Spatial Variability of $PM_{2.5}$ Species in the California Central Valley

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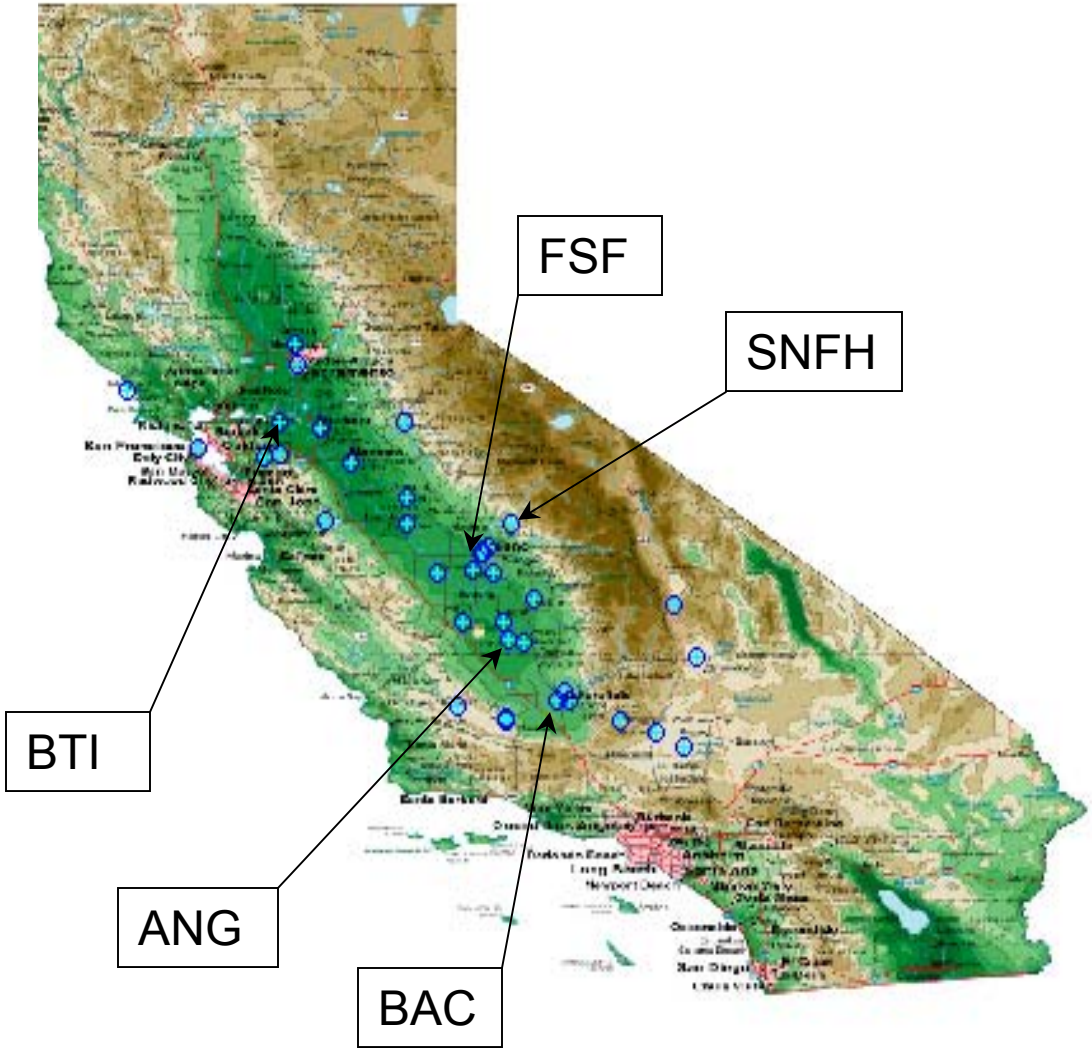
Objectives

- Analyze the spatial variation of $PM_{2.5}$, carbonaceous species, ions, and trace elements in the California central valley on different time scales.
- Determine the zone of representation for major sampling sites.
- Understand the evolution of $PM_{2.5}$ concentration and chemical composition during wintertime pollution episodes.

The California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS)

- Period: Dec. 2, 1999 – Feb. 3, 2001
- Frequency: Every 6th day (Daily 24-hr mass measurement at Fresno and Bakersfield)
- Location: 5 $PM_{2.5}$ anchor sites and 32 satellite sites
- Anchor sites: Bethel Island (BTI), Sierra Nevada Foothill (SNFH) , Fresno (FSF), Angiola (ANG), Bakersfield (BAC).
- Winter IOP periods:
  - –Dec. 15-18, 2000
  - –Dec. 26-28, 2000
  - –Jan. 4-7, 2001
  - –Jan. 31–Feb. 3, 2001



Time Integrated Samplers

RAAS-100
single-channel $PM_{2.5}$ FRM sampler
(Andersen Instruments, Smyrna, GA)

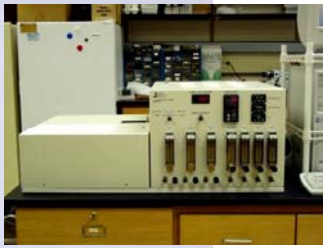
RAAS-400
$PM_{2.5}$ speciation sampler
(Andersen Instruments, Smyrna, GA)

Dual-channel sequential filter sampler
(Desert Research Institute, Reno, NV)

MiniVol filter sampler
(Airmetrics, Springfield, OR)

$PM_{2.5}$ Chemical Speciation

Observables	Chemical Analysis Method
Mass	– Gravimetric Analysis
Elements (Na to U)	– X-Ray Fluorescence (XRF)
Anions (Cl^-, NO_3^-, $SO_4^=$)	– Ion Chromatography (IC)
Ammonium (NH_4^+)	– Automated Colorimetry (AC)
Soluble Sodium (Na^+) Soluble Potassium (K^+)	– Atomic Absorption Spectrophotometry (AAS) (flame or graphite)
Carbon (OC, EC)	– Thermal/Optical Reflectance (TOR)

