Five Decades of Air Quality Studies in Central California

John G. Watson (john.watson@dri.edu)
www.researchgate.net/profile/John_Watson13

Desert Research Institute
Nevada System of Higher Education
Reno, Nevada, USA

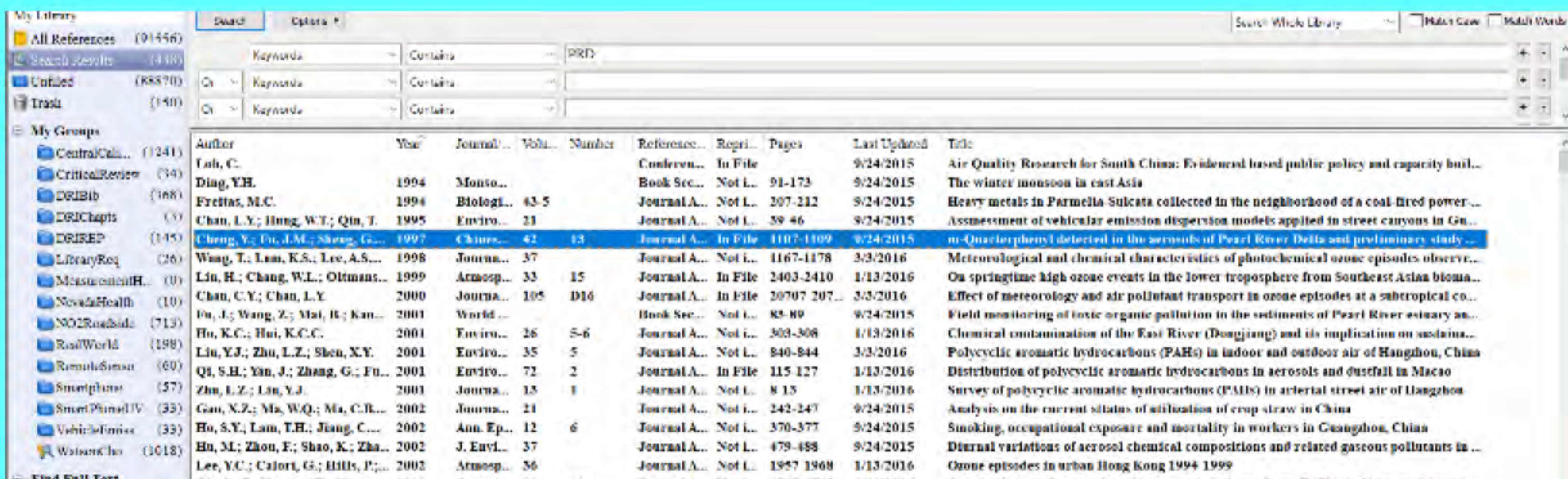
Presented at:
Clean Air Leadership Talks
Air Resources Board
Sacramento, CA
February 20, 2019

Objectives

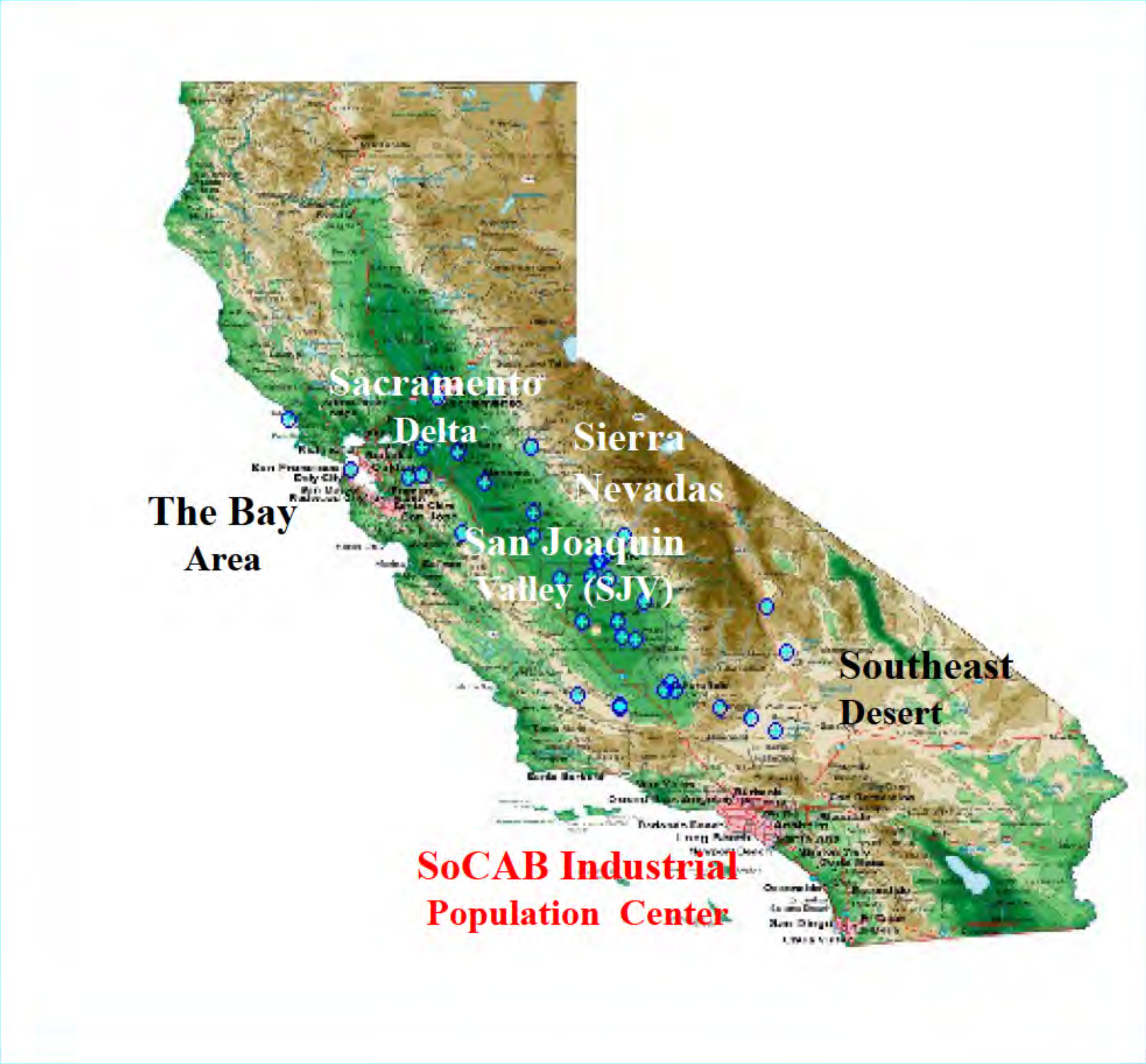
- Explain why central California is one of the world's most important air quality laboratories
- Trace the evolution of knowledge about central California air quality through scientific study
- Identify challenges to improving central California's air quality

California air basins are among the most studied areas in the world, with many of the same phenomena being found in highly polluted Asian Regions

Study Area	No. Publications and Reports	Publication Years
Southern California	1495	1949-2018
Central California	1222	1960-2018
Beijing-Hebei-Tianjin (JingJin Ji)	810	1980-2018
Yangtze River Delta	483	1981-2018
Pearl River Delta	979	1978-2018
Indo-Gangetic Plain of northern India	492	1973-2018



Central California is a complex mixture of populations, emissions, terrain, and meteorology that has commonality with other highly-polluted parts of the world



Central California's pollution has been studied for decades with a combination of short-term and long-term campaigns

- 1970: Project Lo-Jet
(identified summertime low-level jet and Fresno eddy)
- 1972: Aerosol Characterization Experiment
(ACHEX, first TSP chemical composition and size distributions)
- 1979-1980: Inhalable Particulate Network
(first long-term $PM_{2.5}$ and PM_{15} mass and elemental measurements in Bay Area, Five Points)
- 1978: Central California Aerosol and Meteorological Study
(seasonal TSP elemental composition, seasonal transport patterns)
- 1979-1982: Westside Operators
(first TSP sulfate and nitrate compositions in western Kern County)
- 1984: Southern San Joaquin Valley ozone study
(first major characterization of O_3 and meteorology in Kern County)
- 1984-86: Caltech Acid Fog studies

Central California's pollution has been studied for decades with a combination of short-term and long-term campaigns

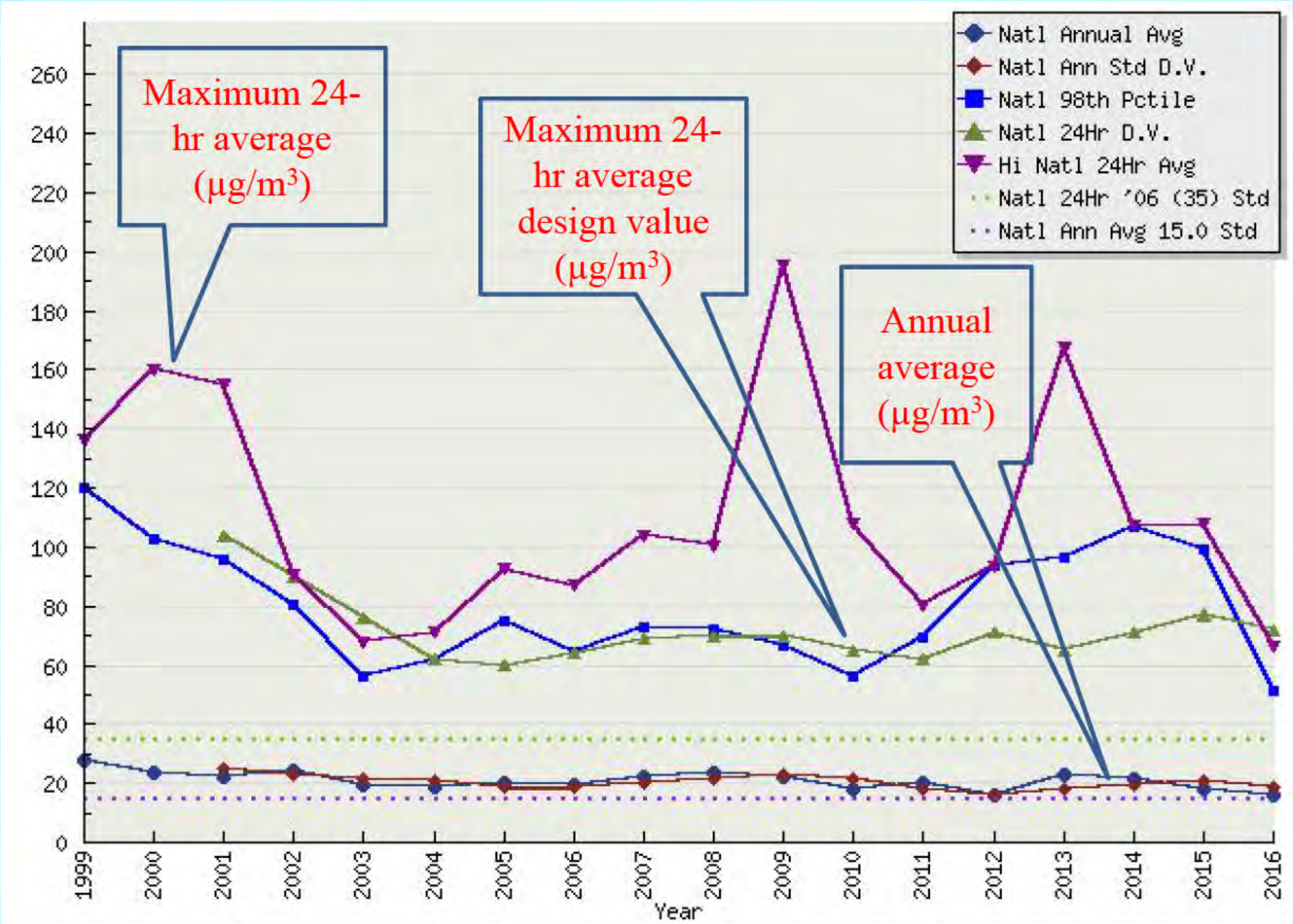
- 1986-1988: California Source Characterization Study
  (quantified chemical composition of source emissions)
- 1988-89: Valley Air Quality Study
  (first spatially diverse, chemical characterized, annual and 24-hour $PM_{2.5}$ and PM_{10} seasonal)
- Summer 1990: San Joaquin Valley Air Quality Study/Atmospheric Utilities Signatures Predictions and Experiments
  (SJVAQS/AUSPEX, first central California regional study of O_3 and $PM_{2.5}$)
- Winter 1995: CRPAQS Pilot Study (IMS95[a])
  (first sub-regional winter study)
- December 1999 to February 2001: CRPAQS and SCOS
- July 1999 to 2007: Fresno Supersite
  (first multi-year experiment with advanced monitoring technology

