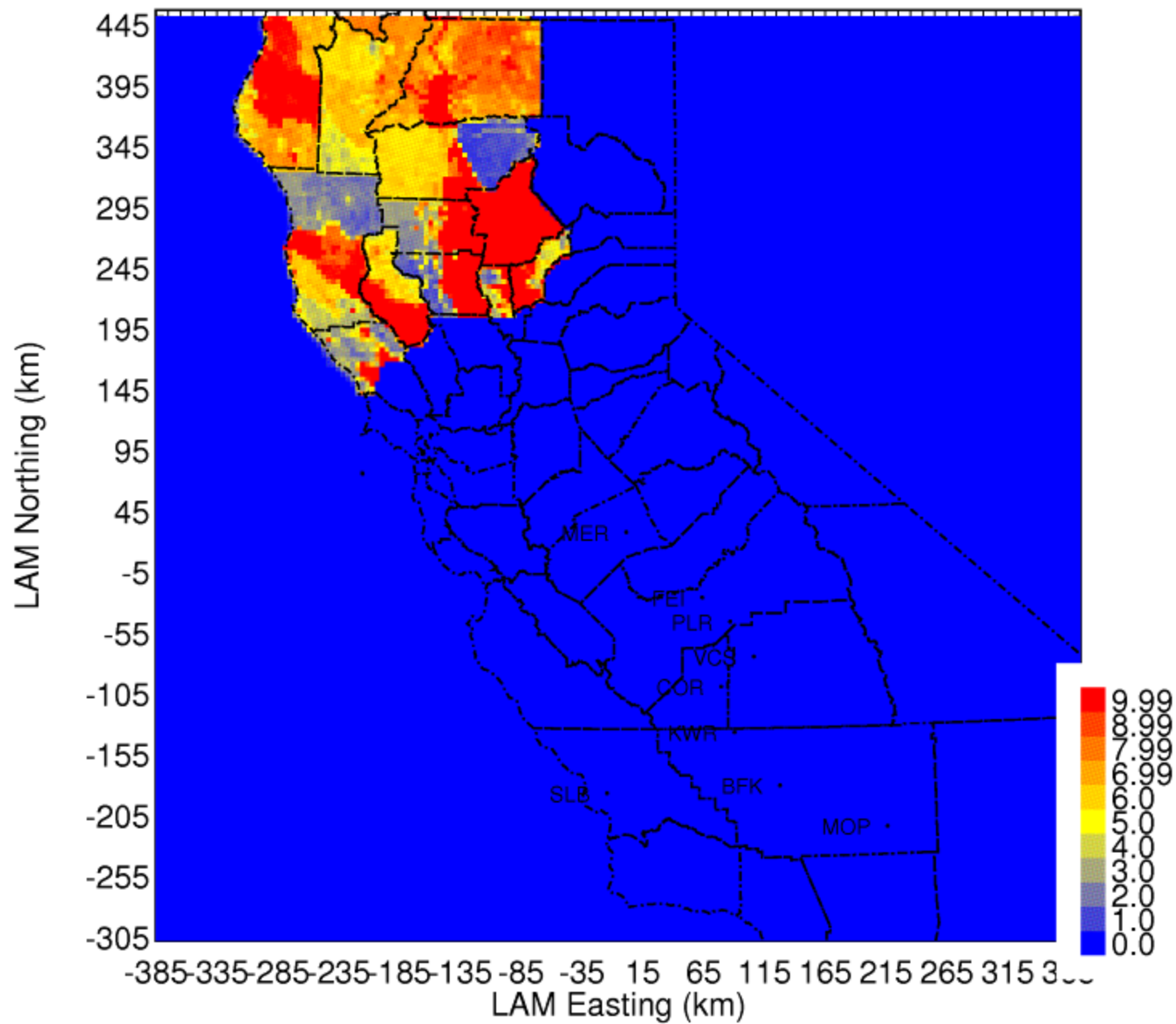


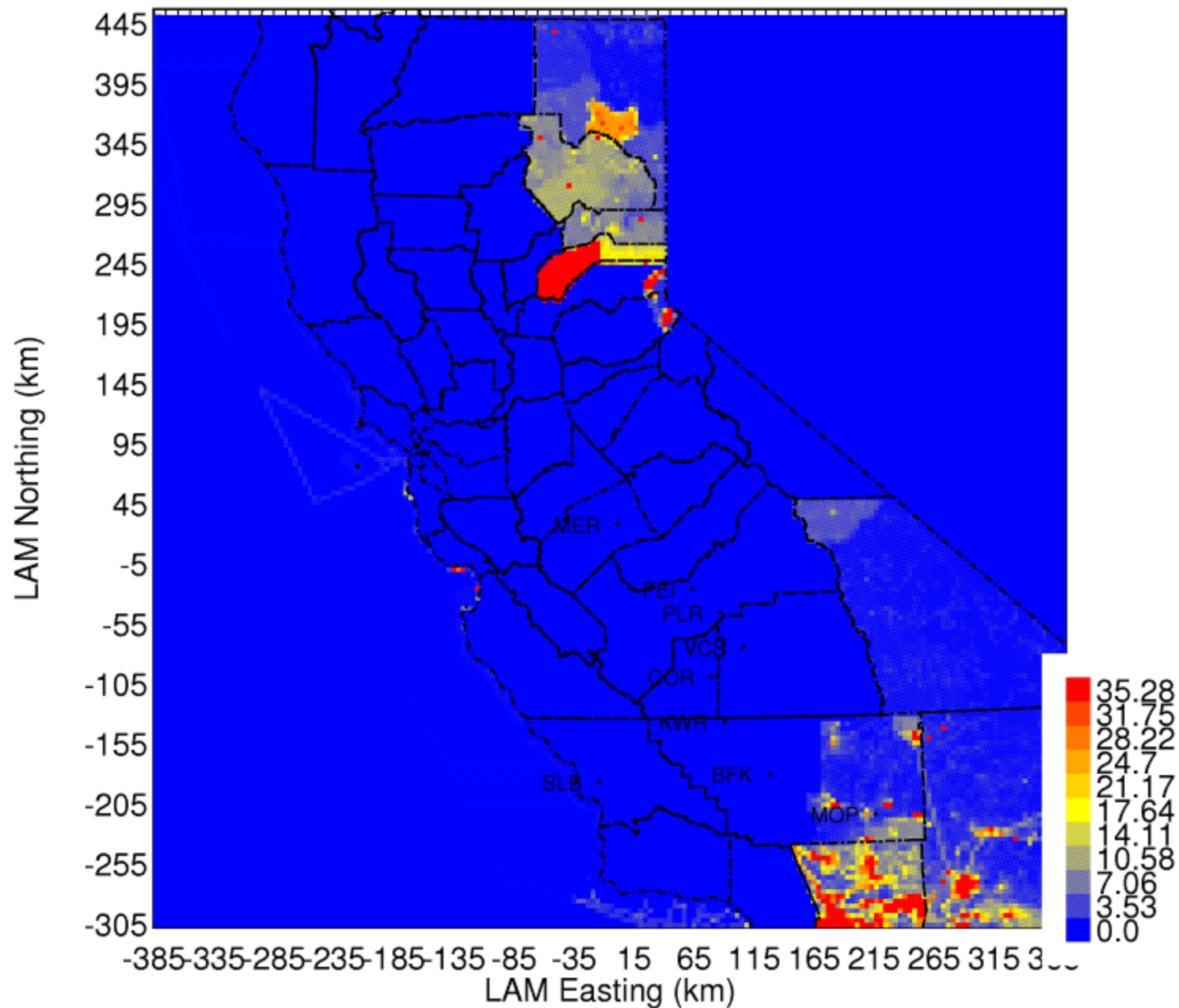




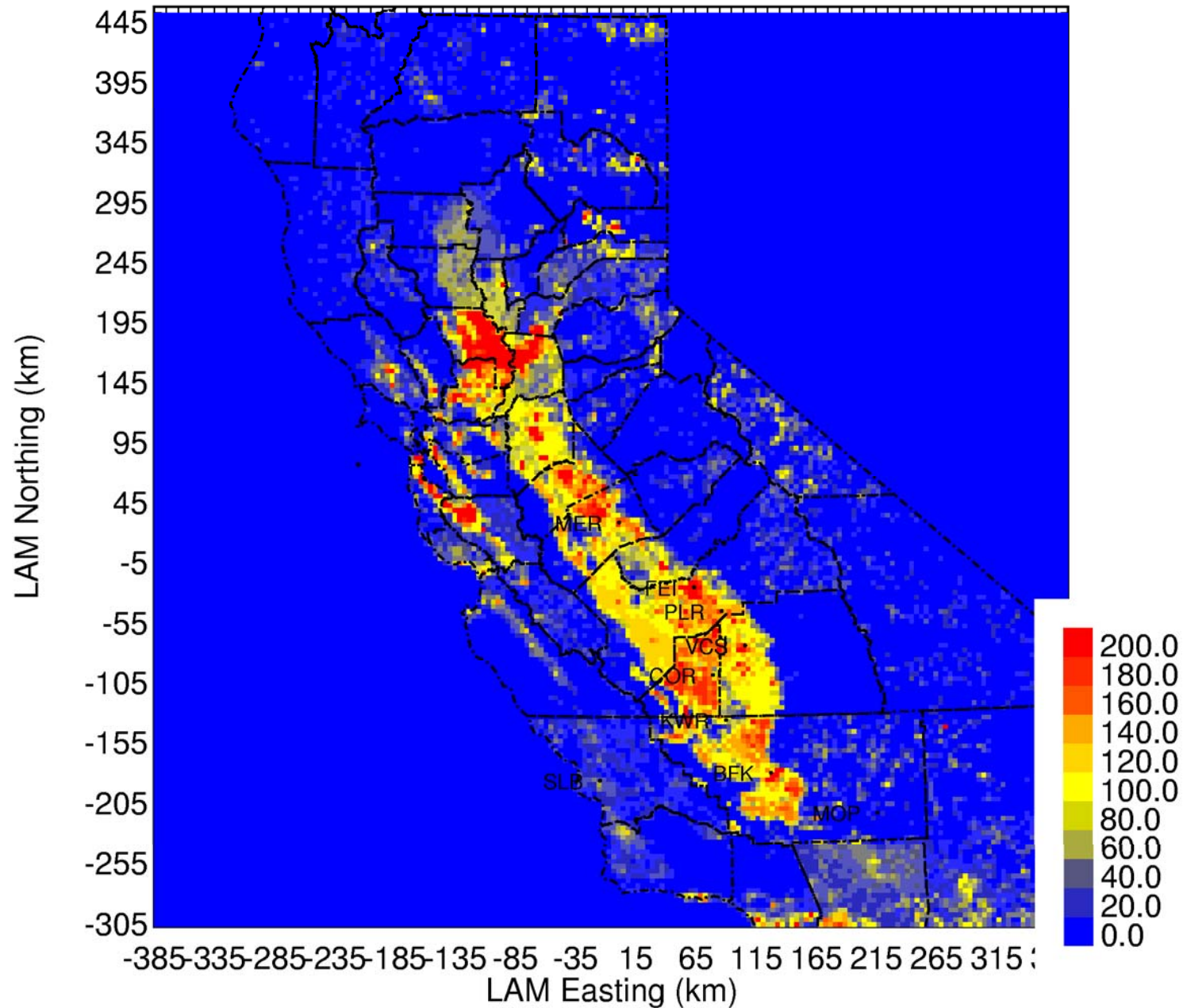




