The Role of Nighttime Chemistry in Winter Ammonium Nitrate Formation in the San Joaquin Valley

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Objectives

As part of a larger study examining wintertime PM in the SJV, CRPAQS gas and aerosol data were used to address two questions:

What precursors limit ammonium nitrate formation?

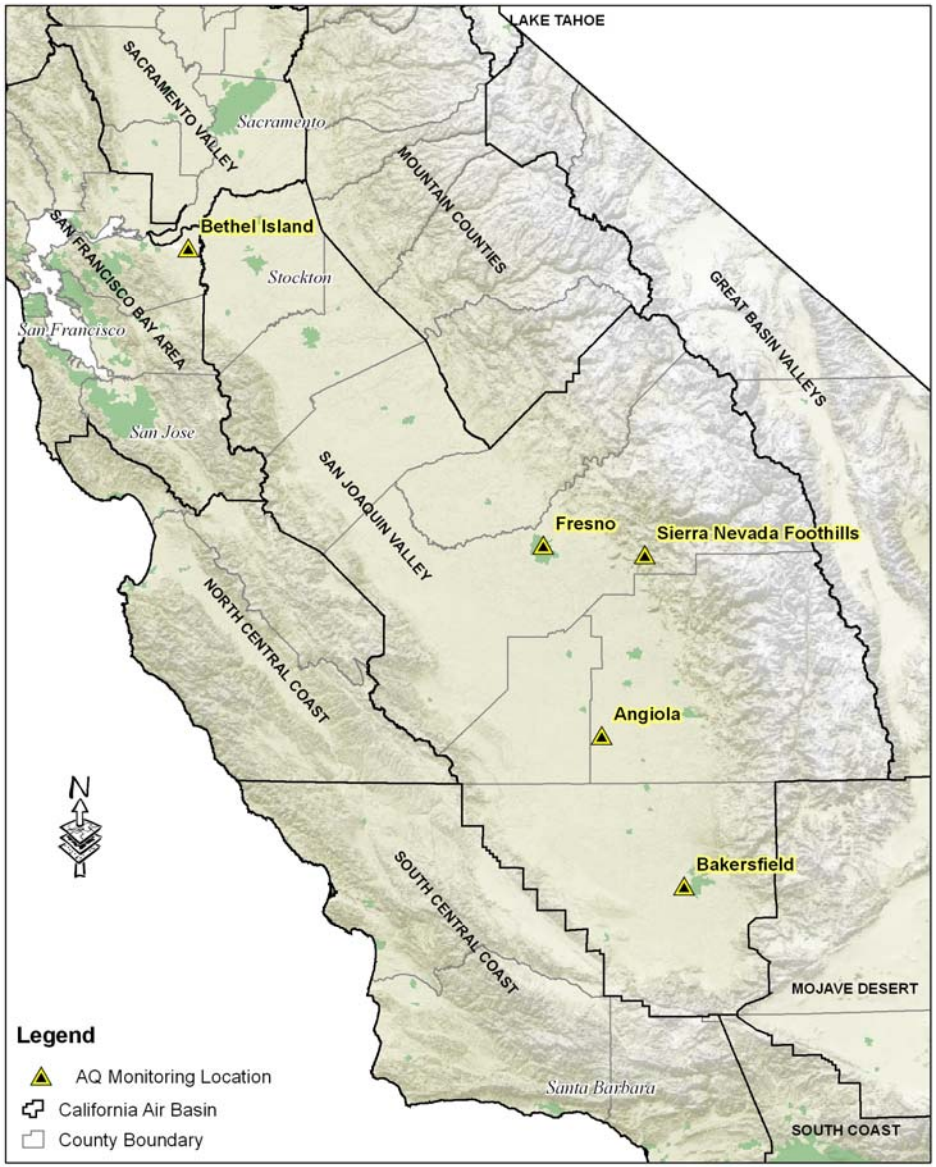
NH3 or HNO3?

Which nitric acid formation pathways are important?