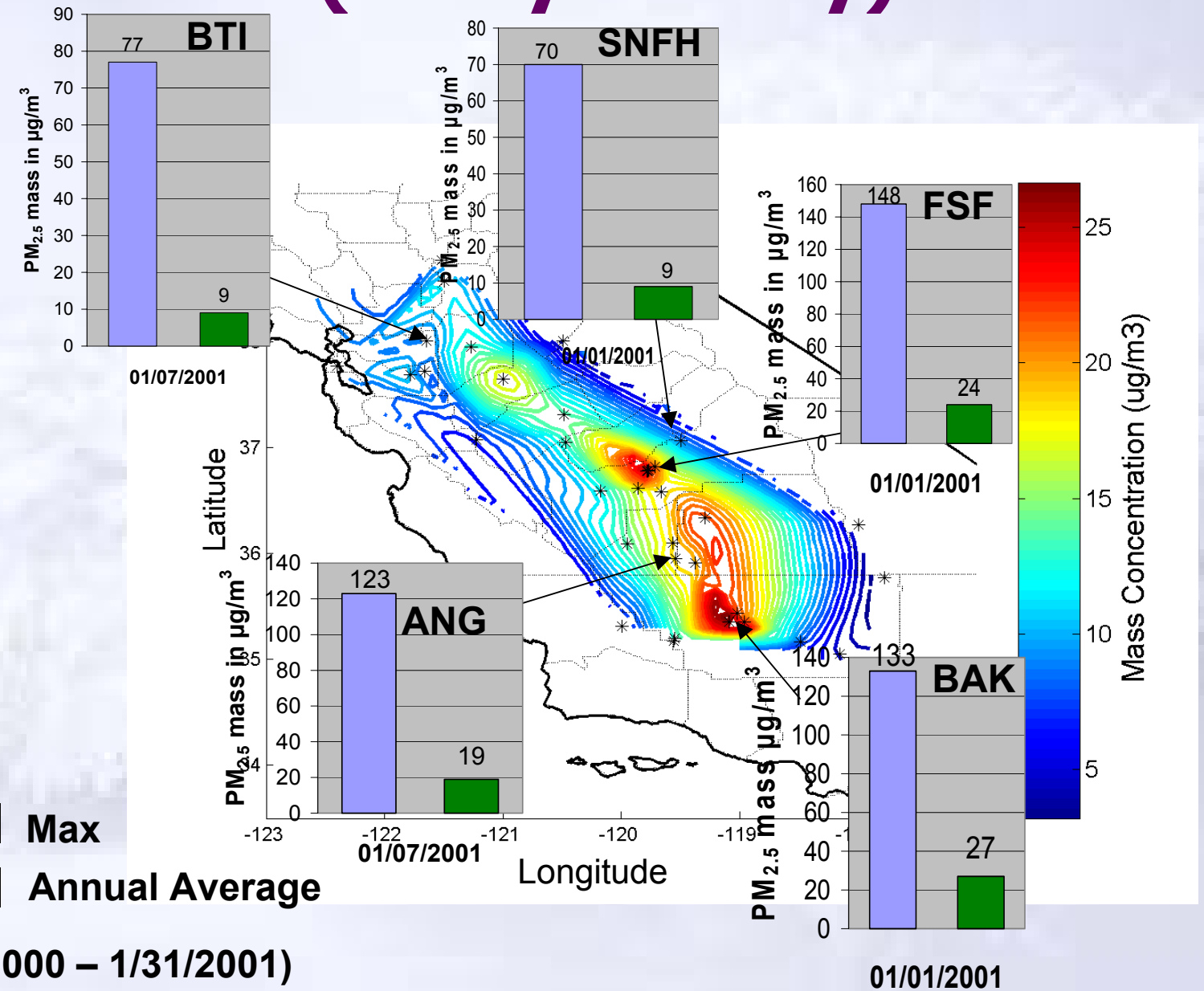


Organic Speciation

- Composite Minivol samples annually (~60 samples/site) at 20 sites.

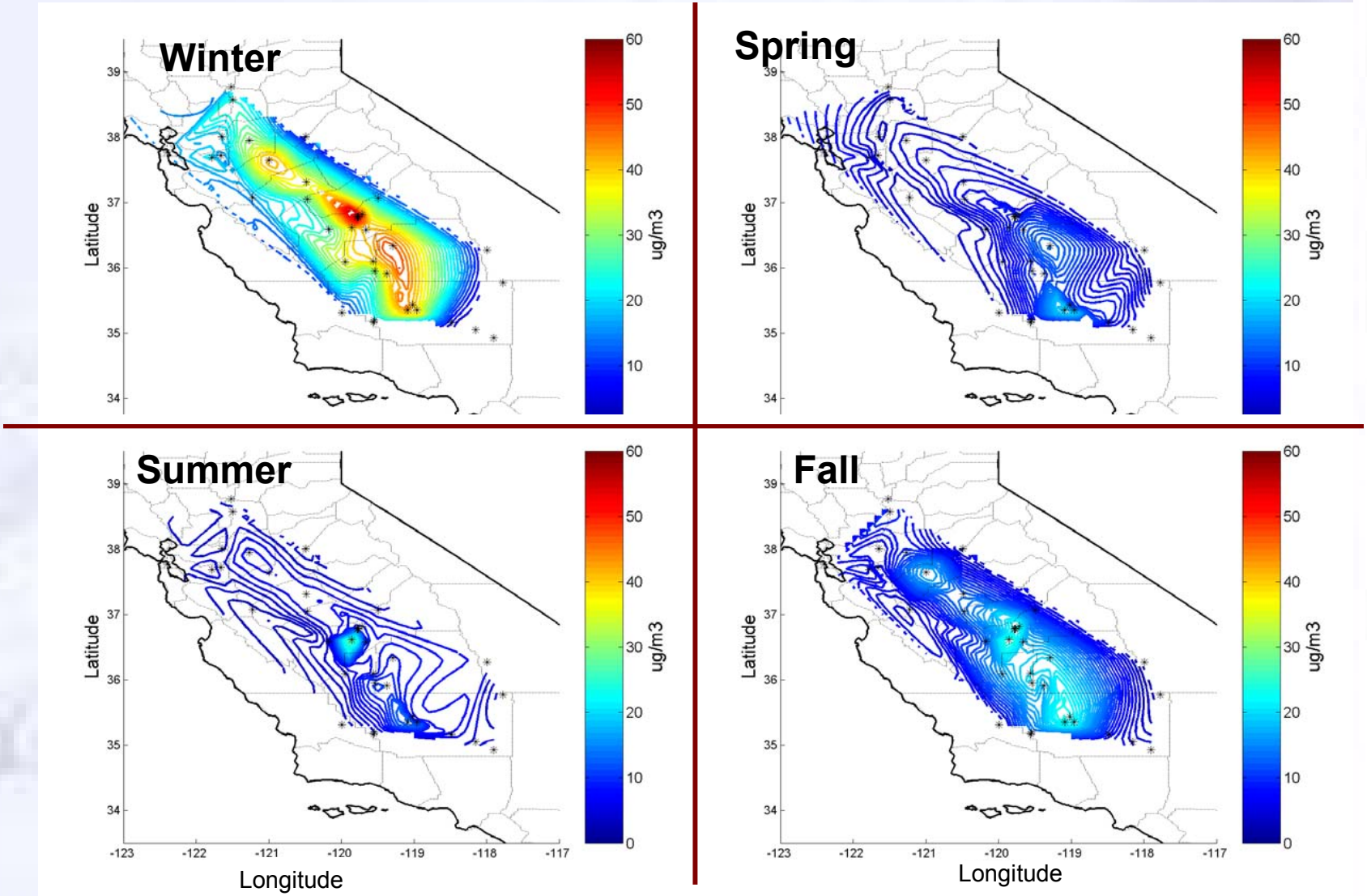
- Perform GC/MS analyses for: PAH, aliphatic alkanes, organic acids, methoxylated phenols, cholesterol, & anhydro-glucose isomers (Levoglucosan & Mannosan).

Annual Average $PM_{2.5}$ Concentration (Every 6th Day)