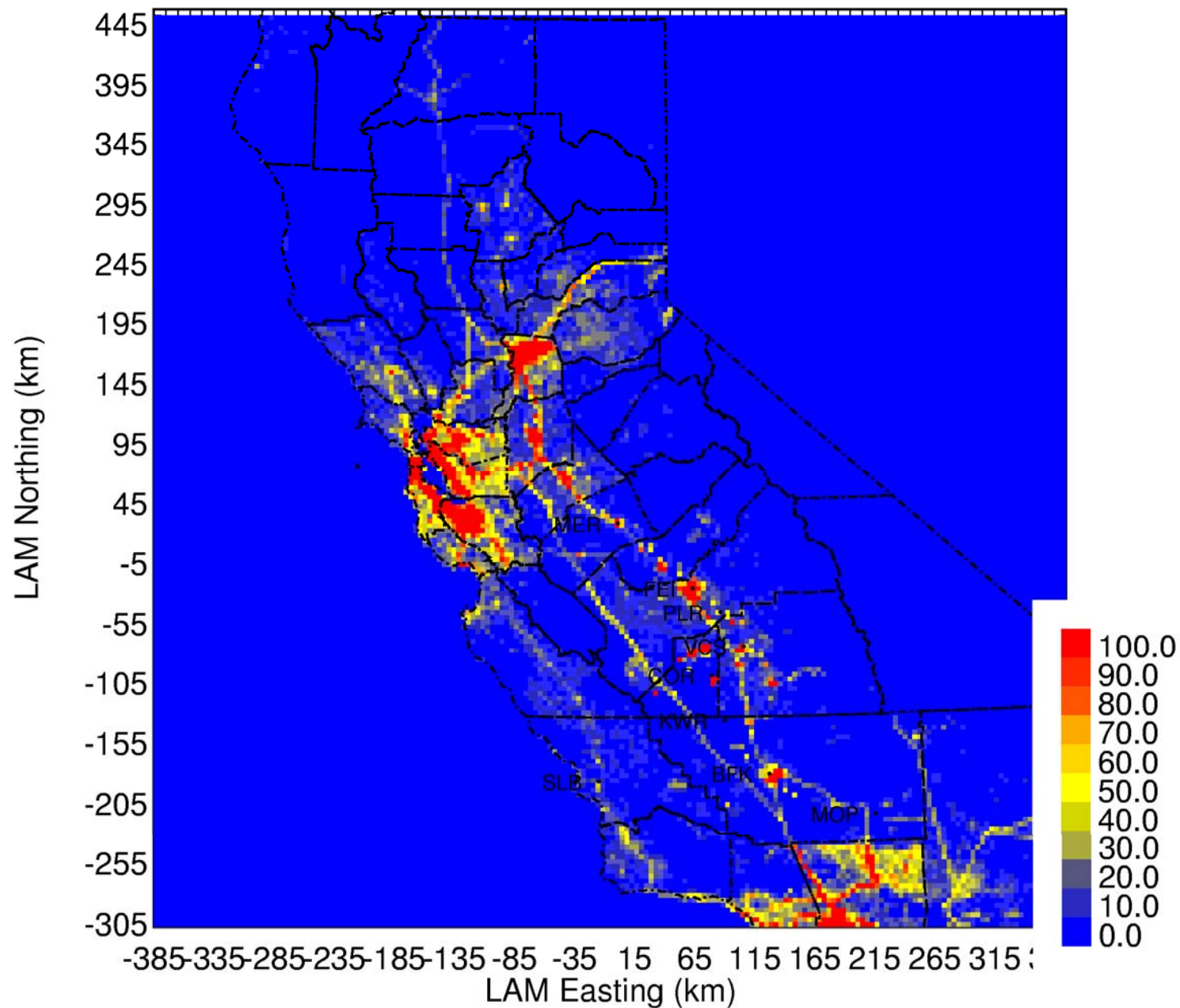




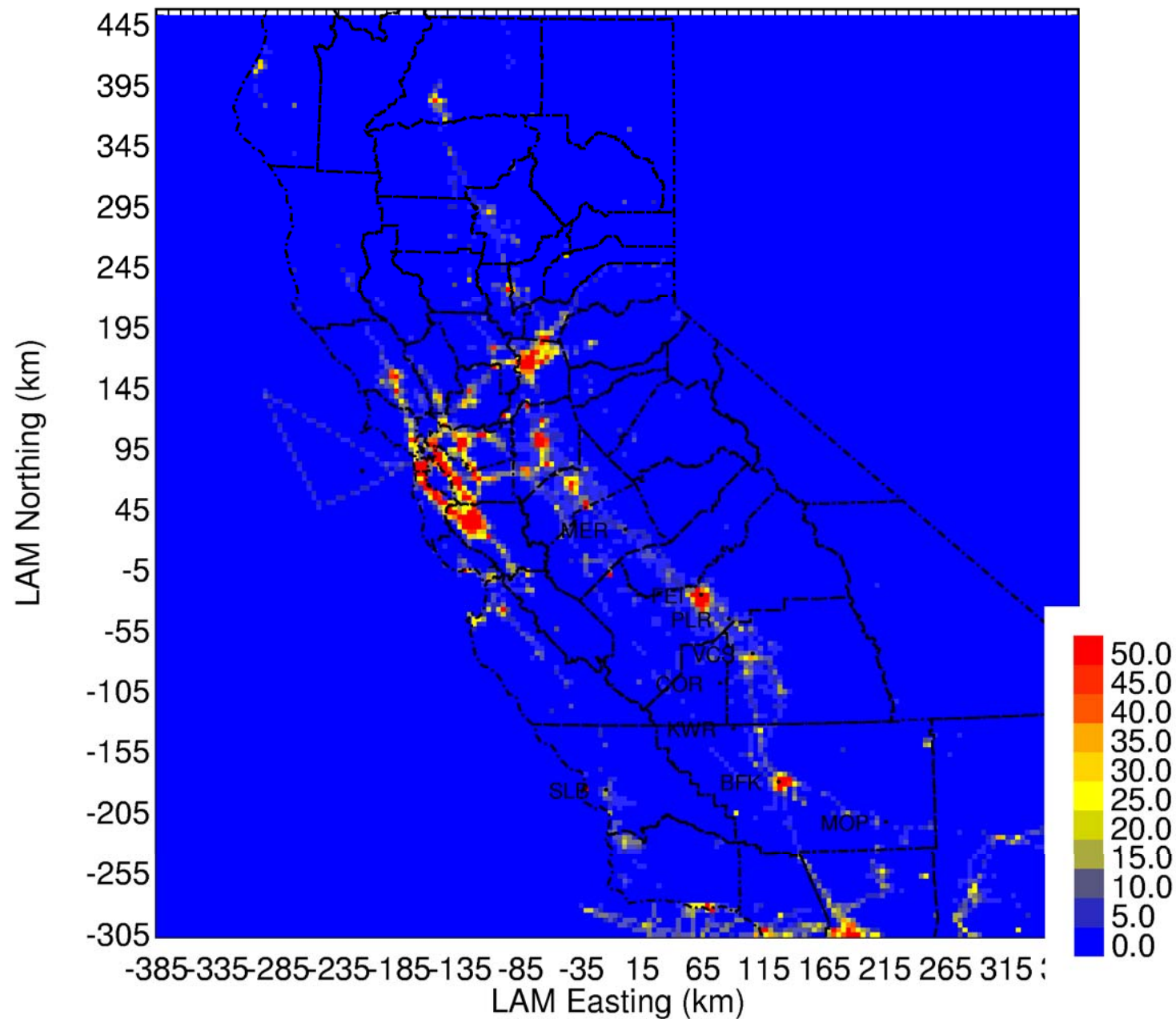
Unpaved Road Dust MASS



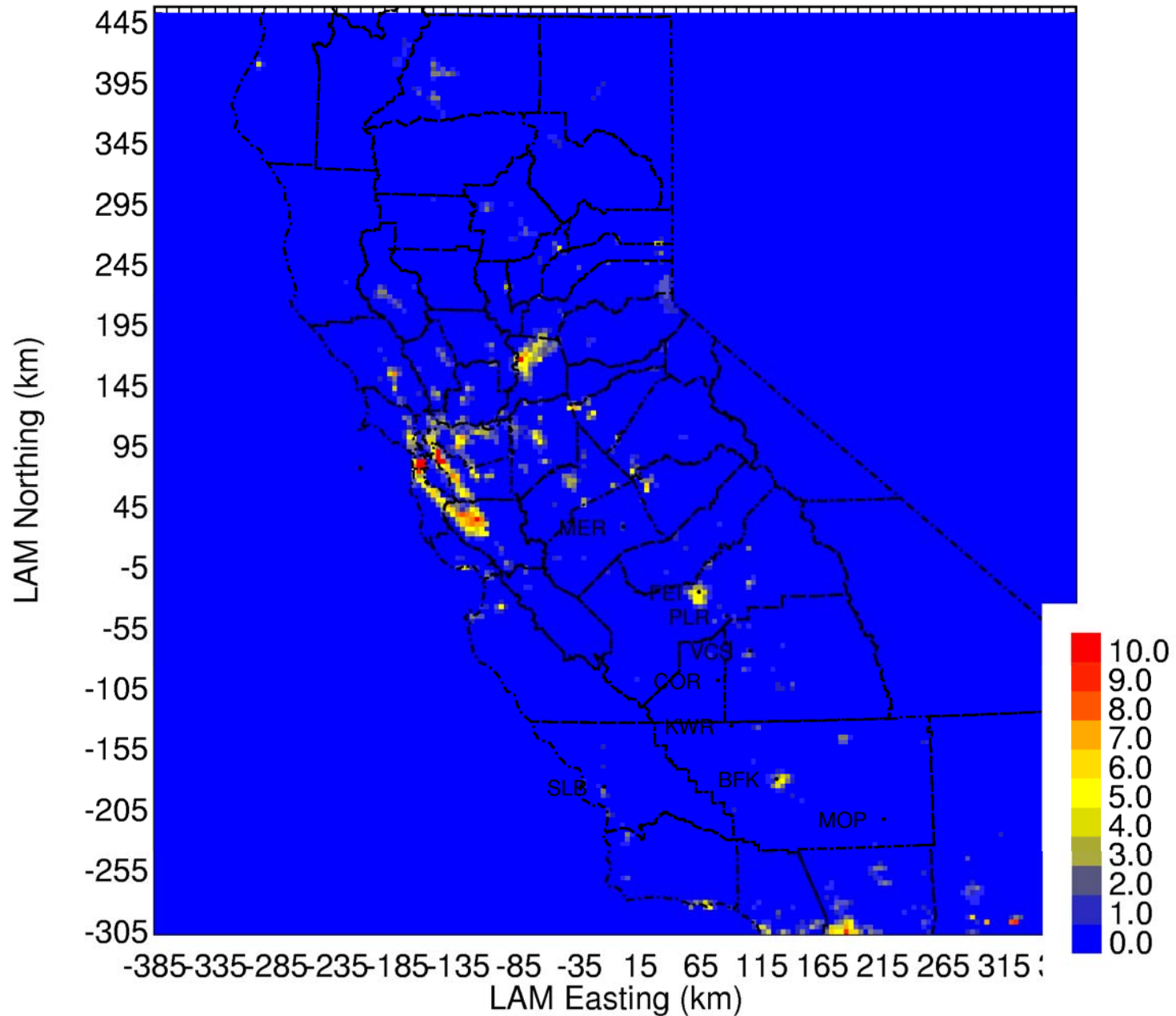
Paved Road Dust MASS