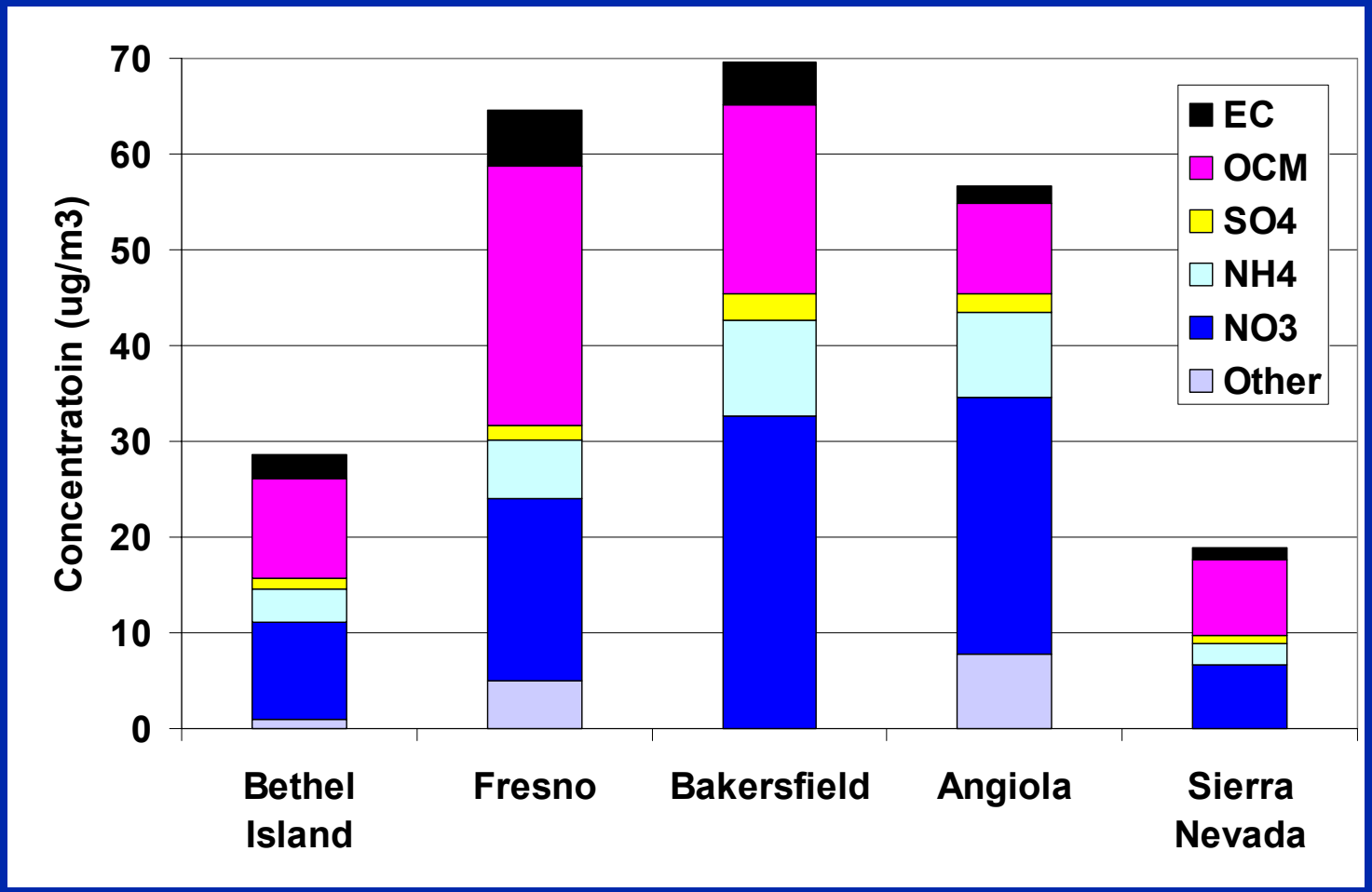
Daytime or Nighttime or Both?