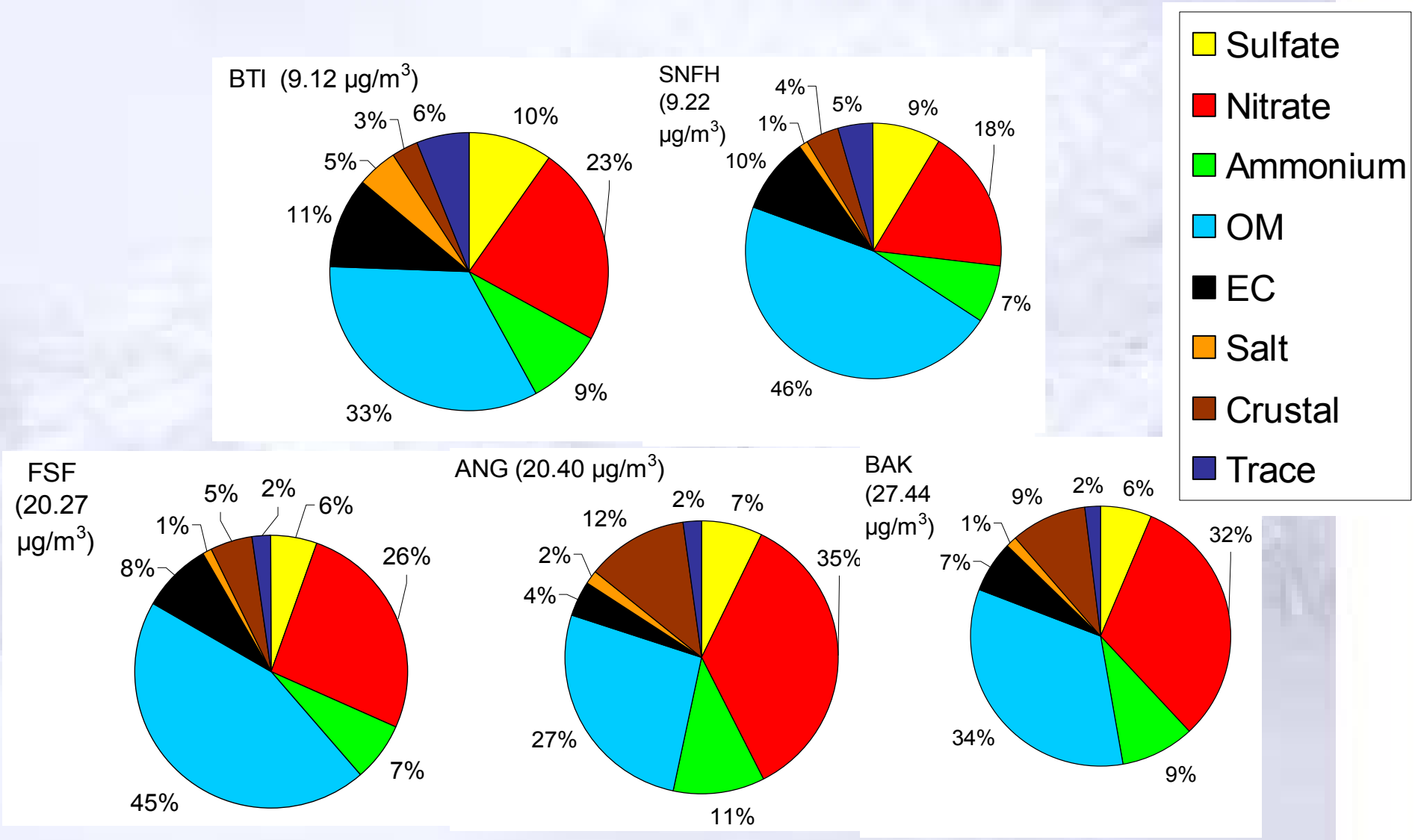


(2/1/2000 – 1/31/2001)

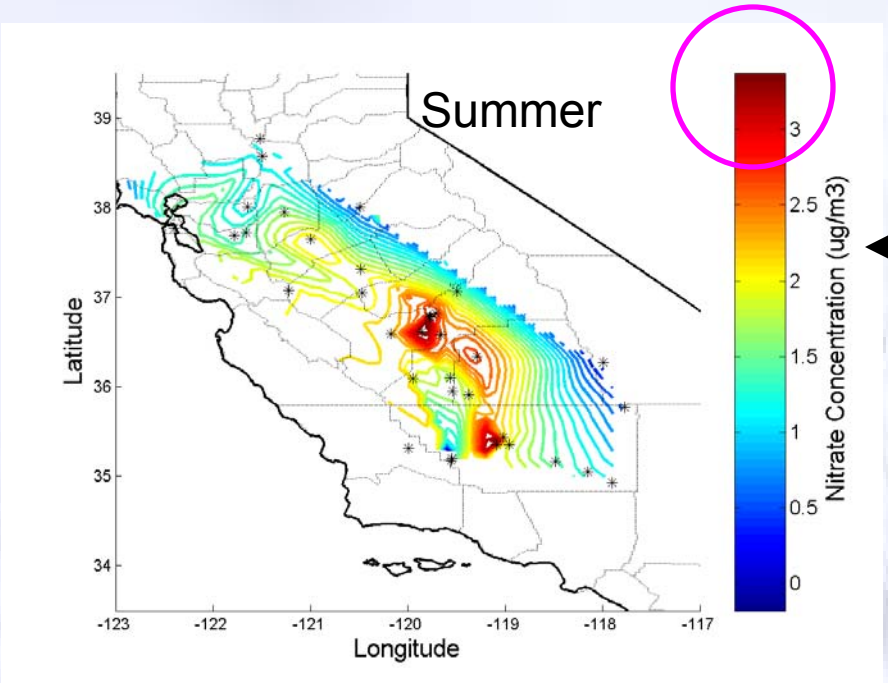
Seasonal Variations of $PM_{2.5}$



Annual $PM_{2.5}$ Chemical Composition

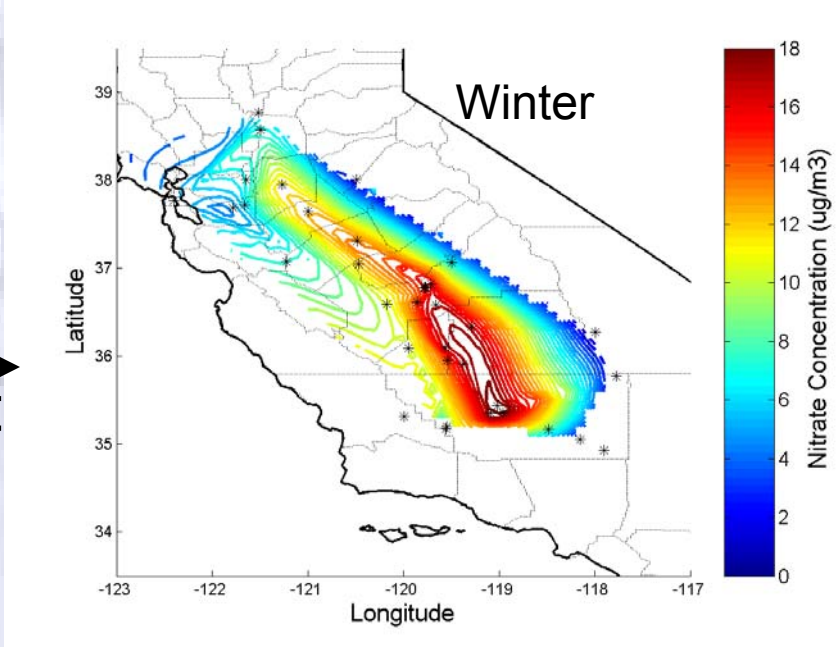


Variation of Nitrate (NO_3^-)

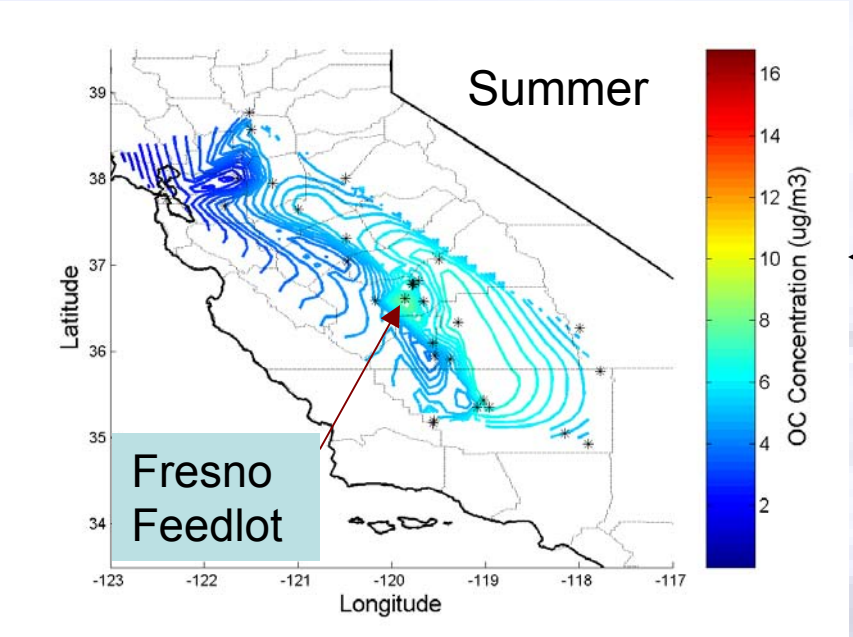


- Low NO_3^- found in summer (<3.5 μg/m^3) (Note: different scales)
- Nitrate highest near urban areas.

- High NO_3^- found in winter.
- Nitrate high throughout SJV.