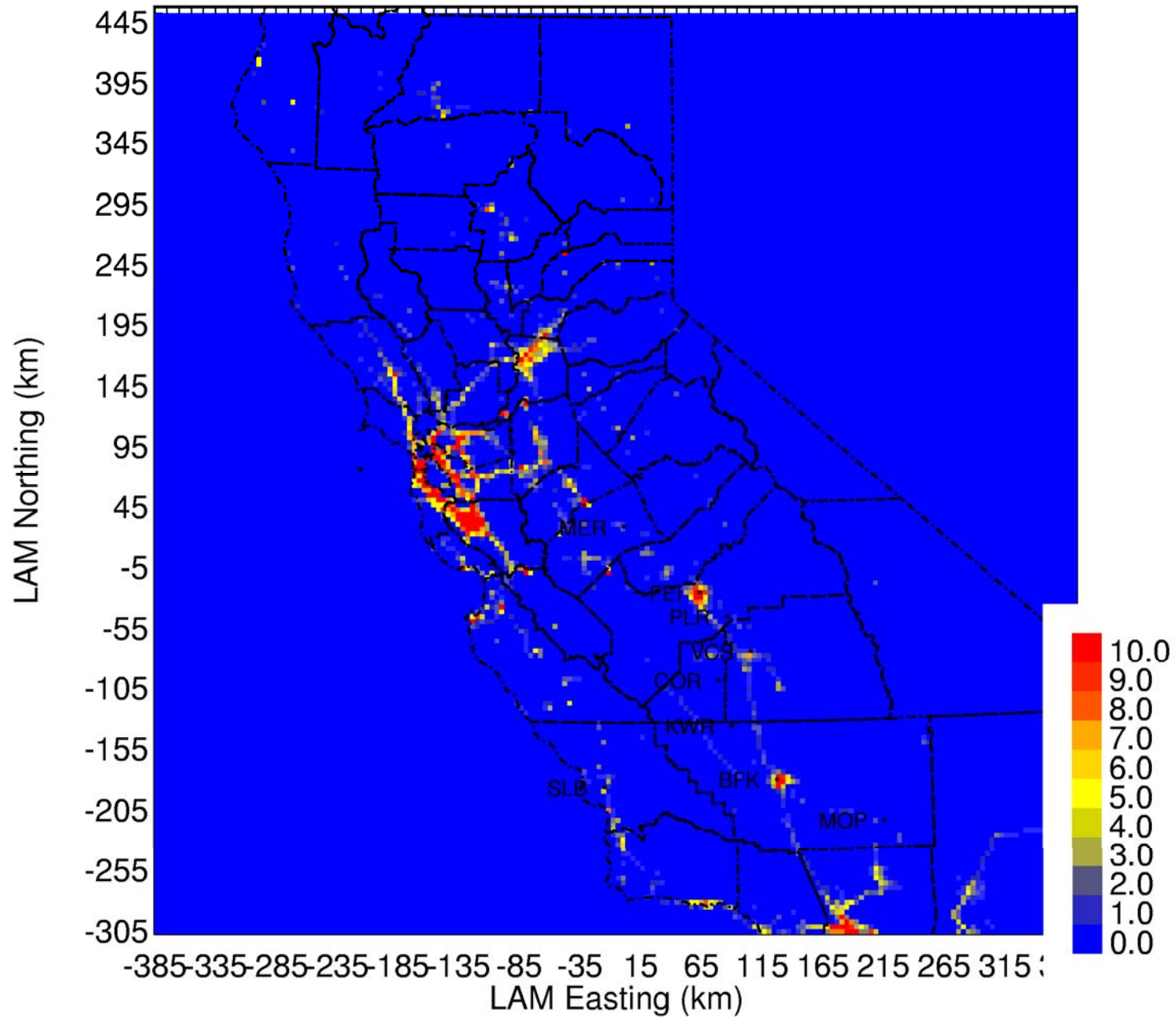
Diesel Engines MASS



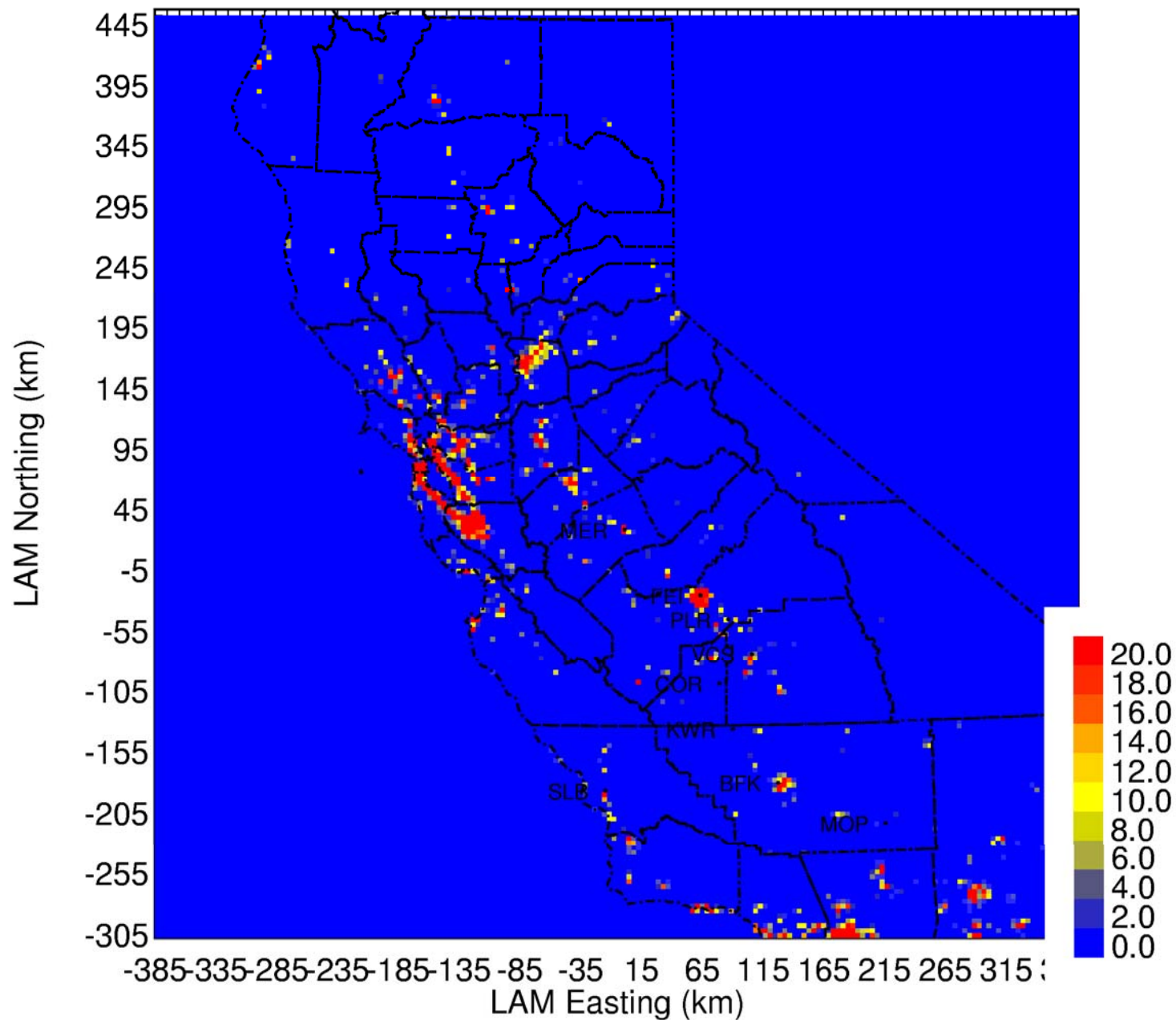
Non Catalyst Gasoline Engines MASS