CRPAQS = California Regional PM10/PM2.5 Air Quality Study

CRPAQS - 5 Core Sites



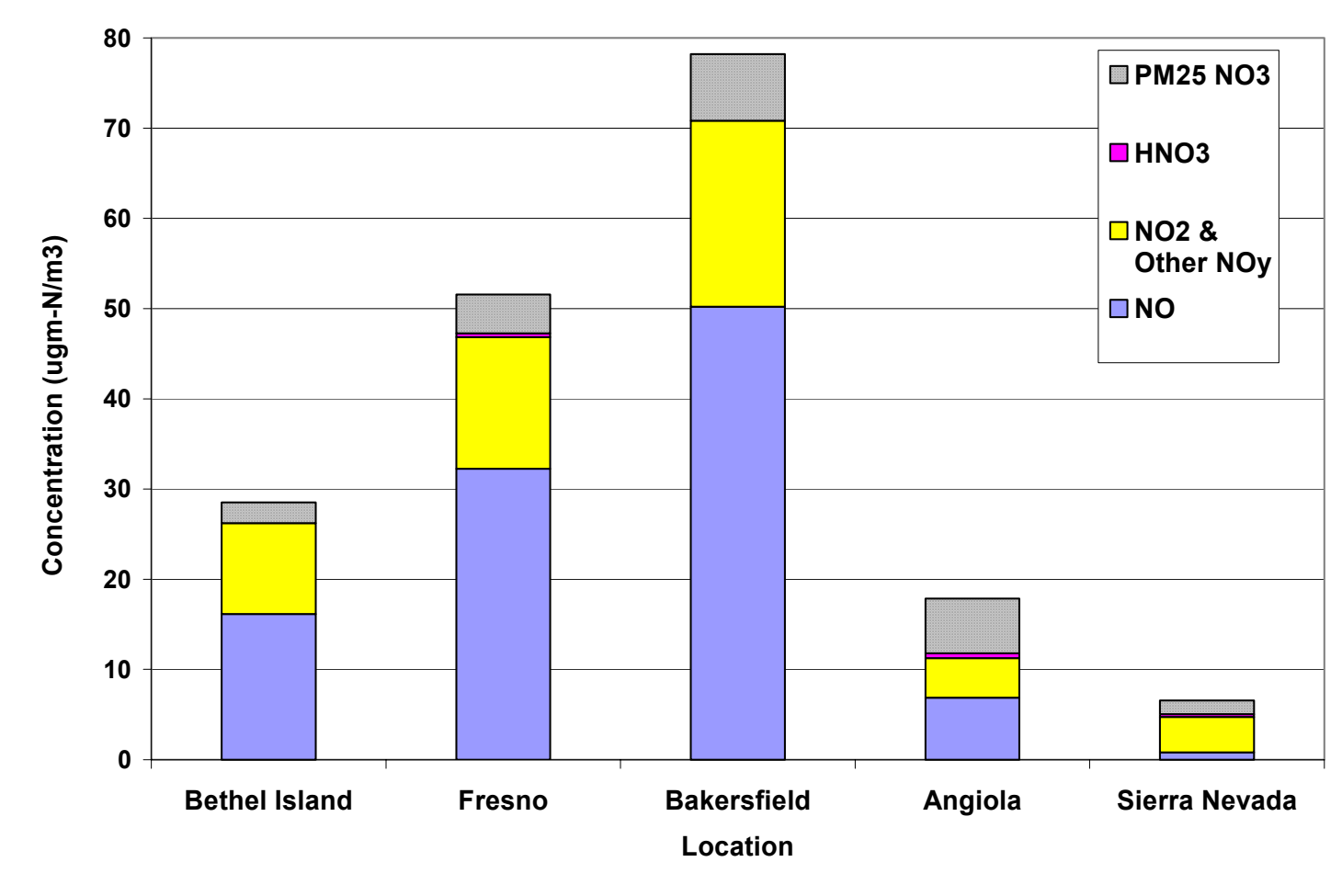
Average Distribution of PM2.5 Chemical Components at the Five Core CRPAQS Sites in Winter (15 IOP days in Dec 2000 – Feb 2001)