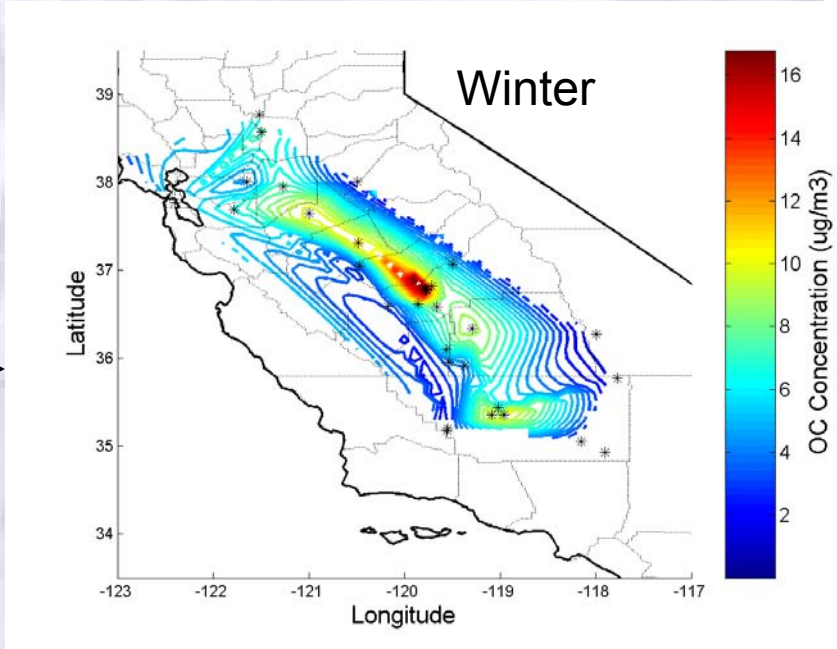


Variation of Organic Carbon (OC)

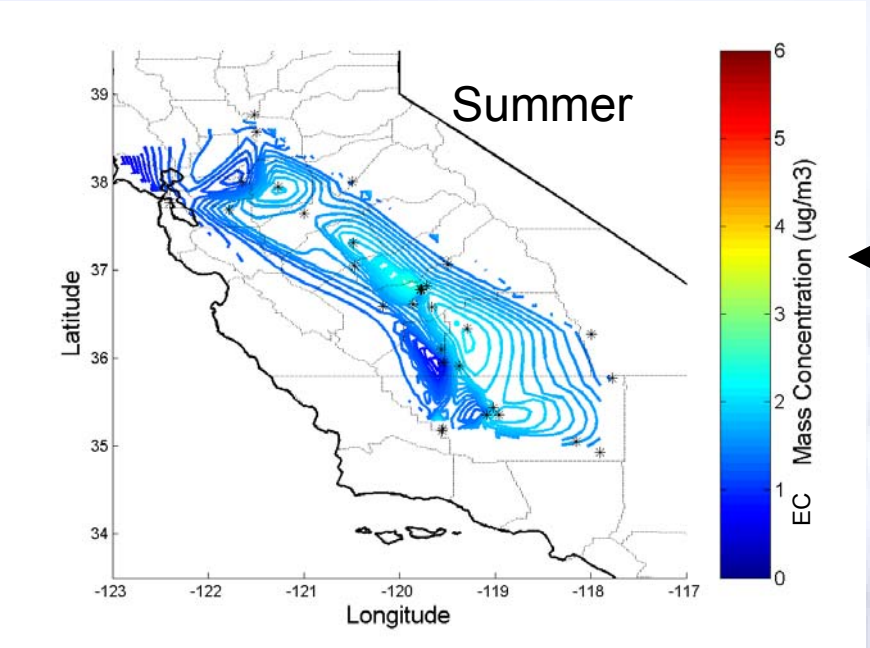


- Uniform OC in the southeastern valley. Highest OC near a dairy.

- Elevated OC at urban centers, especially near the Fresno Supersite. OC in rural areas was lower in winter than in summer.

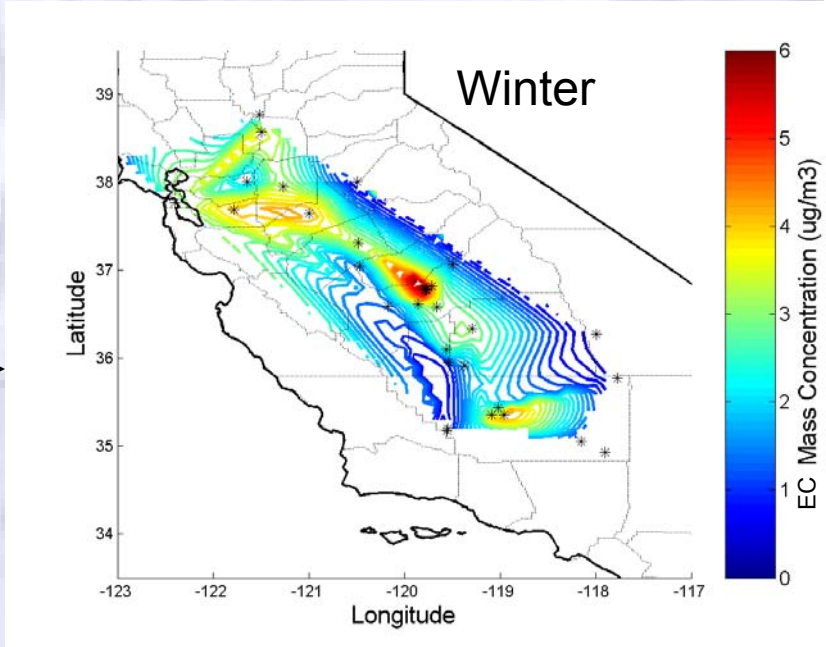


Variation of Elemental Carbon (EC)

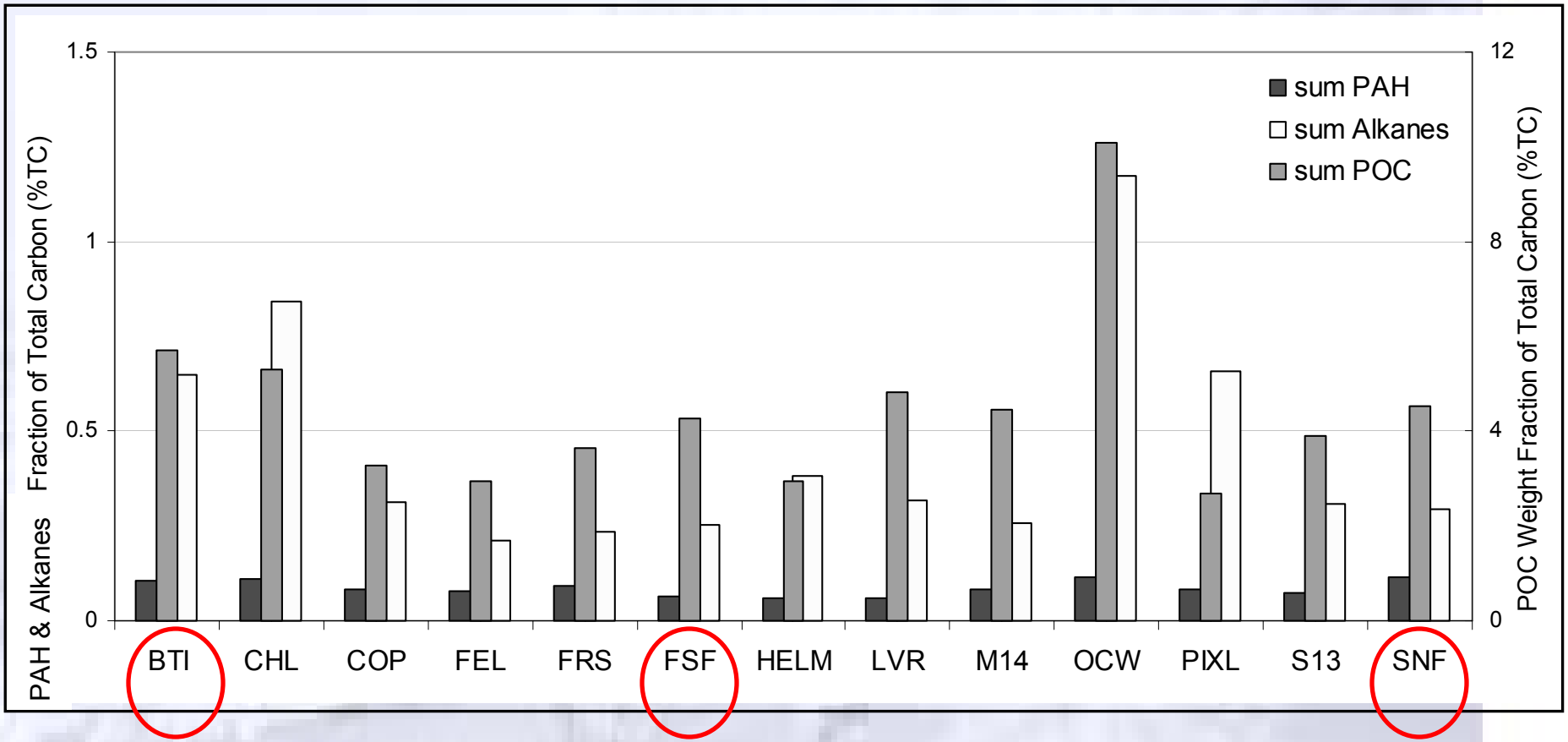


- Higher EC around urban centers.