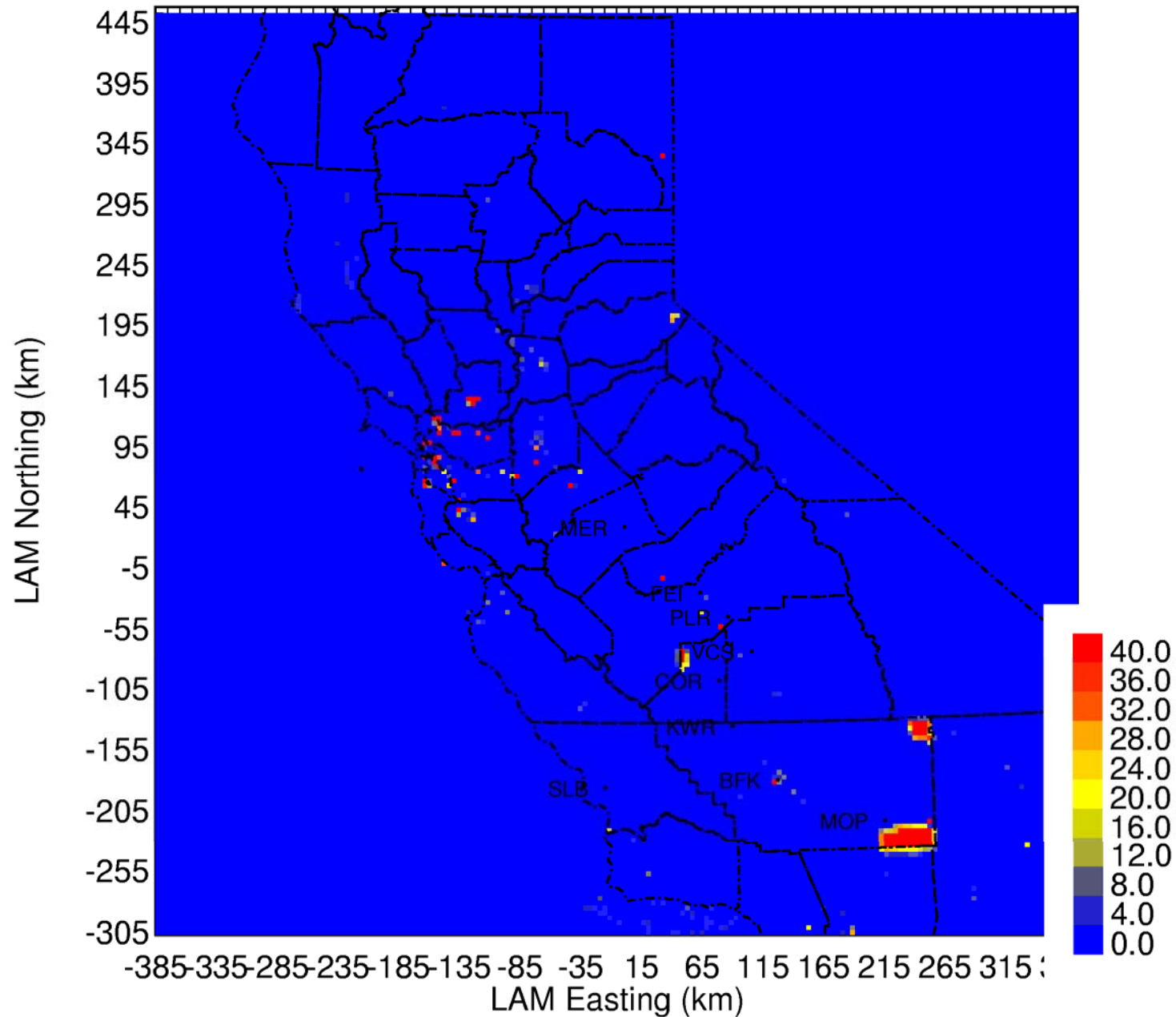
Catalyst Gasoline Engines MASS



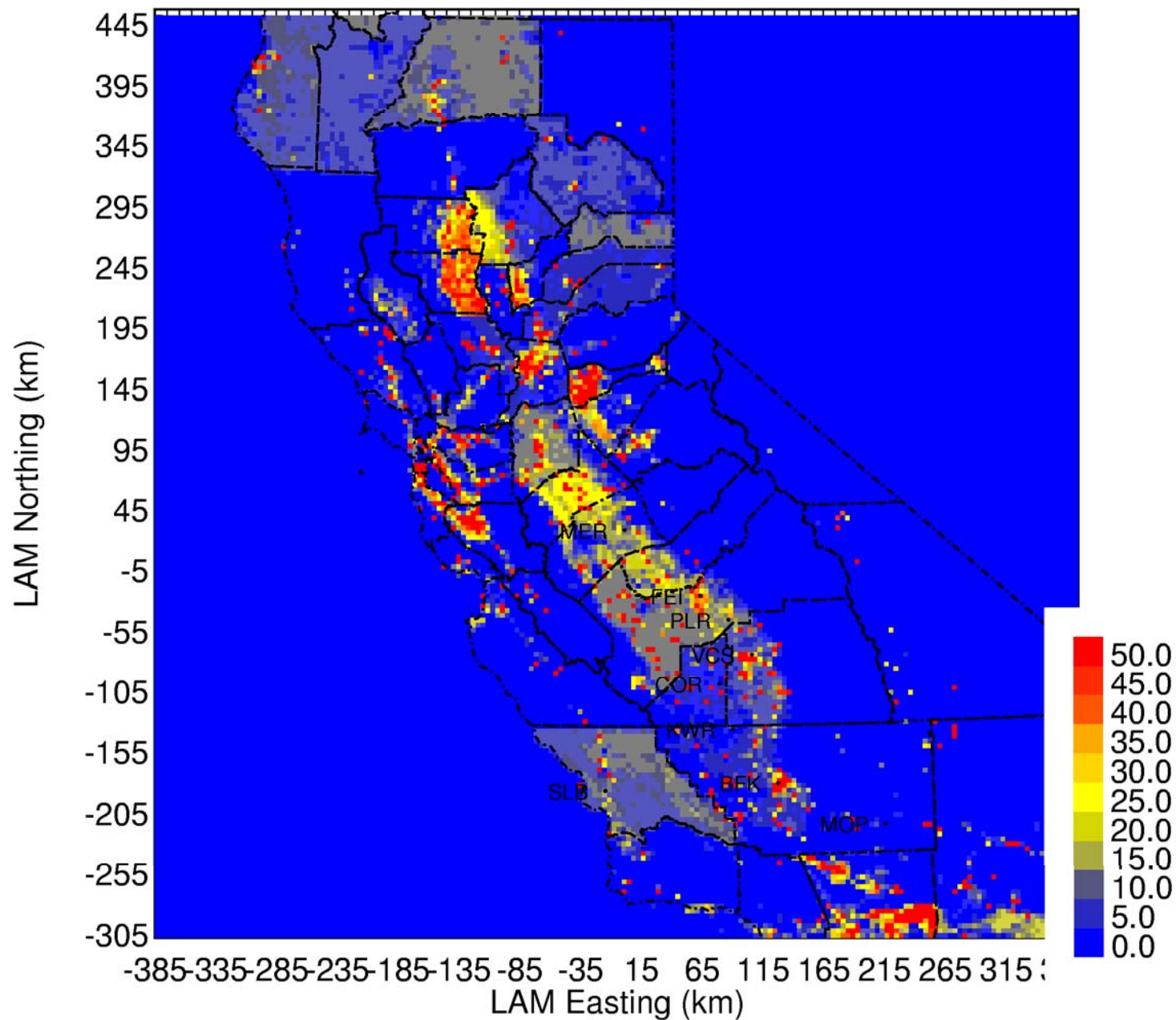
Meat Cooking MASS



High Sulfur Fuel Mass MASS



Other Sources MASS



Conclusions

- Source contributions to primary PM
 - Wood smoke at urban locations
- Source contributions to secondary nitrate
 - Diesel engines contribute most of the NO_x
 - Gasoline engines also significant
 - Ammonium ion from agriculture dominates

Conclusions

- Primary and secondary PM concentrations are dominated by local sources
- Transport distance for Nitrate > Ammonium Ion > Organic Carbon
- Transport between regions seems relatively low during CRPAQS stagnant conditions
 - Material mixed to upper layers is quickly transported out of the domain.