[a]IMS95: 1995 Integrated Monitoring Study of the California Regional PM_{10}/$PM_{2.5}$ Air Quality Study/
Central California Ozone Study

Central California's pollution has been studied for decades with a combination of short-term and long-term campaigns

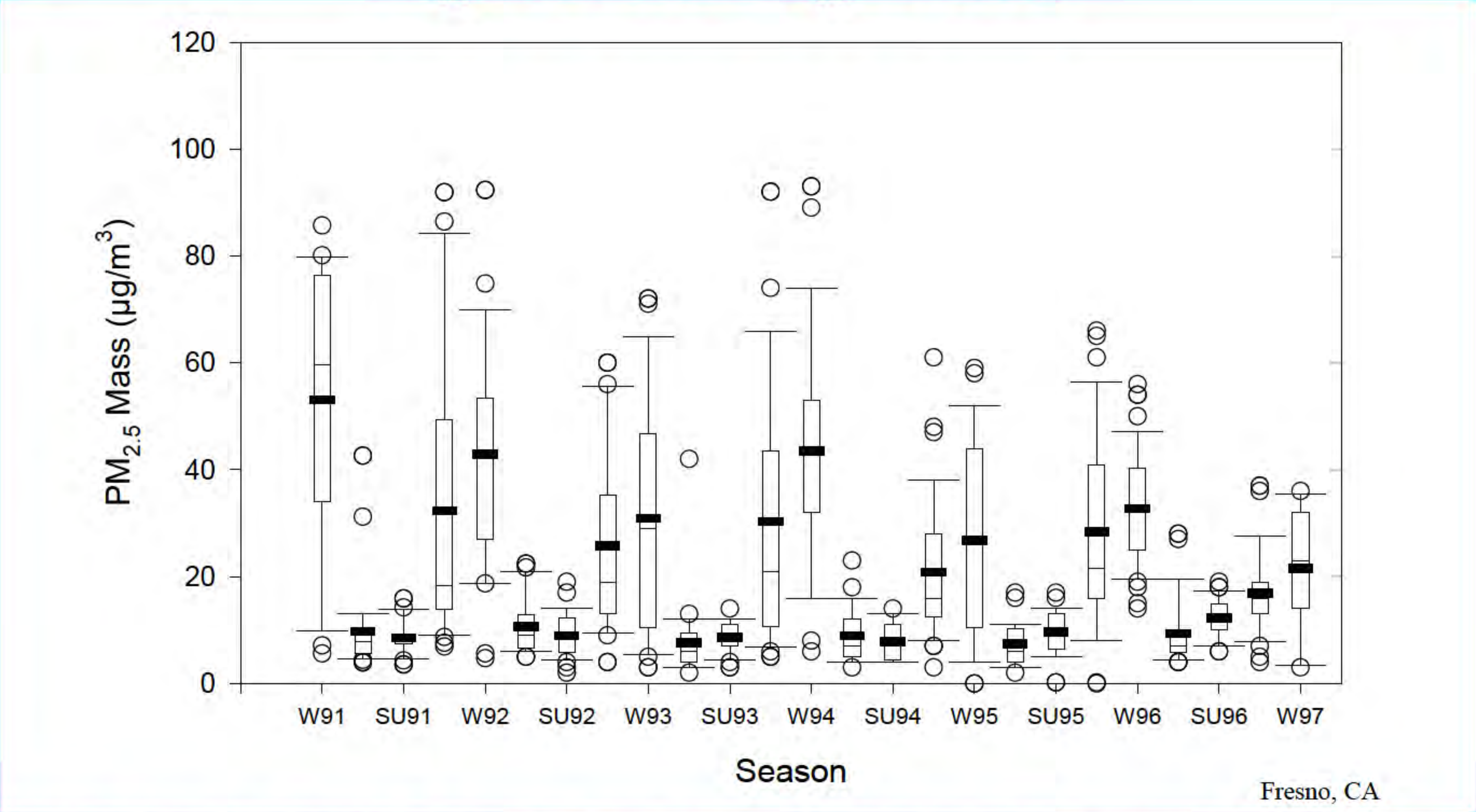
- 1984-1999: Dichotomous sampler network, $PM_{2.5}$ and PM_{10} elements
- 1988-1999: California Acid Deposition Monitoring Program (CADMP), $PM_{2.5}$ and PM_{10} ions
- 1989-present: IMPROVE $PM_{2.5}$ speciation monitoring at California National Parks
- 2000-present: EPA Chemical Speciation Network (CSN) at urban sites
- 2002-present: Trinidad Head global background monitoring
- 2008: ARCTAS-CARB aircraft sampling (June)
- 2010: Carbonaceous Aerosols and Radiative Effects Study (CARES) (summer between Sacramento and the Sierras
- 2010: NOAA CALNEX Special Study-Aircraft and ground measurements
- 2013: NASA DISCOVER-AQ: Special Study-Aircraft and ground measurements

$PM_{2.5}$ is the most challenging air quality issue in central California



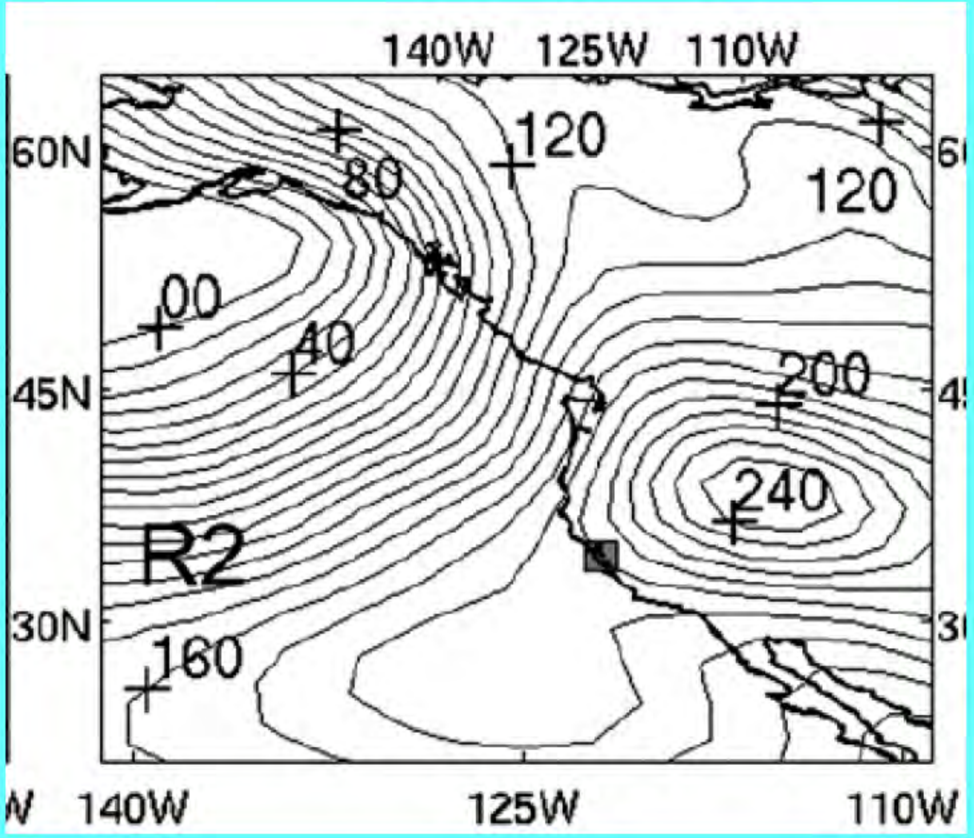
CARB, 2017

Central California $PM_{2.5}$ was, and still is, is highest during winter



Watson, J.G., DuBois, D.W., DeMandel, R., Kaduwela, A.P., Magliano, K.L., McDade, C., Mueller, P.K., Ranzieri, A.J., Roth, P.M., Tanrikulu, S., (1998). Field program plan for the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS). Desert Research Institute, Reno, NV. http://www.arb.ca.gov/airways/crpaqs/publications.htm

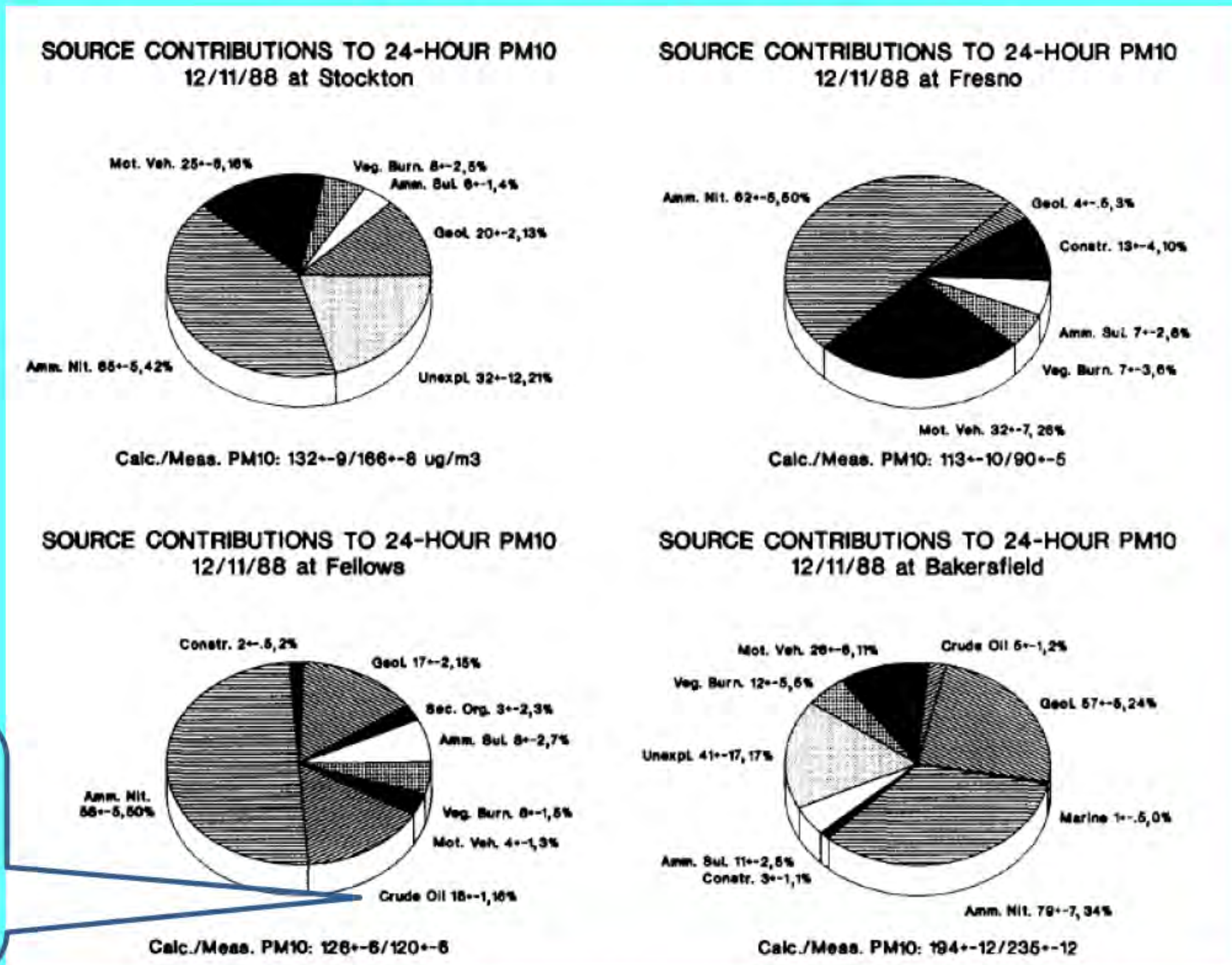
High $PM_{2.}$ concentrations occur with prolonged wintertime high pressure systems that cause subsidence inversions and enhance pollutant accumulation



Beaver, S., Palazoglu, A., Singh, A., Soong, S.T., Tanrikulu, S., (2010). Identification of weather patterns impacting 24-h average fine particulate matter pollution. Atmospheric Environment, 44, 1761-1771.