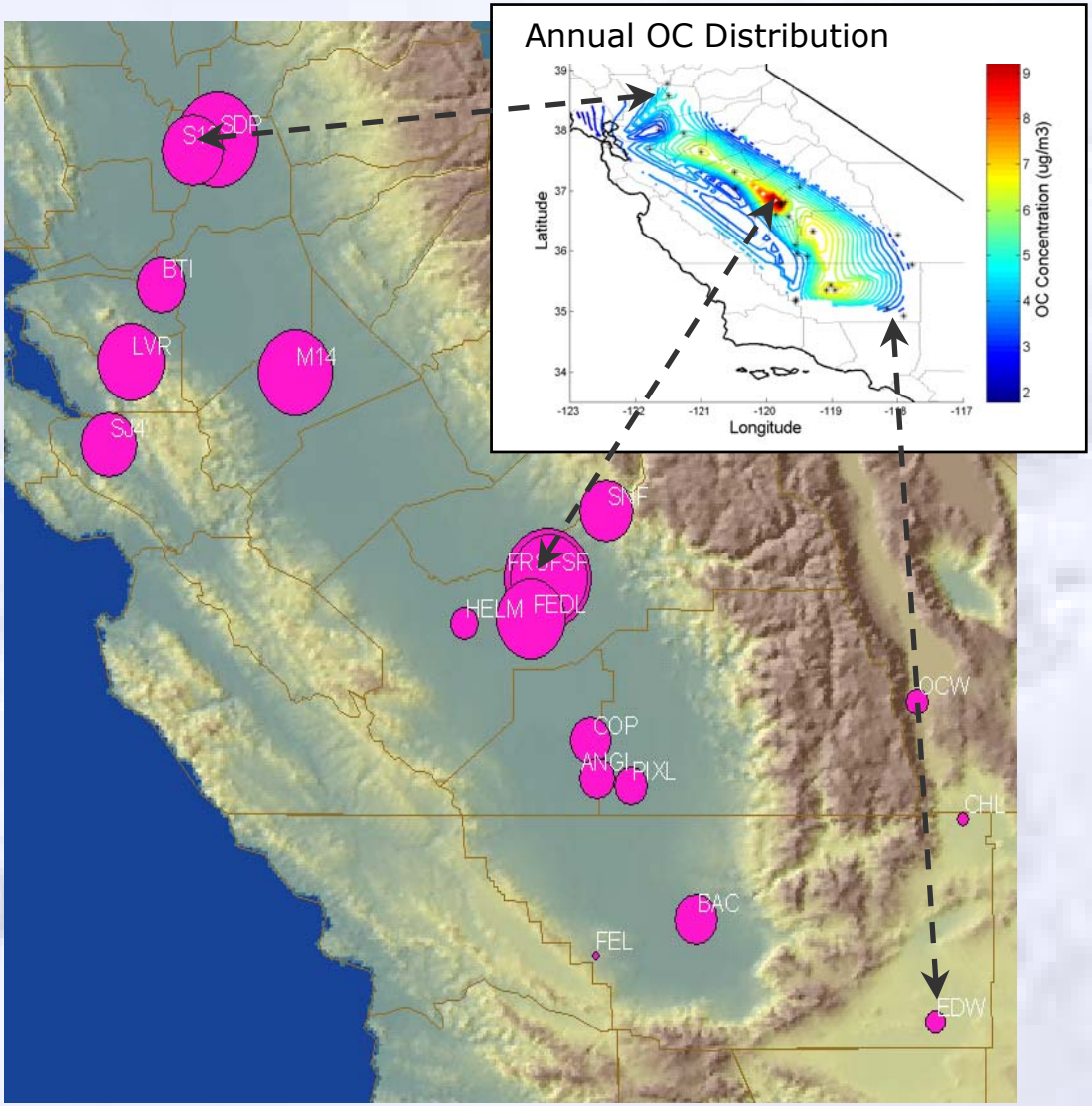
- Elevated EC found near the Fresno Supersite and Bakersfield. Rural sites show limited summer-winter contrast.



Annual Average $PM_{2.5}$ Organics



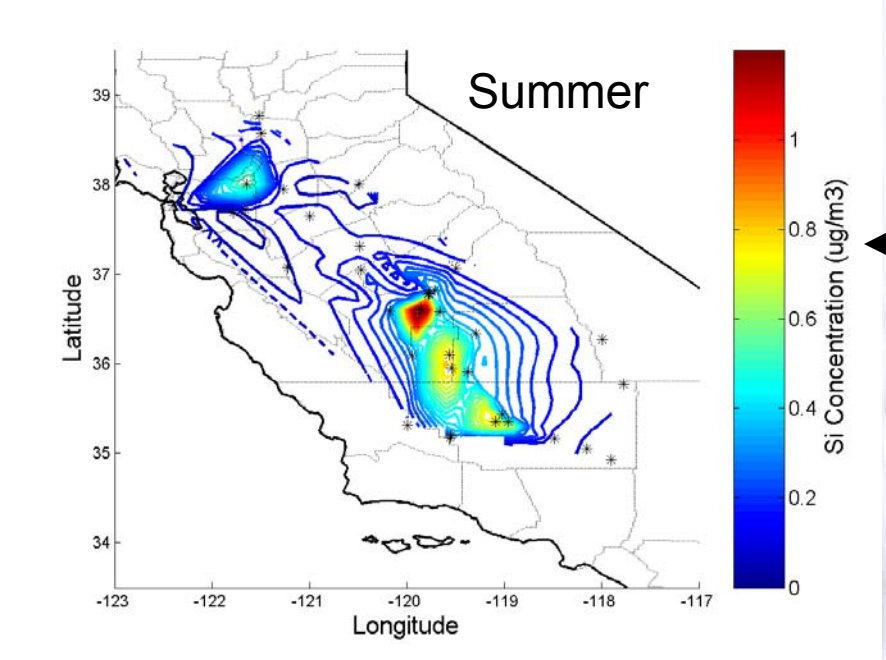
Distribution of Levoglucosan, a Wood-Burning Marker, Compared to OC Distribution



Levoglucosan Concentrations (ng/m3)		
	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	57	244
SJ4	58	247
S13	63	269
LVR	68	291
FEDL	75	323
M14	101	433
FRS	121	521
SDP	128	551
FSF	202	868

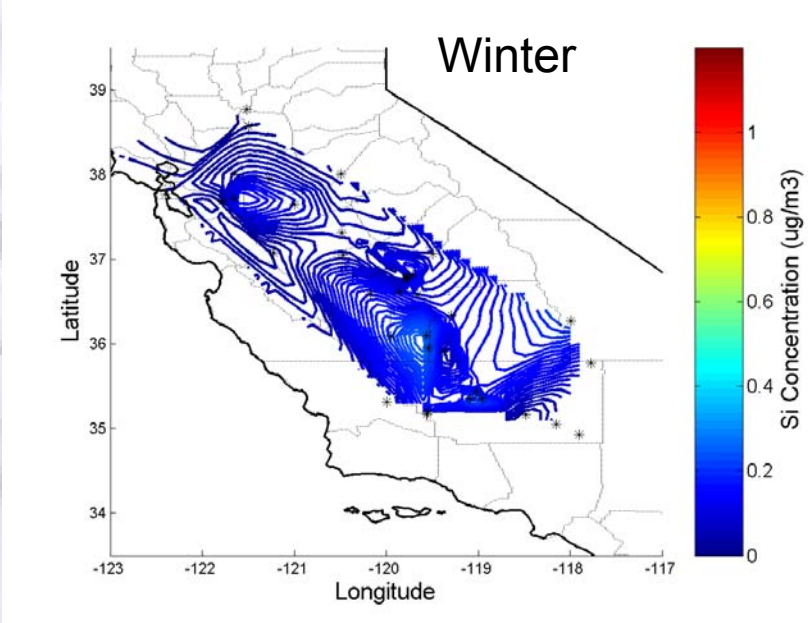
** Predicted concentration based on mass concentration measurements*

Variation of $PM_{2.5}$ Silicon (Si)