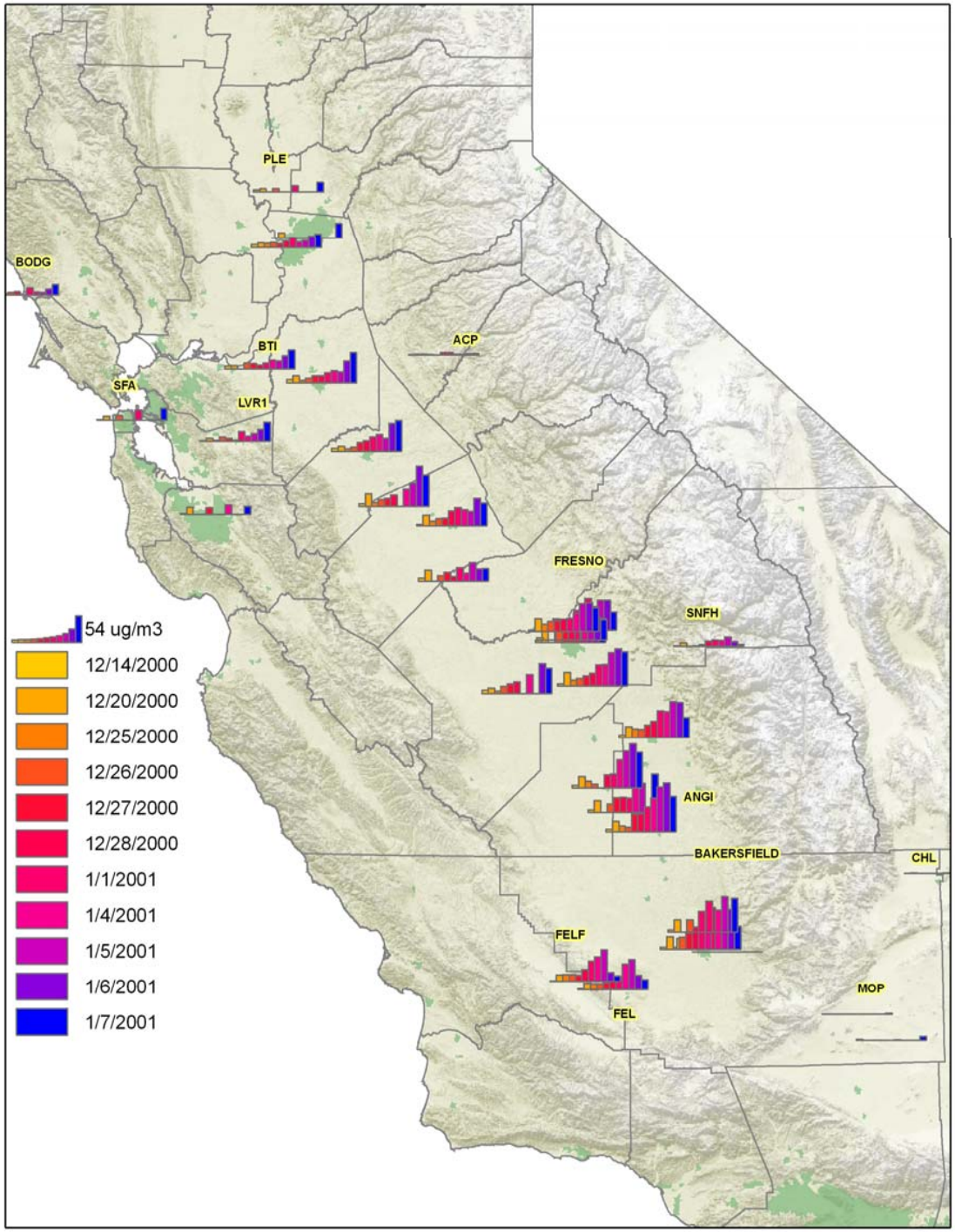
OCM = 1.4 x OC

Based on 3-hr to 8-hr samples from DRI's Sequential Filter Sampler

15-day Average Phase Distribution of NO_x-Related Species CRPAQS Winter 2000/2001 IOP Days