Early source apportionment implicated crude oil burning and its SO_2 emissions in west side steam generators as a large contributor

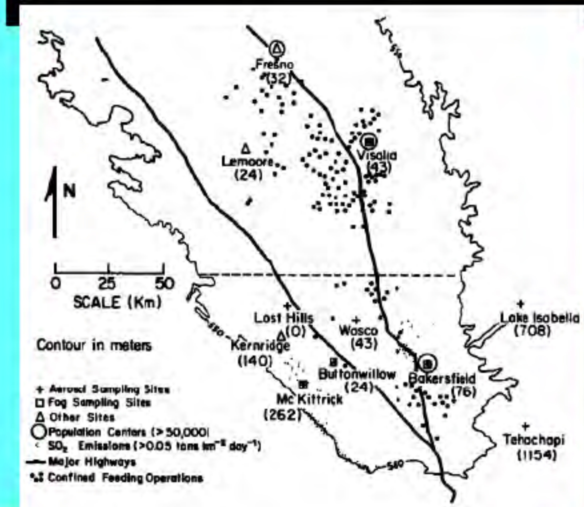
(1988-1989 Valley Air Quality Study)



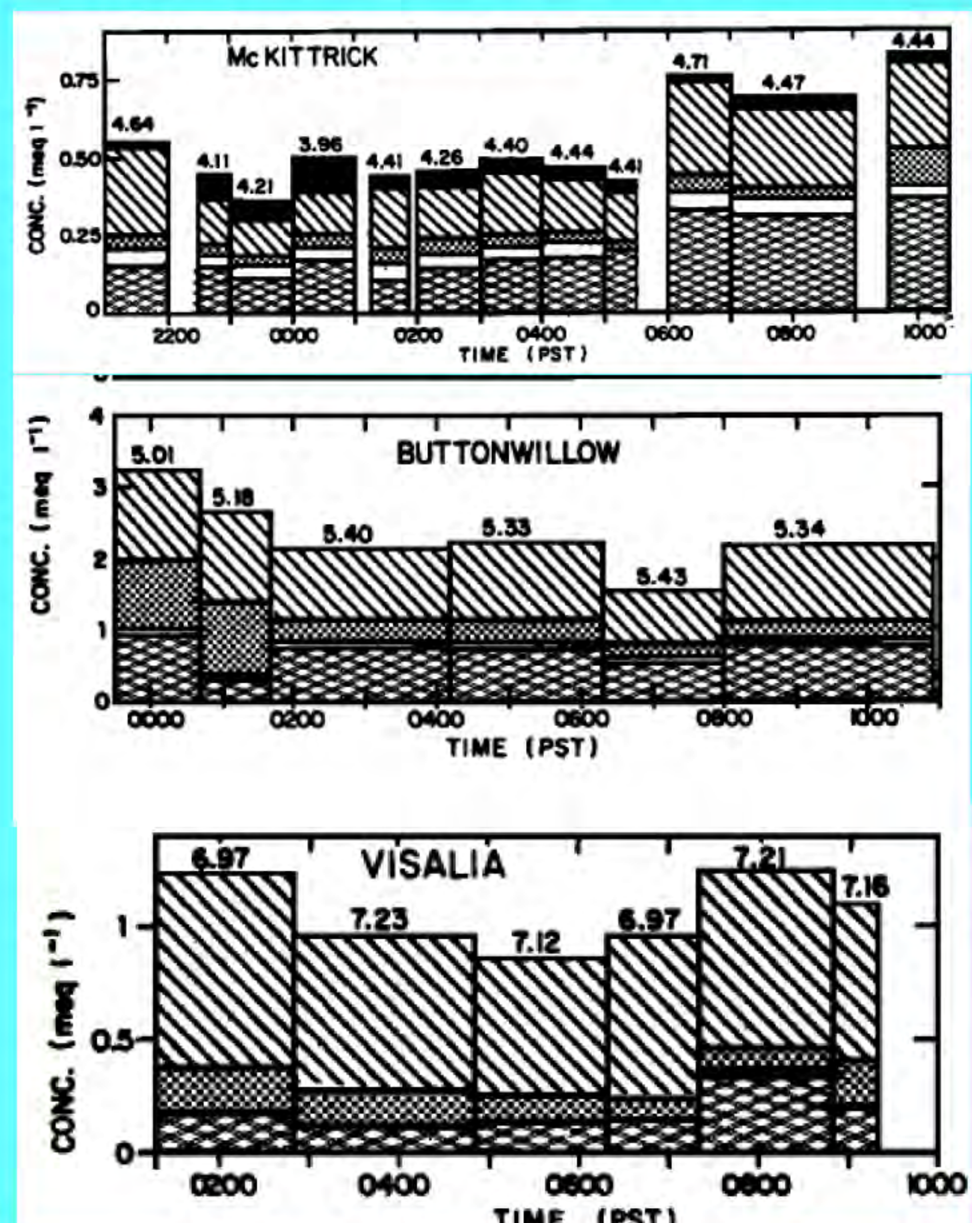
Crude oil combustion

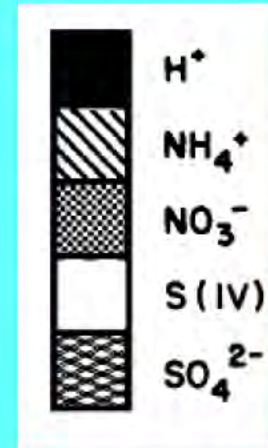
Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., (1992). PM_{10} source apportionment in California's San Joaquin Valley. Atmospheric Environment, 26A, 3335-3354.

Ground fogs turned gases into particles, especially in the southern SJV oil extraction region



Source	Emissions, t d⁻¹
SO₂[a]	
Oil production	
east side	116
west side	69
Agriculture	1
Mobile sources	6
Total emissions	1972
NOₓ[b]	
Stationary sources[c]	138
Mobile sources	52
Total emissions	190
NH₃[d]	
Livestock	46
Soil	18
Fertilizer use	10
Domestic	3
Fuel combustion	2
Total emissions	79

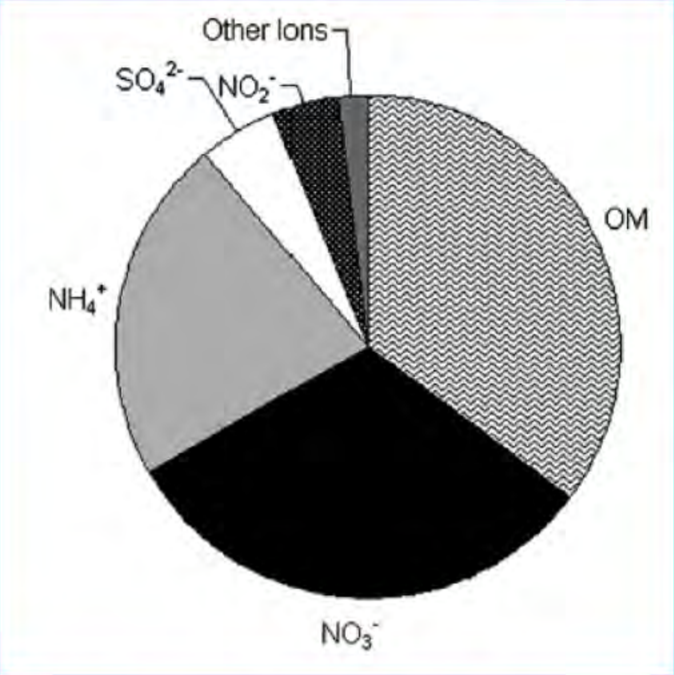




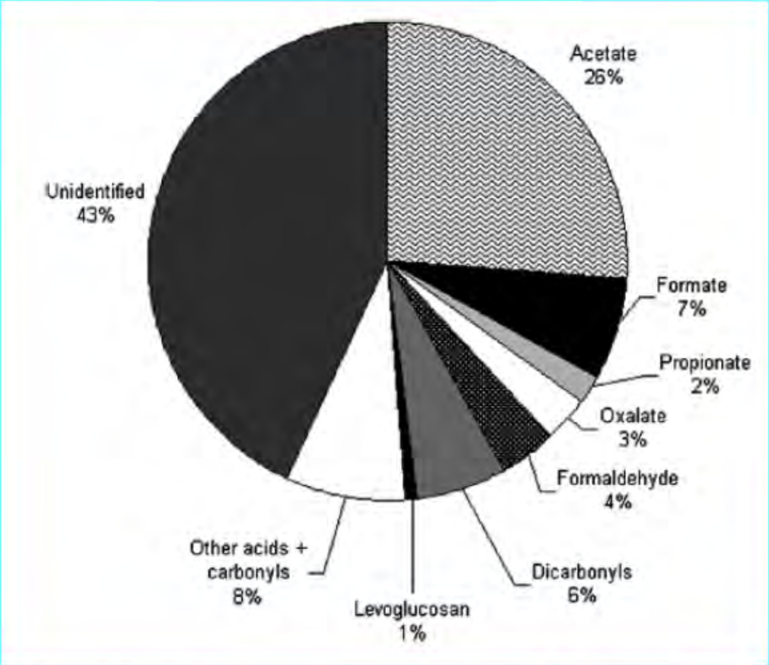
- NH_4 and SO_4 dominated the composition
- Acidic fogs were soon neutralized by NH_3

Jacob, D.J., Munger, W., Waldman, J.M., Hoffmann, M.R., (1986). The H_2SO_4-HNO_3-NH_3 system at high humidities and in fogs. 1. Spatial and temporal patterns in the San Joaquin Valley of California. Journal of Geophysical Research, 91, 1073-1088.

Fog compositions changed in California after crude oil was no longer burned for steam generation in the west side oil fields



Average fog water mass composition at Fresno



Dissolved organic carbon at Fresno shows evidence of wood burning and secondary organic end-products

Fog scavenging efficiencies (η) for organic, elemental, and total carbon

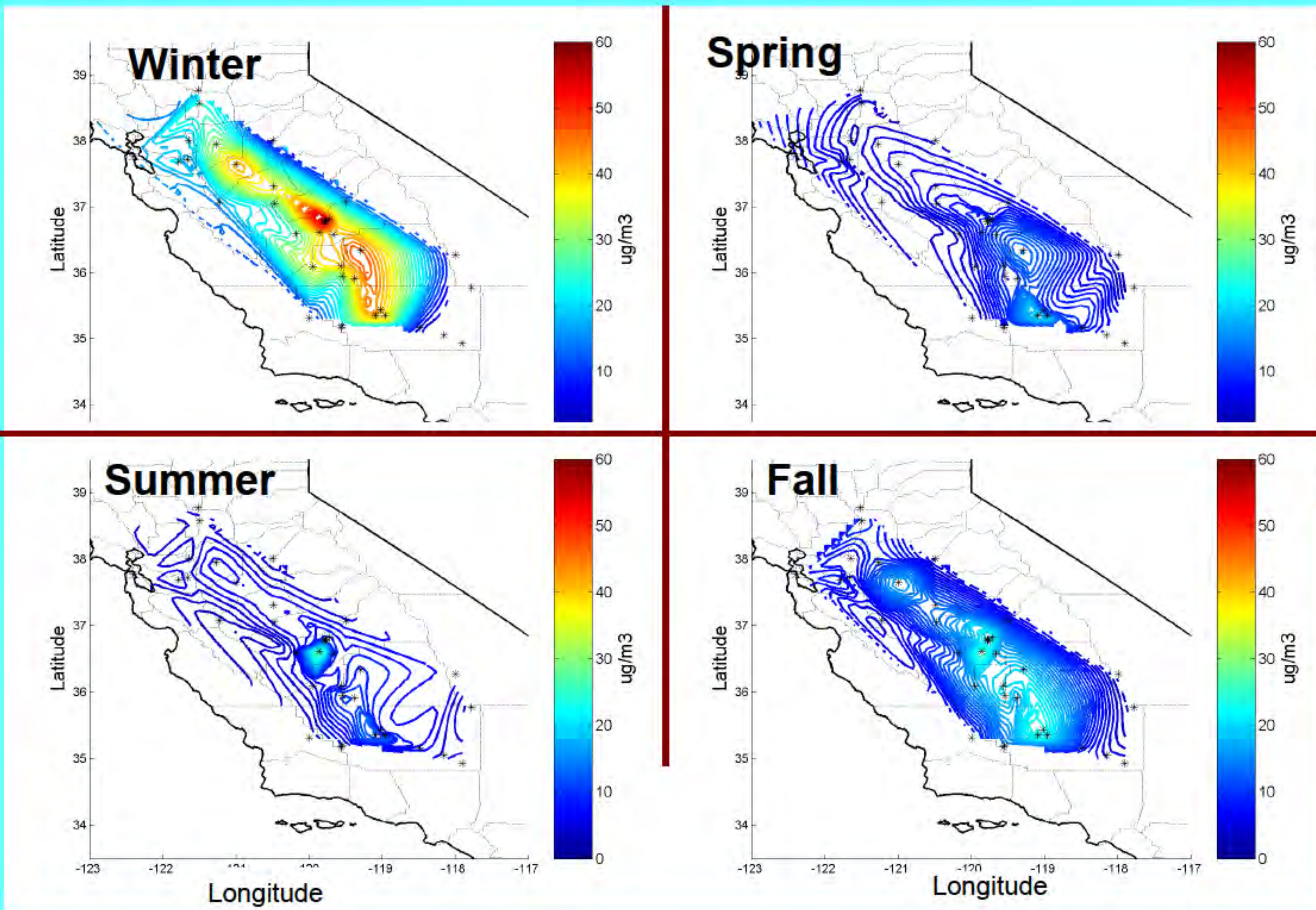
	η_{OC}	η_{EC}	η_{TC}
Angiola 12/19/00	0.90	0.12	0.84
Angiola 1/15/01	0.59	0.05	0.54
Angiola 1/17/01	0.33	0.06	0.29
Fresno 1/11/04	0.41	0.0[a]	0.36

[a] No significant difference between pre-fog and interstitial EC concentrations.