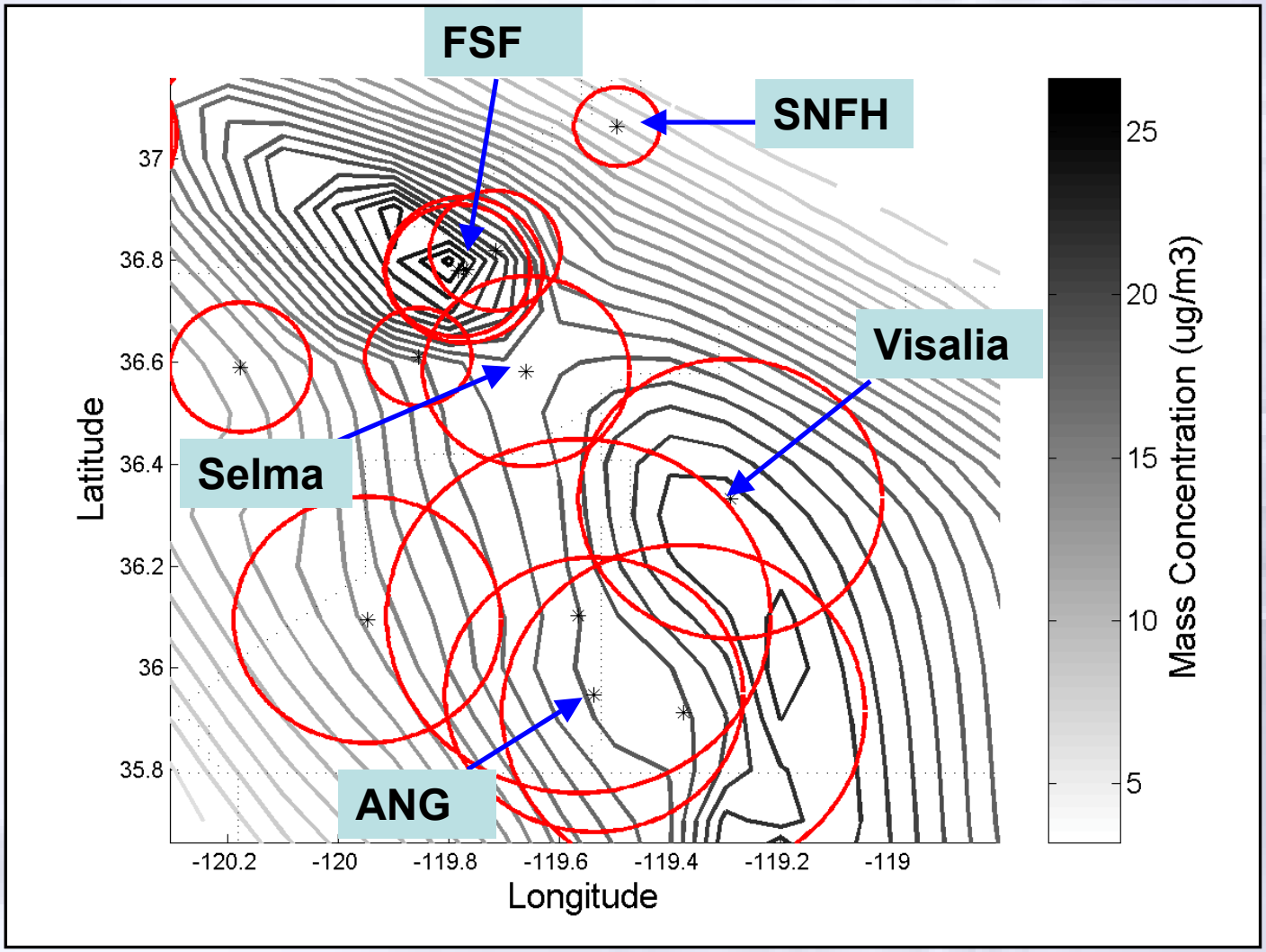


- Higher concentration found around the Fresno Feedlot and the southwestern valley. This reflects the relatively dry surface due to low precipitation.

- Si concentration was much lower in winter.

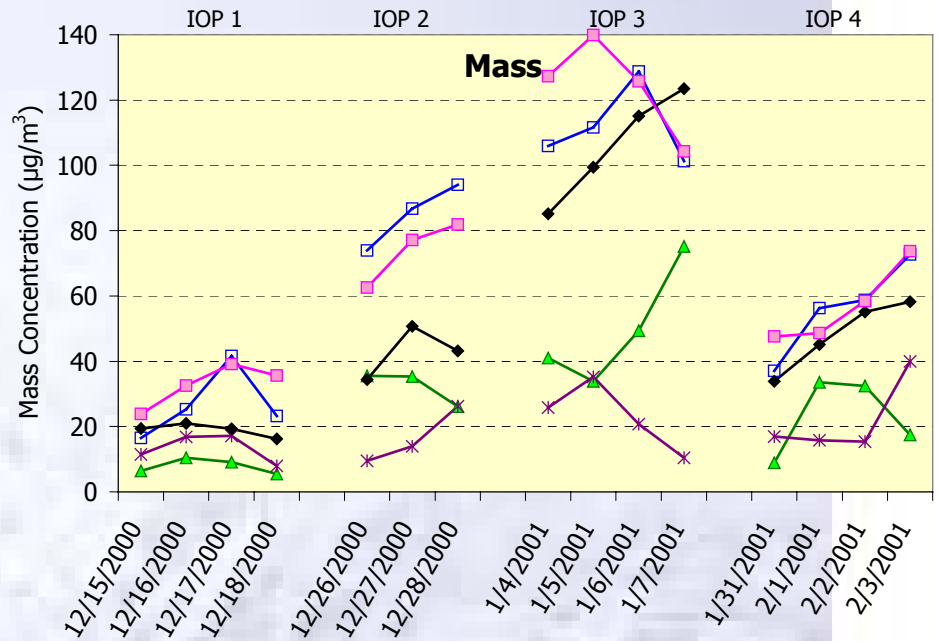


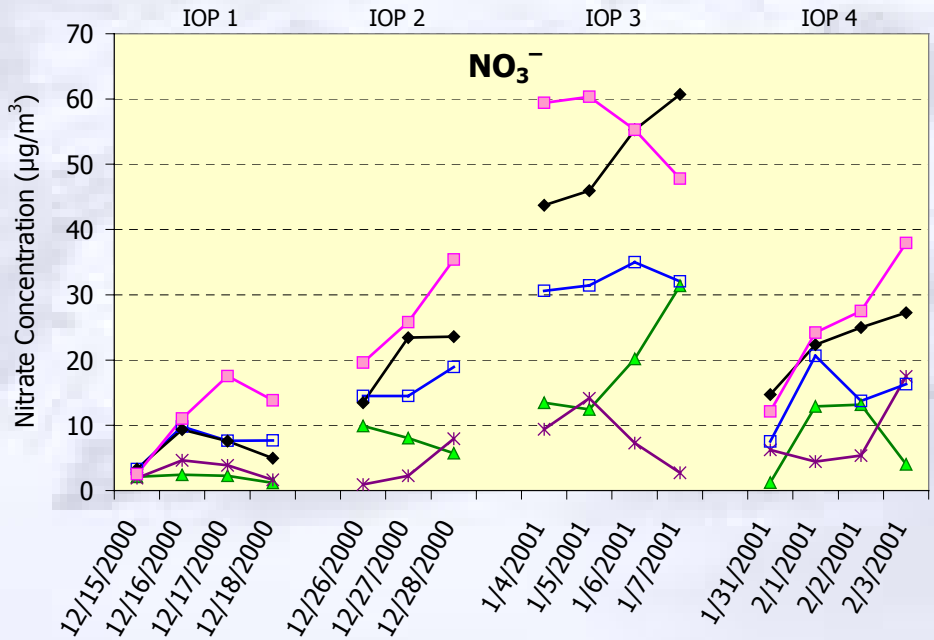
Zone of Representation (±25%) for Annual $PM_{2.5}$