Fogs may have a cleansing action due to large droplet scavenging and deposition

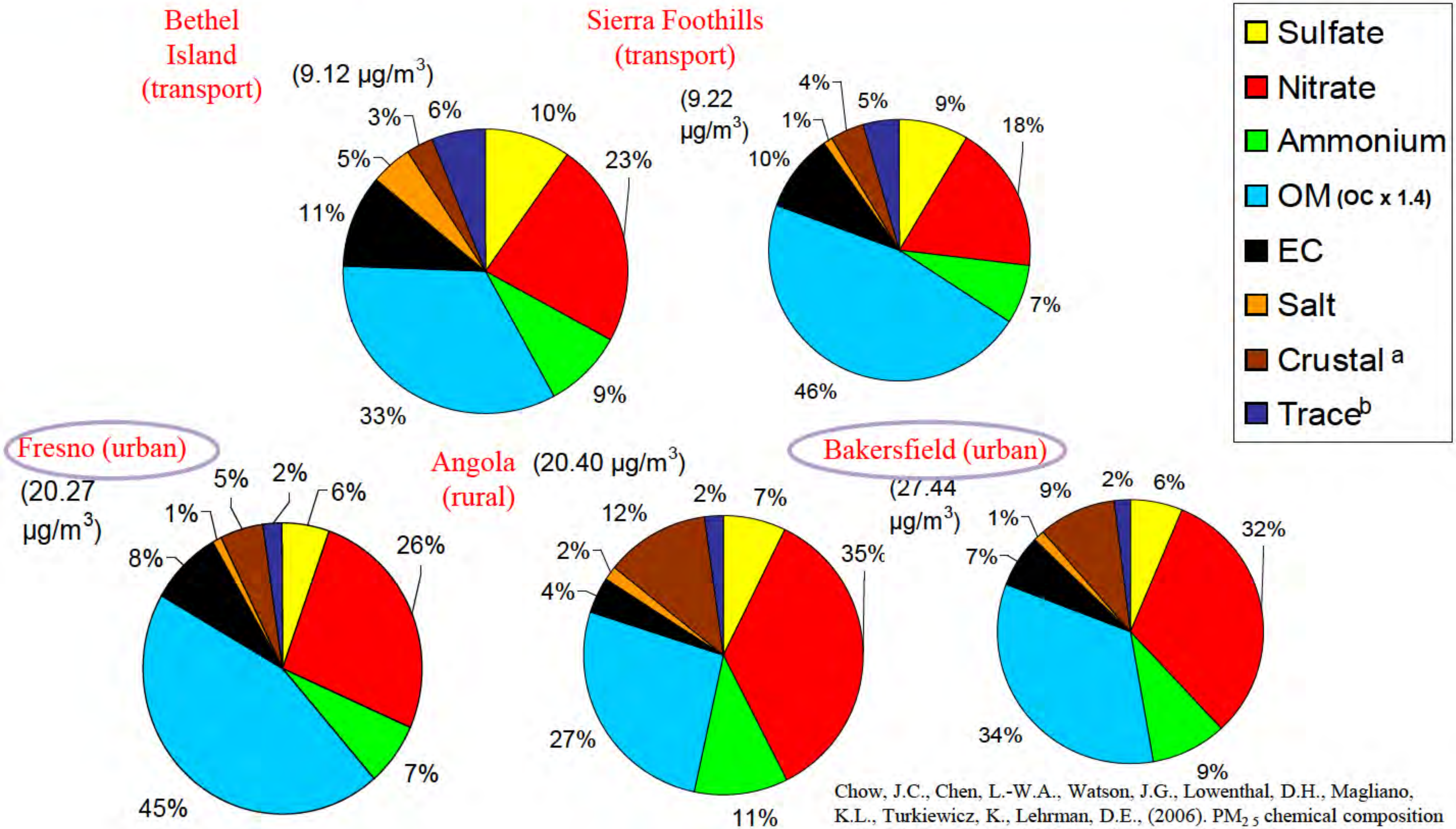
Collett, J.L., Jr., Herckes, P., Youngster, S., Lee, T., (2008). Processing of atmospheric organic matter by California radiation fogs. Atmospheric Research, 87, 232-241.

High spatial density sampling revealed that high $PM_{2.}$ mass concentrations are found throughout central California in winter



Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.L., Turkiewicz, K., Lehrman, D.E., (2006). $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). Journal of Geophysical Research-Atmospheres, 111, 1-17.

Nitrate and carbon are major components of annual $PM_{2.5}$ after major reductions in SO_2 emissions from oil extraction

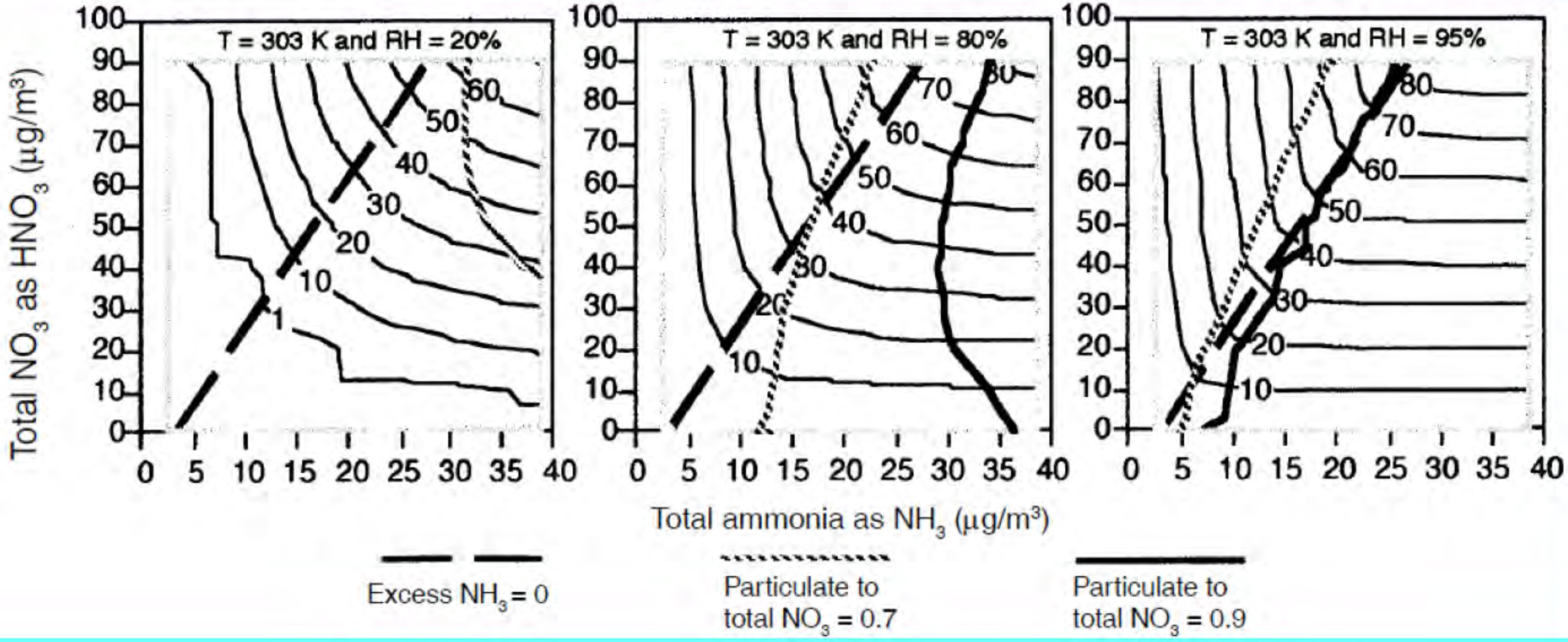


[a] 2.2 x Al + 2.49 x Si + 1.63 x Ca + 2.42 x Fe + 1.94 x Ti
[b] All elements except for Al, Si, Ca, Fe, and Ti

Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.L., Turkiewicz, K., Lehrman, D.E., (2006). $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). Journal of Geophysical Research-Atmospheres, 111, 1-17.

Ammonium nitrate results from both ammonia (NH_3) and nitric acid (HNO_3)

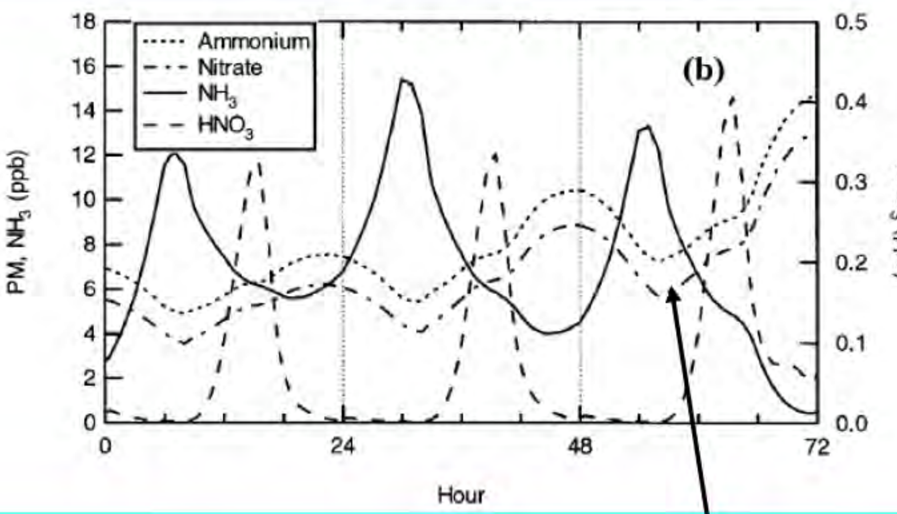
Which one should be reduced? It seemed that HNO_3 availability was the limiting factor

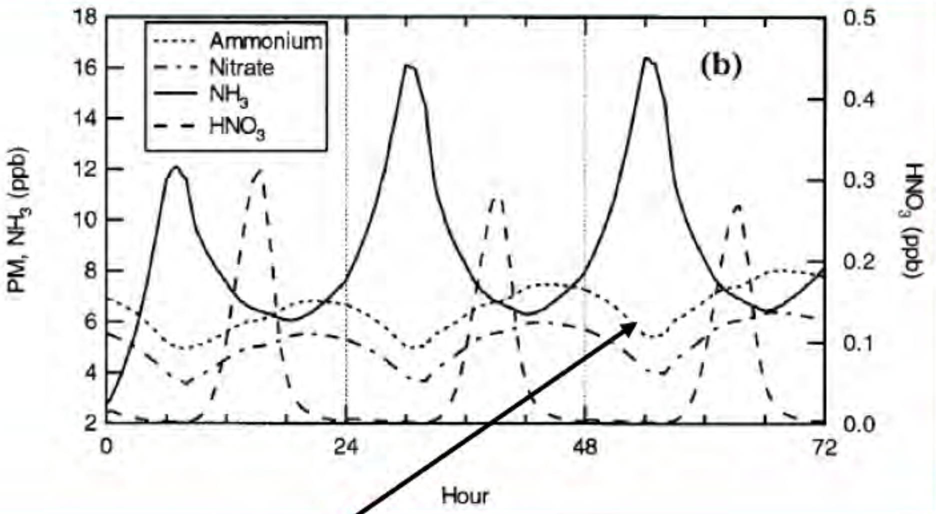


Blanchard, C.L., Roth, P.M., Tanenbaum, S.J., Ziman, S.D., Seinfeld, J.H., (2000). The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. Journal of the Air & Waste Management Association, 50, 2073-2084.

But HNO_3 has both NO_x and VOC precursors

Which ones should be reduced? A box model applied to urban (Fresno) measurements indicated that VOC reductions were needed





Base case for Fresno, 1995

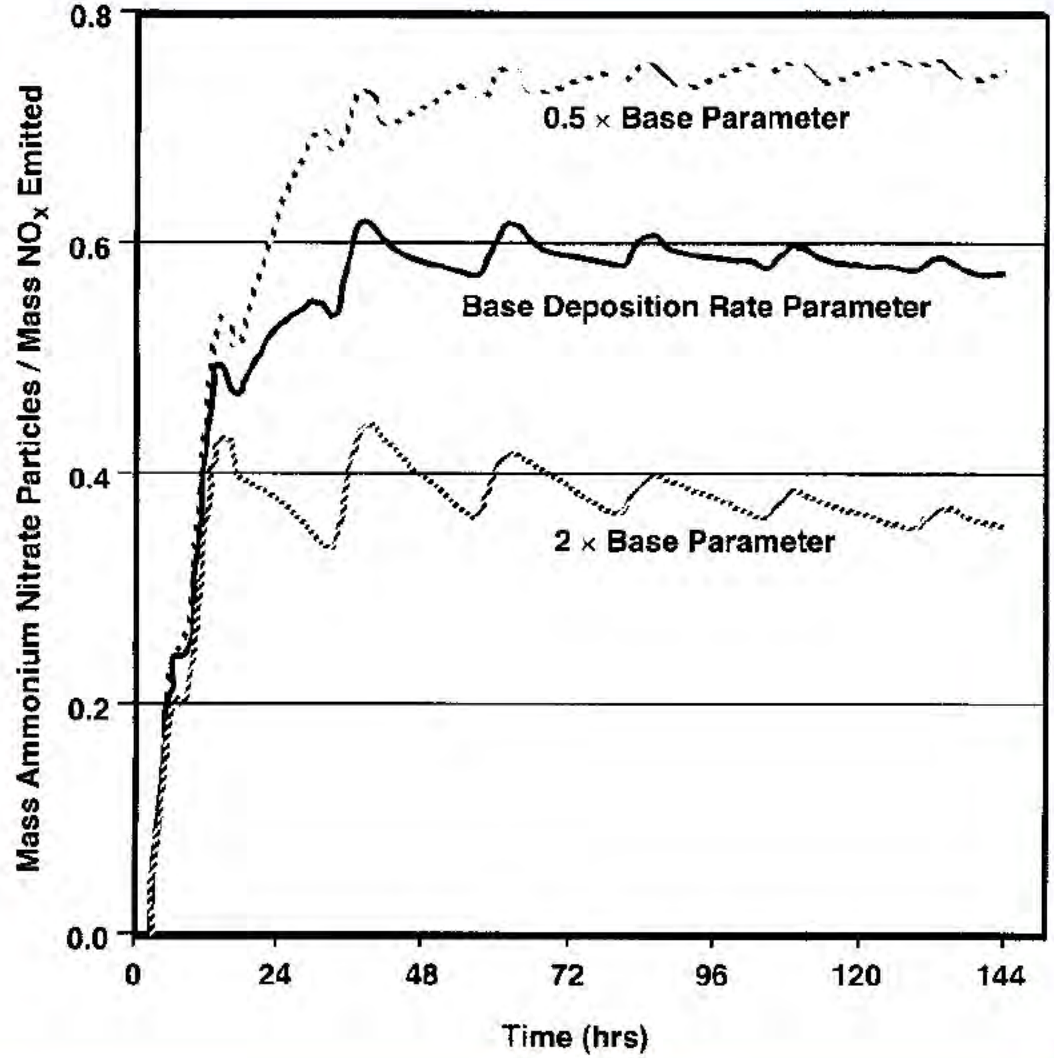
Test case with 50% VOC reduction, Fresno, 1995

NH_4NO decreased with VOC reduction

Pun, B.K., Seigneur, C., (2001). Sensitivity of particulate matter nitrate formation to precursor emissions in the California San Joaquin Valley. Environmental Science & Technology, 35, 2979-2987.

Applying a similar approach at a non-urban location, however, demonstrated a NO_x limitation

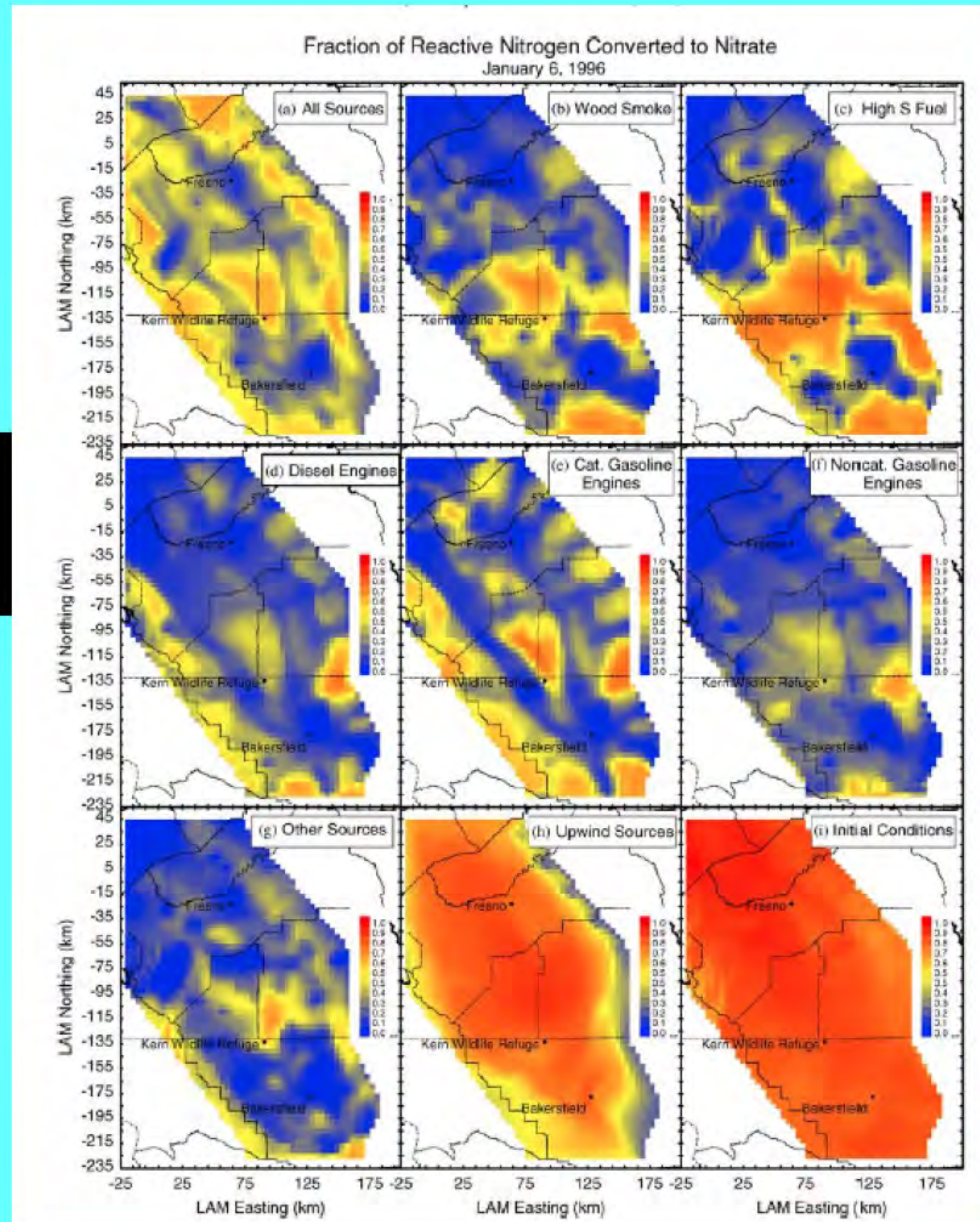
Kern Wildlife Refuge
1995



Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., Sylte, W.W., (2000). The ammonium nitrate particle equivalent of NOx emissions for wintertime conditions in Central California's San Joaquin Valley. Atmospheric Environment, 34, 4711-4717.

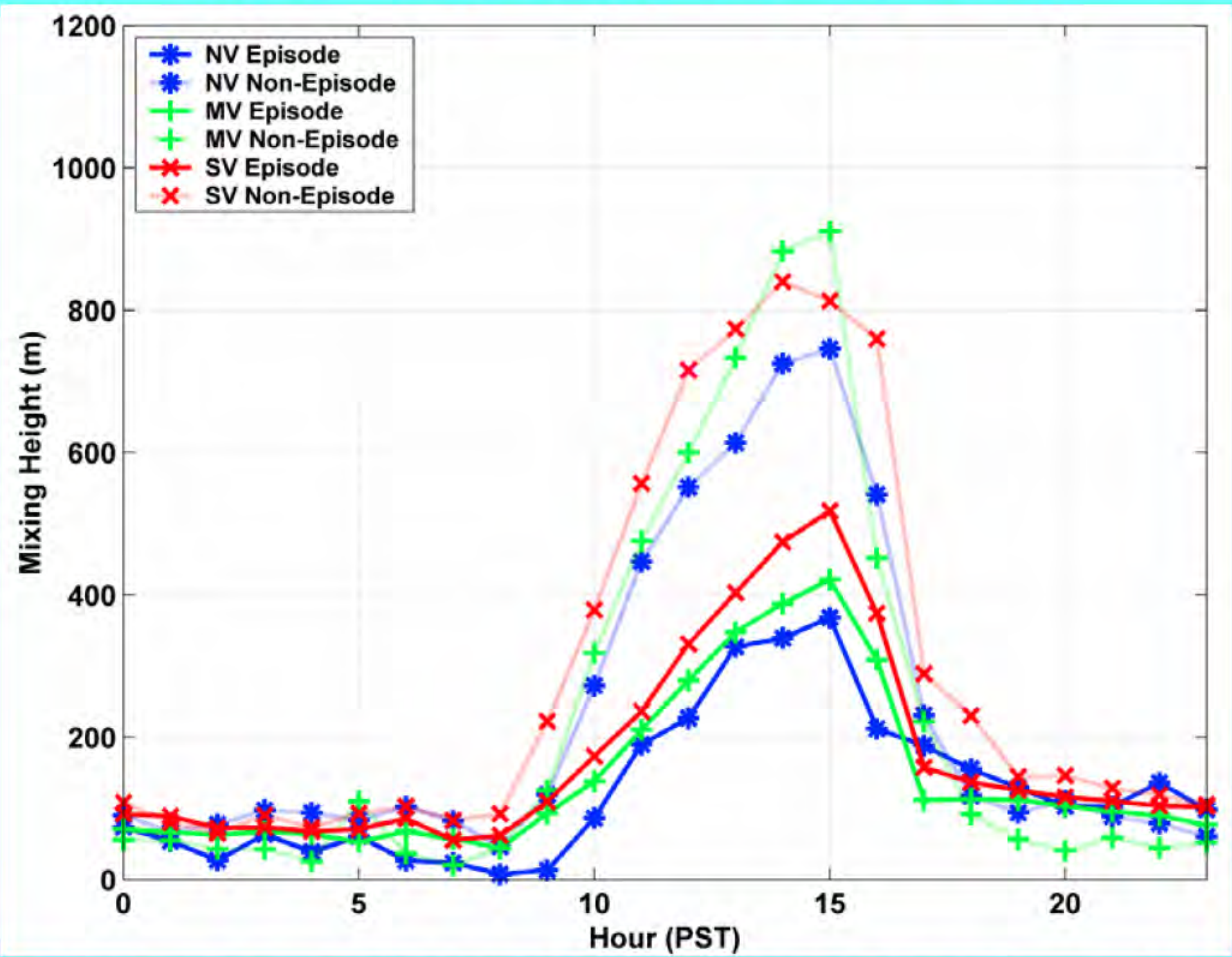
More complete 3-D modeling indicates that most NH_3NO_3 is NO_x limited

Kleeman, M.J., Ying, Q., Kaduwela, A.P., (2005). Control strategies for the reduction of airborne particulate nitrate in California's San Joaquin Valley. Atmospheric Environment, 39, 5325-5341.