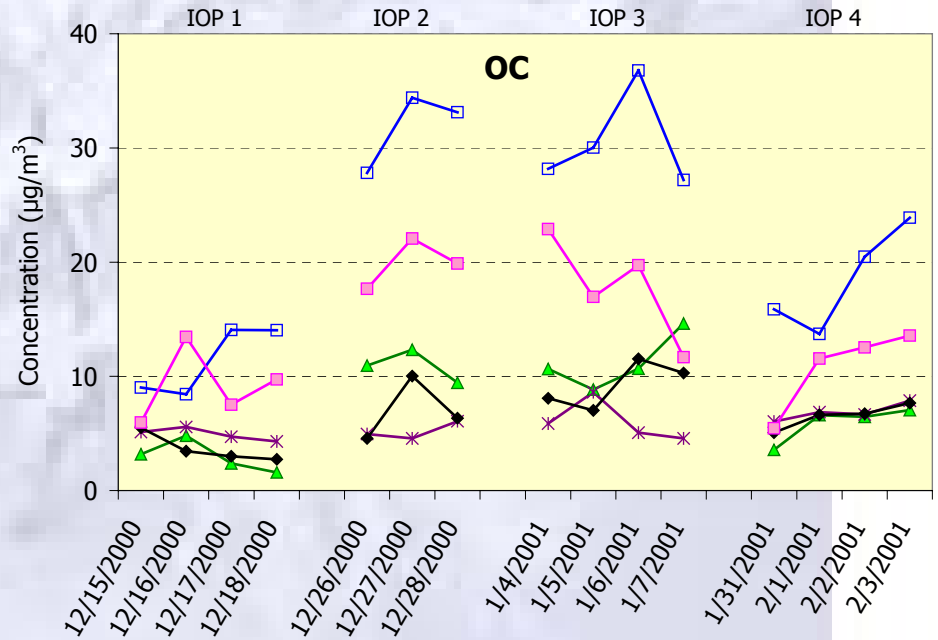


- Visalia and Angiola represent a larger zone, since they are located near the center of the high $PM_{2.5}$ region.

Elevated $PM_{2.5}$ Mass Coincides with Elevated Nitrate and OC (Winter IOPs)

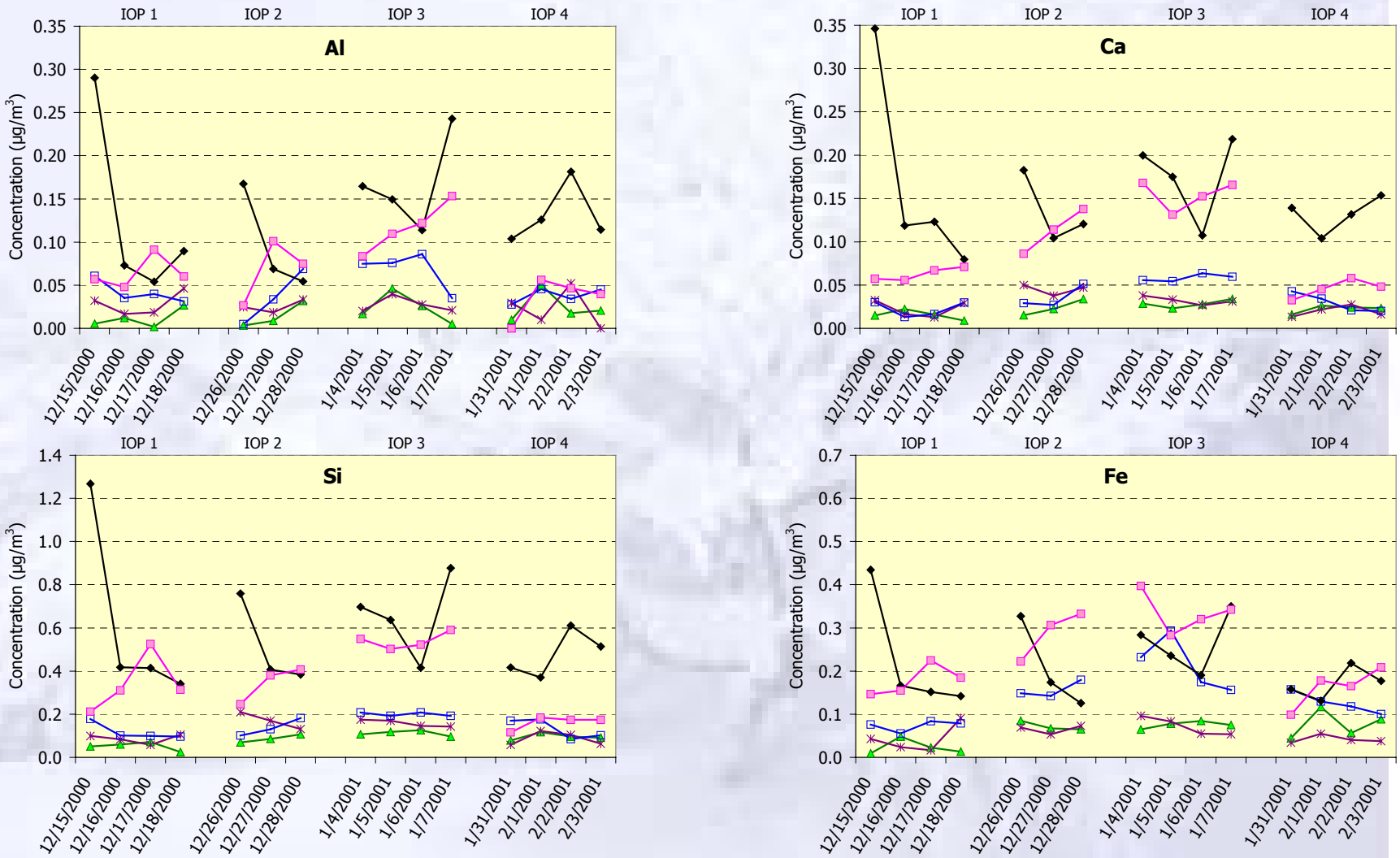






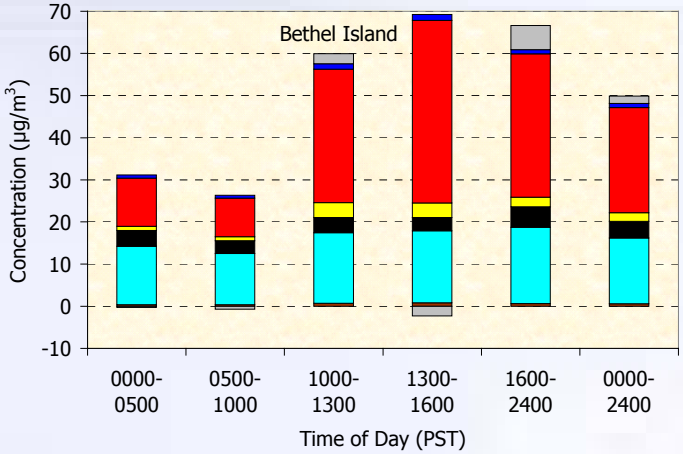
Angiola — Bakersfield — Bethel Island — Fresno — Sierra NV

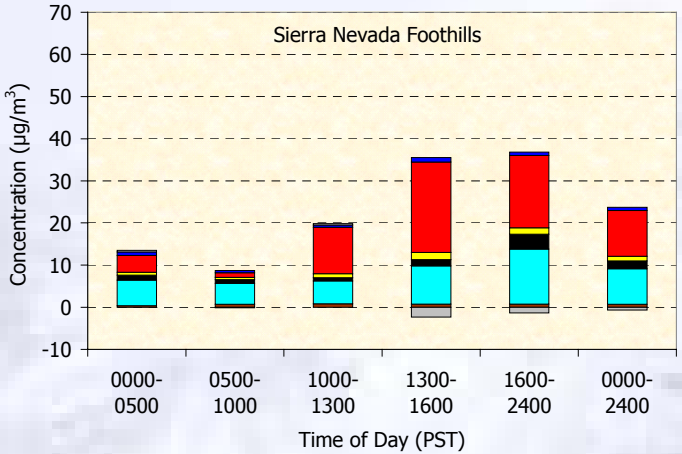
Crustal Species are Elevated at the Angiola and Bakersfield Sites