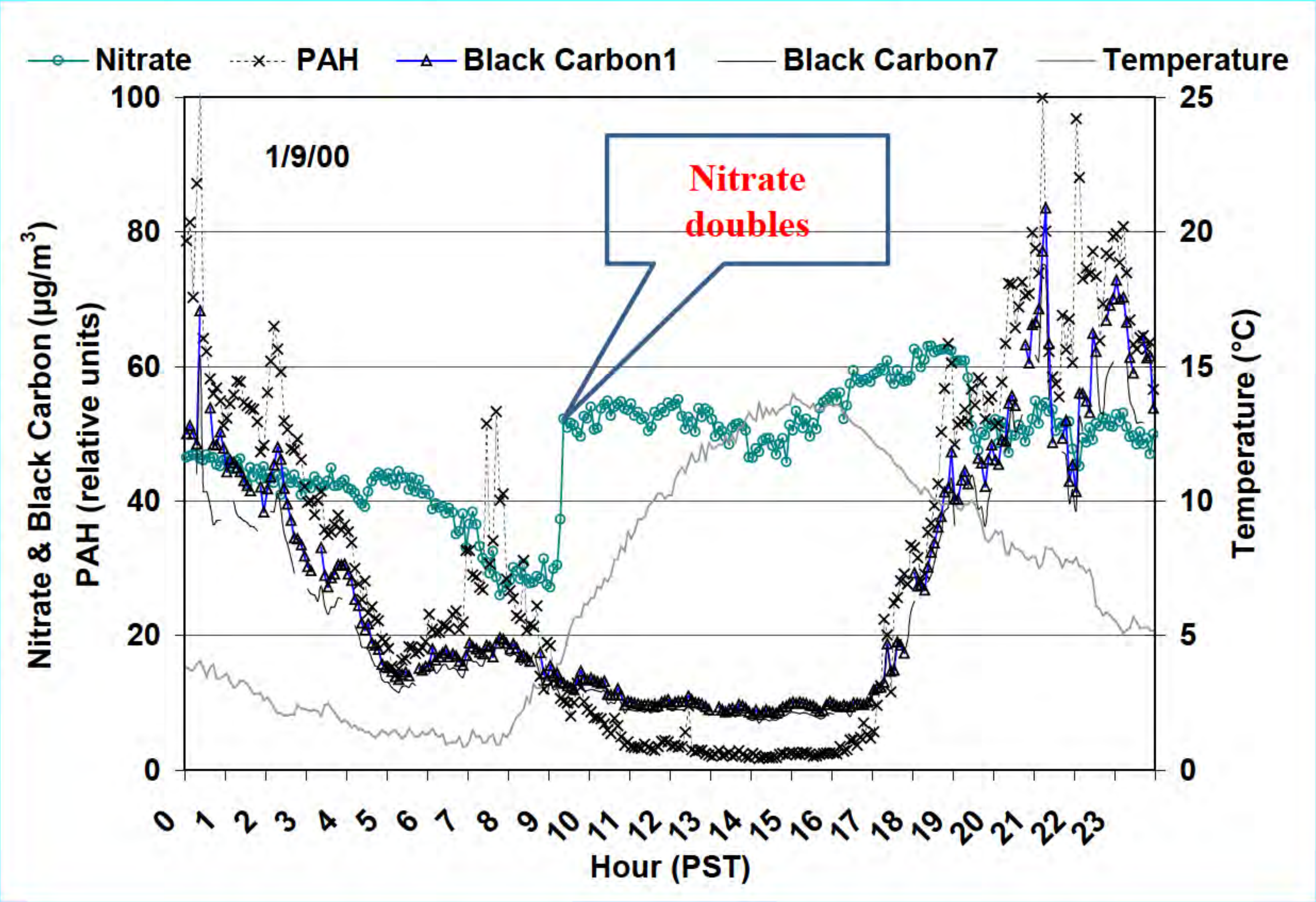
Wintertime meteorology is different from that in other seasons

Shallow surface layers separate pollutants aloft from those at the surface at night, but they mix together during the day



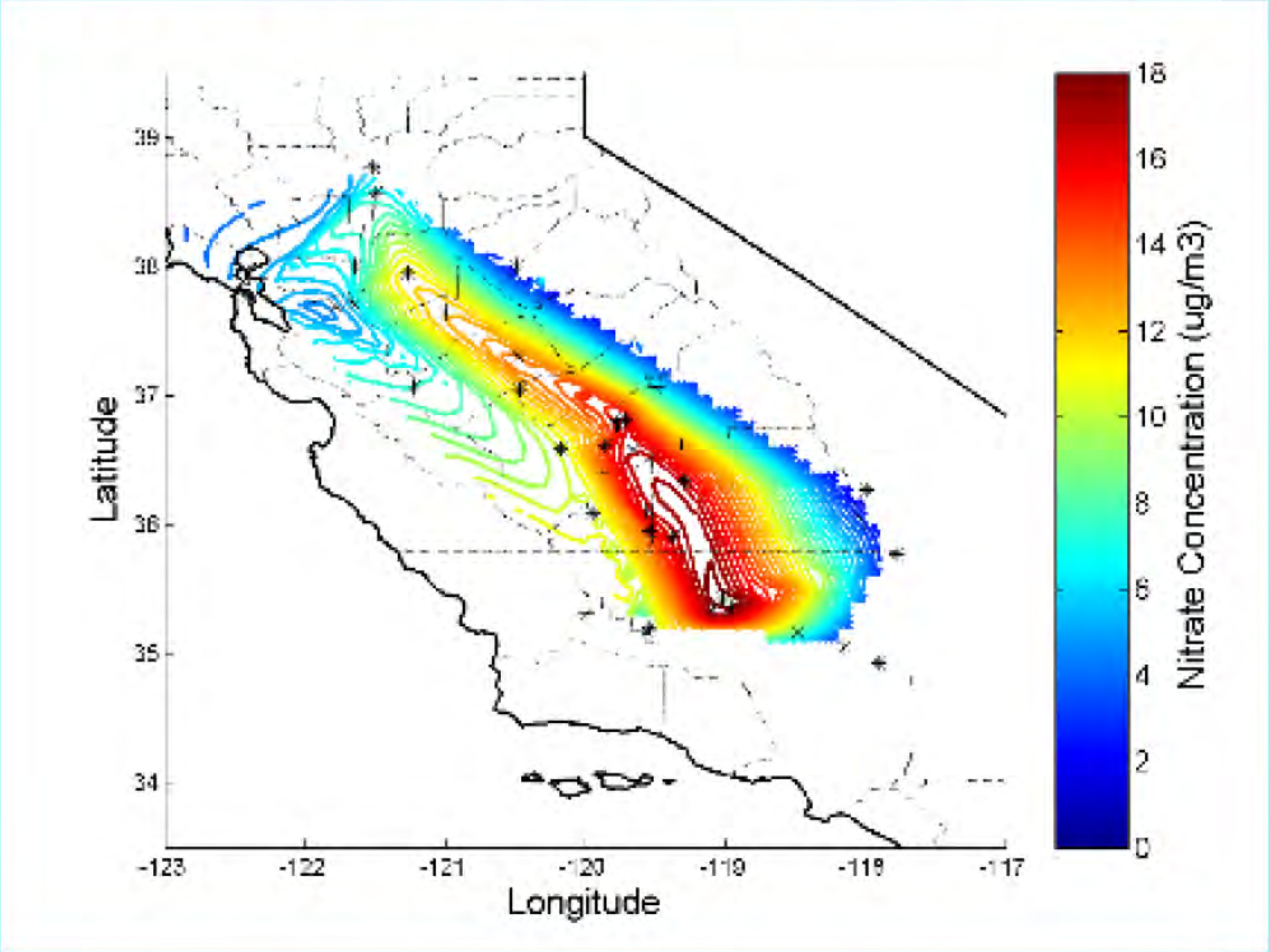
MacDonald, C.P., McCarthy, M.C., Dye, T.S., Wheeler, N.J.M., Hafner, H.R., Roberts, P.T., (2006). Transport and dispersion during wintertime particulate matter episodes in the San Joaquin Valley, California. Journal of the Air & Waste Management Association, 56, 961-976.

Ammonium nitrate formed aloft mixes to the surface when the surface inversion couples to the valley-wide layer soon after sunrise



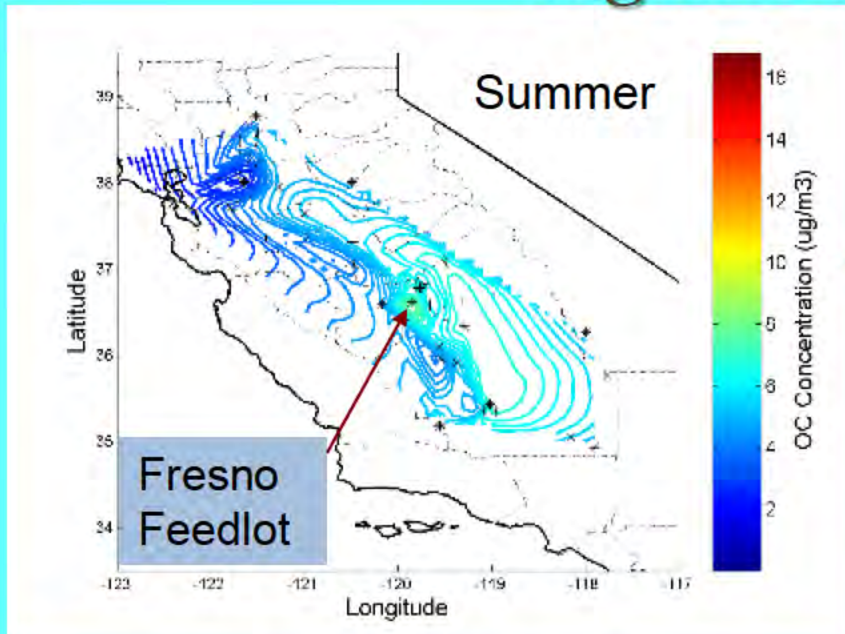
Watson, J.G., Chow, J.C., (2002). A wintertime $PM_{2.5}$ episode at the Fresno, CA, supersite. Atmospheric Environment, 36, 465-475.

As a result $PM_{2.5}$ nitrate is more evenly mixed throughout the SJV, requiring regional NO_x reductions



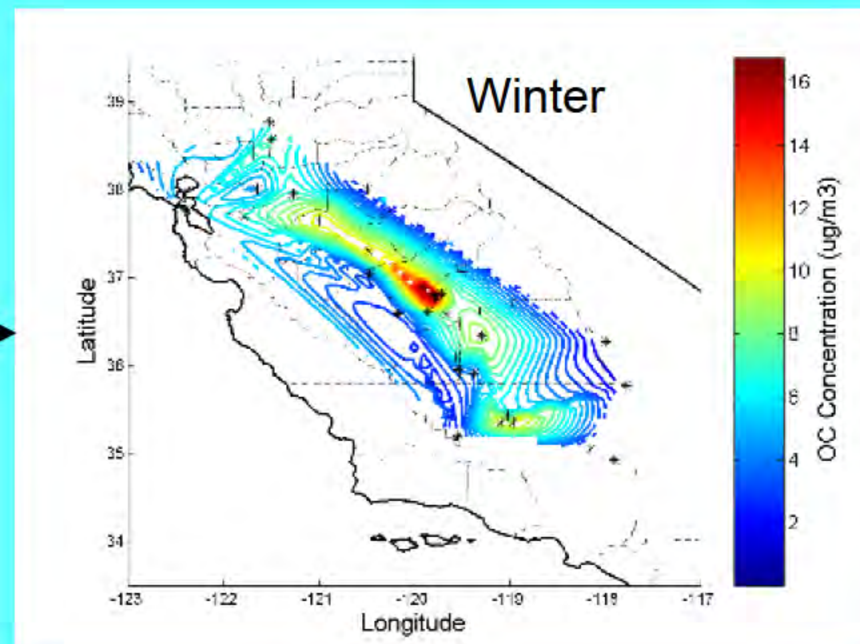
Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.L., Turkiewicz, K., Lehrman, D.E., (2006). $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). Journal of Geophysical Research-Atmospheres, 111, 1-17.

This contrasts with $PM_{2.}$ rgani arbon which is highest in the cities



Uniform OC in the southeastern valley with highest OC near a dairy operation

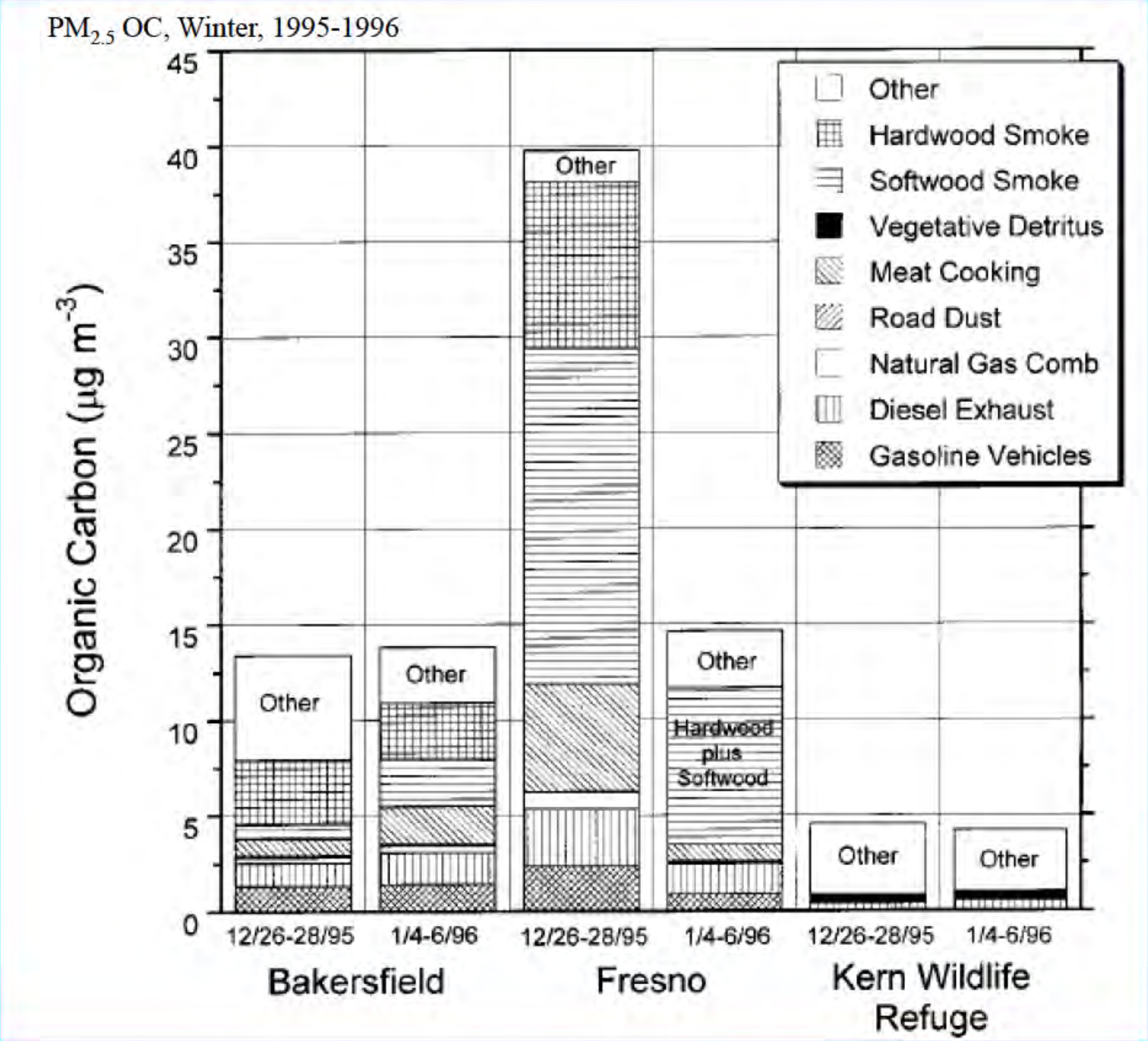
Elevated OC at urban centers, especially near Fresno



Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.L., Turkiewicz, K., Lehrman, D.E., (2006). $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). Journal of Geophysical Research-Atmospheres, 111, 1-17.

More detailed speciation of organic carbon revealed meat cooking and road dust as important OC contributors

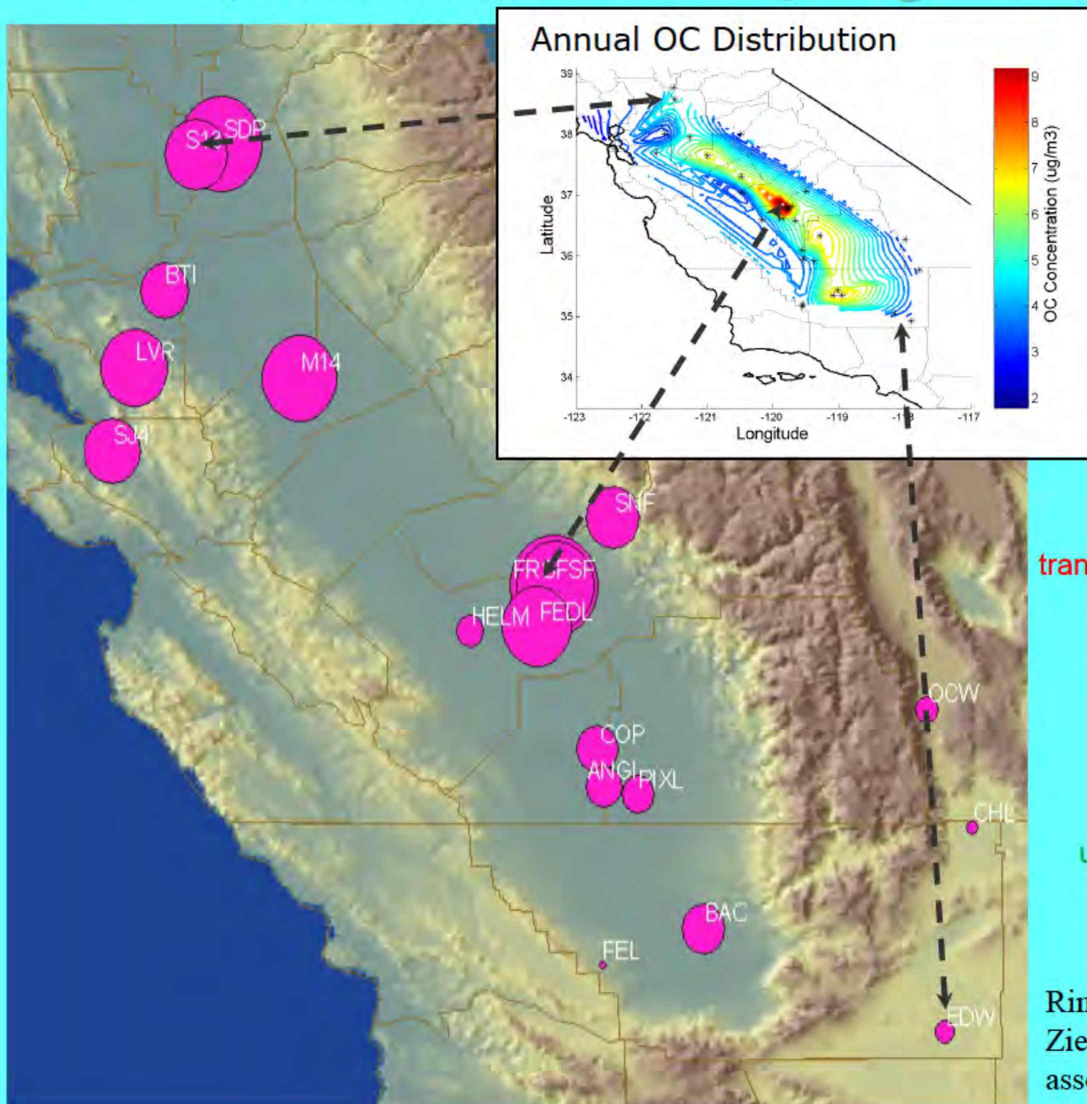
Could "other" be secondary organic aerosol?



Schauer, J.J., Cass, G.R., (2000). Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environmental Science & Technology, 34, 1821-1832.

Wood burning is a large contributor to carbon in urban areas during winter

(Wood smoke marker [levoglucosan] distribution)

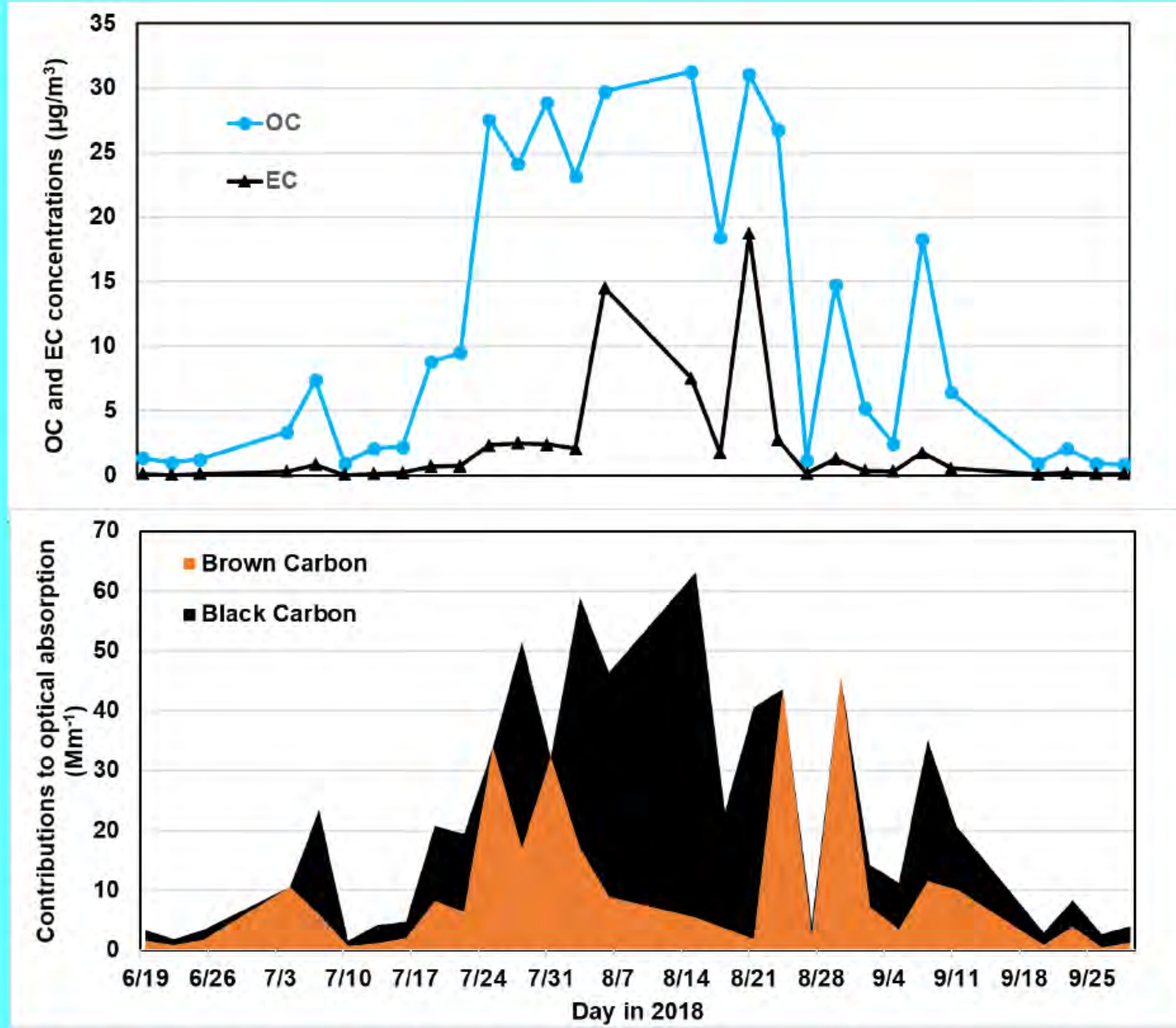


Levoglucosan Concentrations (ng/m3)

Site	Annual Avg	Winter Avg*
FEL	6	26
CHL	7	32
YOSE	9	38
EDW	12	52
OCW	14	58
HELM	19	81
PIXL	19	82
ANGI	23	98
COP	32	138
BAC	49	209
BTI	50	215
SNF (transport site)	57	244
SJ4	58	247
S13	63	269
LVR	68	291
FEDL	75	323
M14	101	433
FRS	121	521
SDP	128	551
FSF (urban site)	202	868

** Predicted concentration based on mass concentration measurements*

Rinehart, L.R., Fujita, E.M., Chow, J.C., Magliano, K.L., Zielinska, B., (2006). Spatial distribution of PM2.5 associated organic compounds in central California. Atmospheric Environment, 40, 290-303.