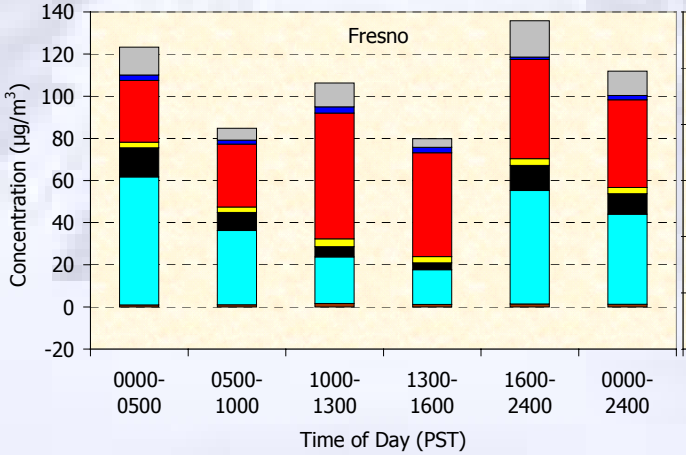


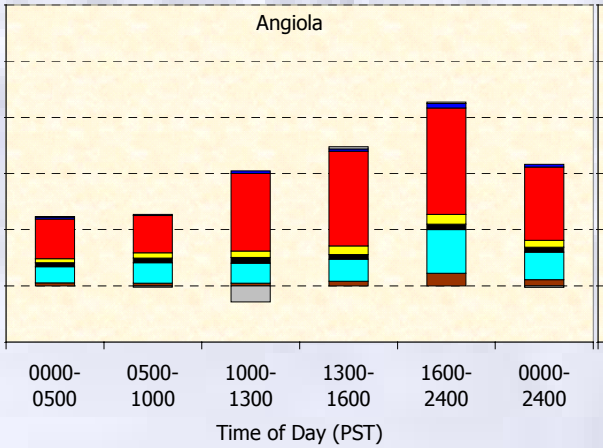
Diurnal Variation During IOP 3 (Jan. 4-7, 2001)

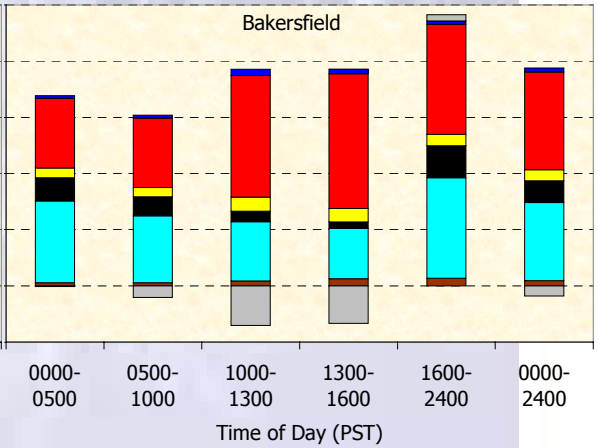
Blue=Organics (1.4)
Black=EC (IMPROVE)
Red=Amm. Nitrate
Yellow=Amm. Sulfate
Brown=Soil



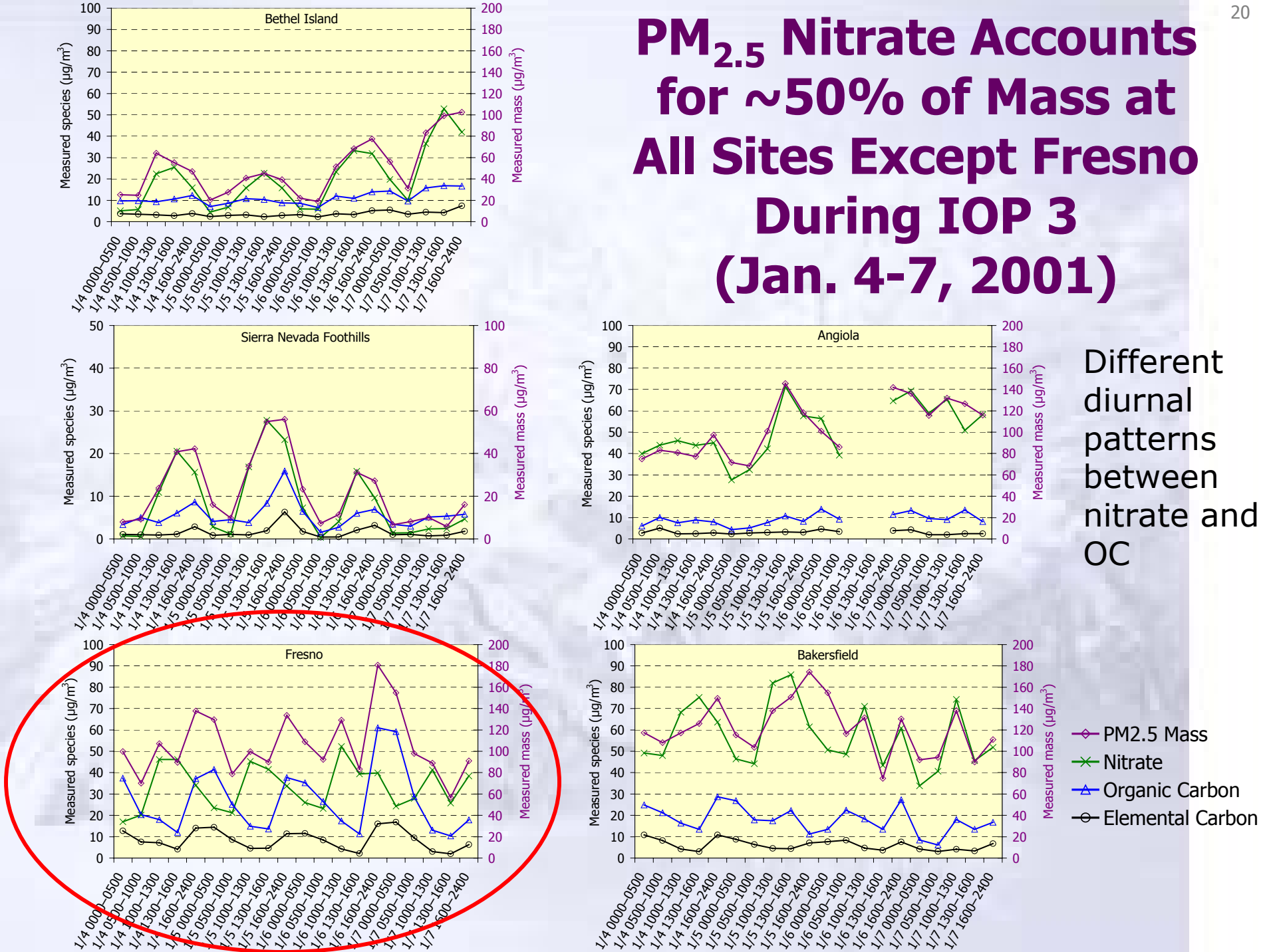








$PM_{2.5}$ Nitrate Accounts for ~50% of Mass at All Sites Except Fresno During IOP 3 (Jan. 4-7, 2001)



Different diurnal patterns between nitrate and OC

Regional- and Urban-Scale Influences

Dates	Bethel Island	Foothills	Fresno	Angiola	Bakersfield
IOP 1 Dec. 15-18	mix	carbon	mix	nitrate	mix
IOP 2 Dec. 26-28	carbon	carbon	carbon	nitrate	mix
IOP 3 Jan. 4-7	nitrate	nitrate	mix	nitrate	nitrate
IOP 4 Jan. 31-Feb. 1	nitrate	mix	carbon	nitrate	carbon

Conclusions

- Annual $PM_{2.5}$ mass ranged from 3.8 μg/m^3 (Angels Camp, Sonora) to 27.0 μg/m^3 (Bakersfield).
- Annual $PM_{2.5}$ exceedances are due to very high wintertime $PM_{2.5,}$ wintertime episodes, which are dominated by ammonium nitrate and organic matter.
- Elevated wintertime $PM_{2.5}$ in the cities caused by urban-scale carbonaceous material superimposed on regional ammonium nitrate.
- Wood smoke and traffic constitute much of the urban carbon.

Conclusions (continued)

- The urban Fresno Supersite zone of representation is of 15 – 20 km zone of representation. The non-urban Angiola site as a 25-30 km zone of representation.
- During the IOPs, nitrate and organics showed distinct diurnal cycles, reflecting their different origins. $PM_{2.5}$ nitrate peaked in the afternoon when boundary layer mixing was intense. Carbon accumulated at night.