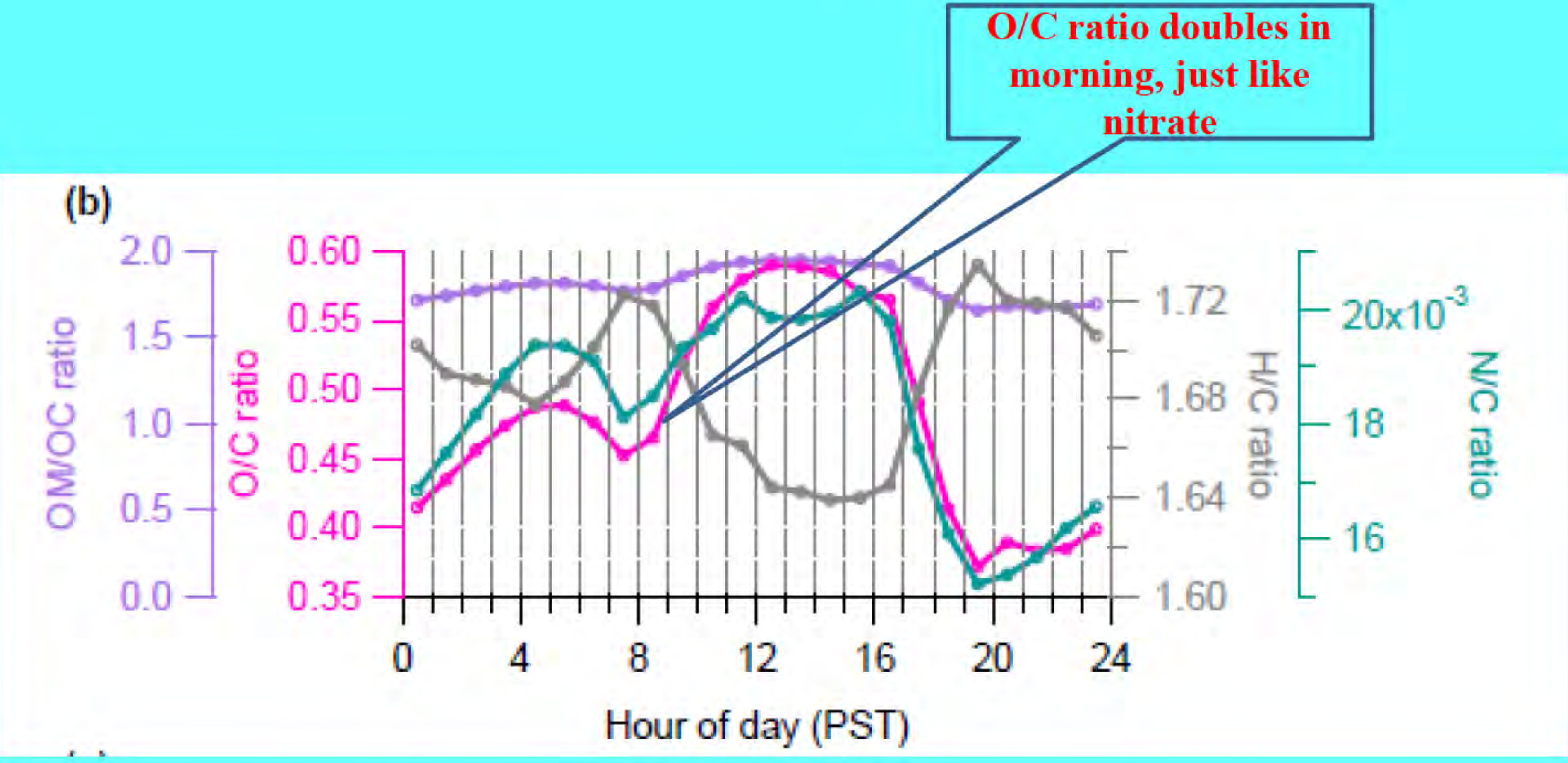
Organic carbon, elemental carbon, and brown carbon measured at Lava Beds National Monument during the 2018 northern California Carr Fire

As of 2016, thermal/optical carbon measurements at CSN and IMPROVE sites contain both black and brown carbon (BC and BrC) that indicate biomass burning, and possibly other, source contributions

Chow, J.C., Riggio, G.M., Wang, X.L., Chen, L.-W.A., Watson, J.G., (2018). Measuring the organic carbon to organic matter multiplier with thermal/optical carbon mass spectrometer analyses. Aerosol Science and Engineering, 2, 165-172.

Chow, J.C., Wang, X.L., Green, M.C., Watson, J.G., (2019). Obtaining more information from existing filter samples in $PM_{2.5}$ speciation networks. EM, 23, accepted.

Recent evidence shows increasing O/C ratio, indicating possibly of secondary organic aerosol also forming and/or transported aloft at night



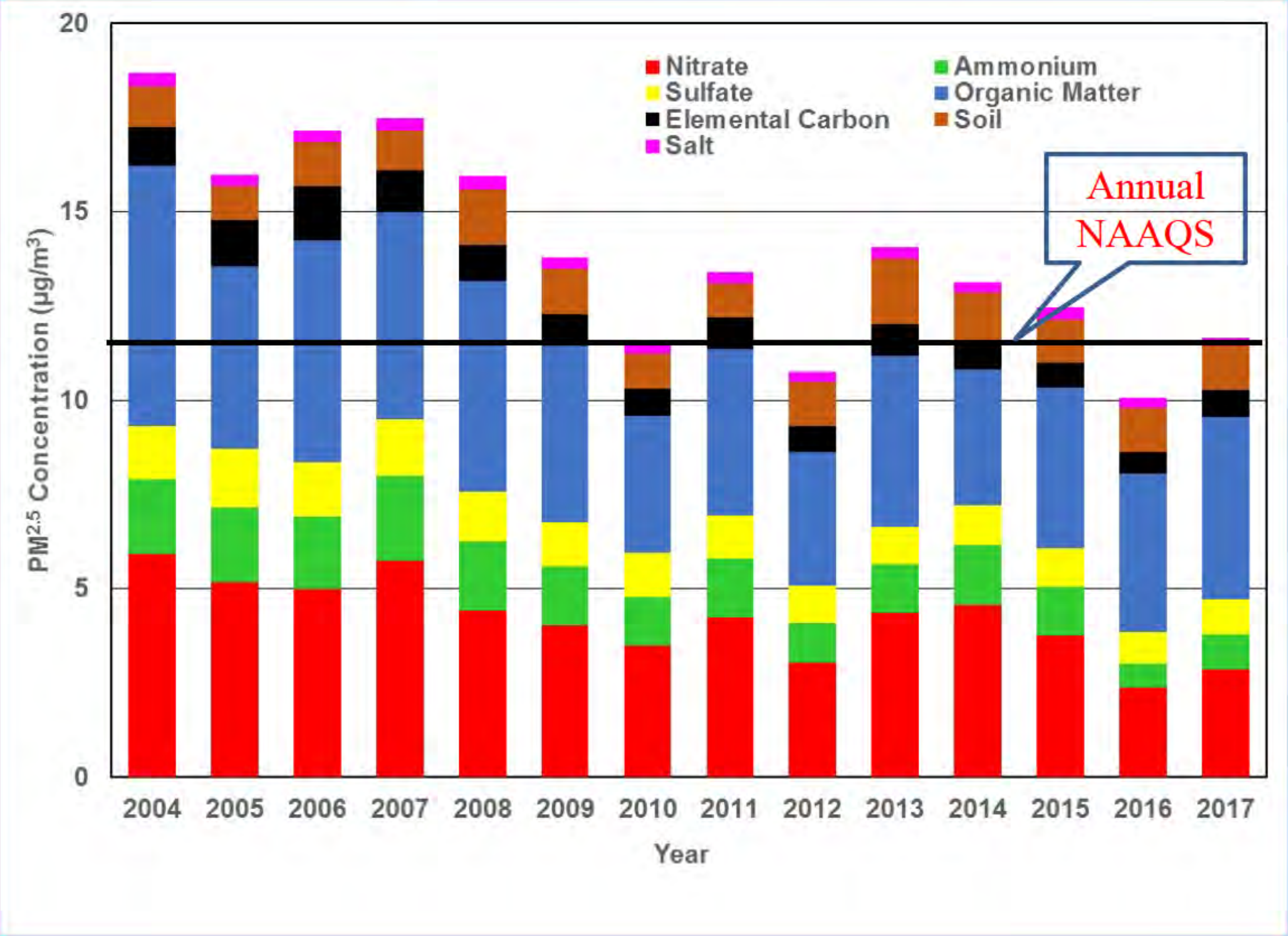
Young, D.E., Kim, H., Parworth, C., Zhou, S., Zhang, X.L., Cappa, C.D., Seco, R., Kim, S., Zhang, Q., (2016). Influences of emission sources and meteorology on aerosol chemistry in a polluted urban environment: results from DISCOVER-AQ California. Atmospheric Chemistry and Physics, 16, 5427-5451. 10.5194/acp-16-5427-2016. http://www.atmos-chem-phys.net/16/5427/2016/

As a result of these studies many emission reduction measures have been implemented in California

- Eliminated the addition of lead to gasoline to prevent contamination of catalytic converters
- Provided subsidies to replace older engines with newer engines
- Enforced stricter emission standards for on-road and off-road gasoline and diesel engines
- Reduced sulfur content in on-road and off-road gasoline and diesel fuels
- Replaced diesel irrigation pumps with electric and propane pumps
- Substituted natural gas for crude oil in southern SJV oil field steam generators
- Installed oxides of nitrogen scrubbers on major point sources, including steam generators
- Improved livestock management practices to reduce volatile organic compound and ammonia emissions
- Replaced old wood burning appliances with certified stoves
- Implemented fugitive dust suppression rules for construction, agriculture, food and minerals processing, and paved and unpaved roads

$PM_{2.5}$ and chemical component concentrations decreased until 2010 (CSN, Fresno), but then they seem to fluctuate in recent years

There are still phenomena that we don't understand!



Overall Conclusions for Central California

- There is no single cause of elevated $PM_{2.5}$ levels in California's Central Valley. All emitters must participate in control strategies
- Annual emission estimates don't correspond with ambient chemical components, especially for fugitive dust
- Wintertime nitrate is regional, while carbon concentrations are highest around population centers
- Oxides of nitrogen, as well as primary PM, emissions must be further reduced, to attain $PM_{2.5}$ NAAQS
- A changing climate may have adverse effects on Central Valley $PM_{2.5}$, with drier conditions engendering more fugitive dust and wildfires

Reynolds, S., Blanchard, C.L., Lehrman, D.E., Reid, S., Harley, R.A., Kleeman, M., Stoeckenius, T.E., Morris, R., Watson, J.G., Chow, J.C., (2012). Synthesis of CCOS and CRPAQS study findings. San Joaquin Valley Unified Air Pollution Control District, Fresno, CA. https://www.researchgate.net/publication/316170523_Synthesis_of_CCOS_and_CRPAQS_study_findings

We're not done yet!
We need to know more

- When will inflection points be met for NH_3, VOC, and NO_x precursors?
- What are the mechanisms and algorithms for modeling wintertime secondary organic aerosol?
- Why are $PM_{2.5}$ trends leveling off?
- How are climate changes enhancing or negating emission reduction measures?
- What comprehensive studies need to be planned to answer these questions?

This knowledge would not be possible without contributions from many air quality scientists

- Bruce Appel
- Jerry Anderson
- Lowell Ashbaugh
- Bob Baxter
- Charles Blanchard
- Don Blumenthal
- Dave Bush
- Glen Cass
- Tom Cahill
- Lyle Chinkin
- Jeff Collett
- Manuel Cunha
- Judith Chow
- Bart Croes
- John DaMassa
- Rob deMandel
- Dave Dubois
- Tim Dye
- Dave Fairley
- Milton Feldstein
- Dennis Fitz
- Eric Fujita
- Kochy Fung
- Alan Gertler
- Dave Grantz
- Rich Hackney
- Alan Hansen
- Suzanne Hering
- Vernon Hughes
- George Hidy
- John Holmes
- James Houck
- Walter John
- Ajith Kadawela
- Michael Kleeman
- Doug Lawson
- Don Lehrman
- Alan Lloyd
- Fred Lurman
- Hillary Main
- Karen Magliano
- Chuck McDade
- K.C. Moon
- Ralph Morris
- Nezhat Motallebi
- Peter Mueller
- Bill Neff
- Liz Niccum
- Spiros Pandis
- Jim Pederson
- Andy Ranzieri
- Cathy Reheis
- Steve Reynolds
- Will Richards
- Paul Roberts
- Phil Roth
- Evan Shipp
- Paul Solomon
- Jim Sweet
- Safet Tanrikulu
- John Trijonis
- Dick Thullier
- Barbara Zielinska
- Steve Ziman