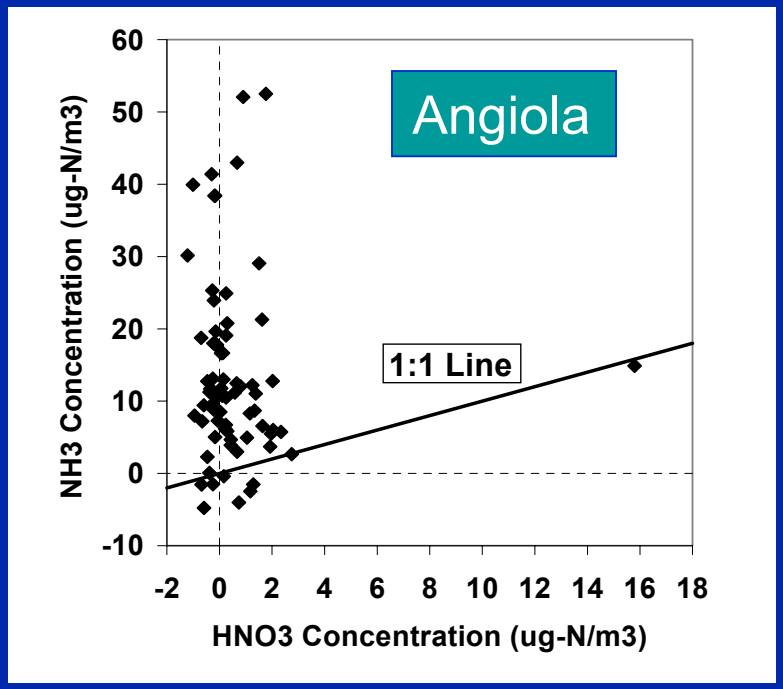
HNO_3 data were not available at Bethel Island and Bakersfield

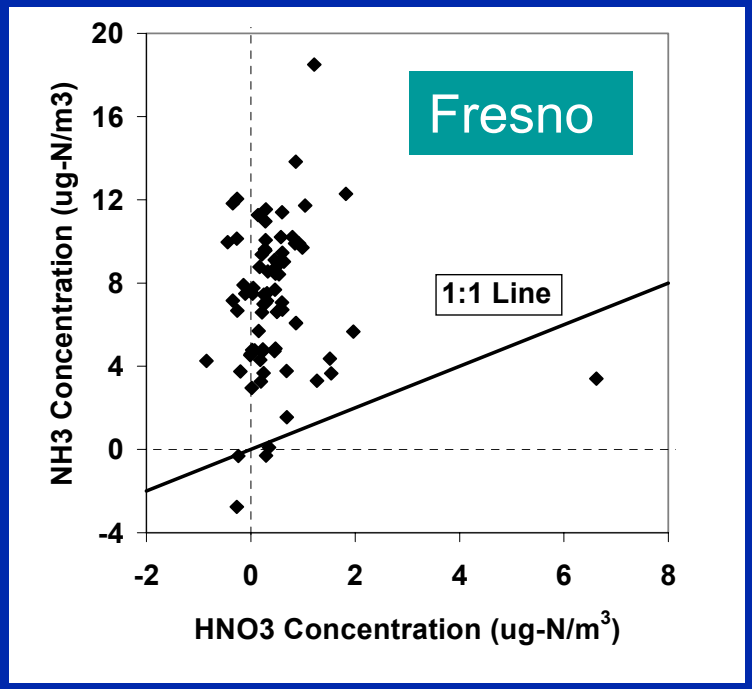


Regional Buildup of PM2.5 NO3 in San Joaquin Valley

Dec 14 - Jan 7 at CRPAQS sites

Comparison of Ammonia and Nitric Acid

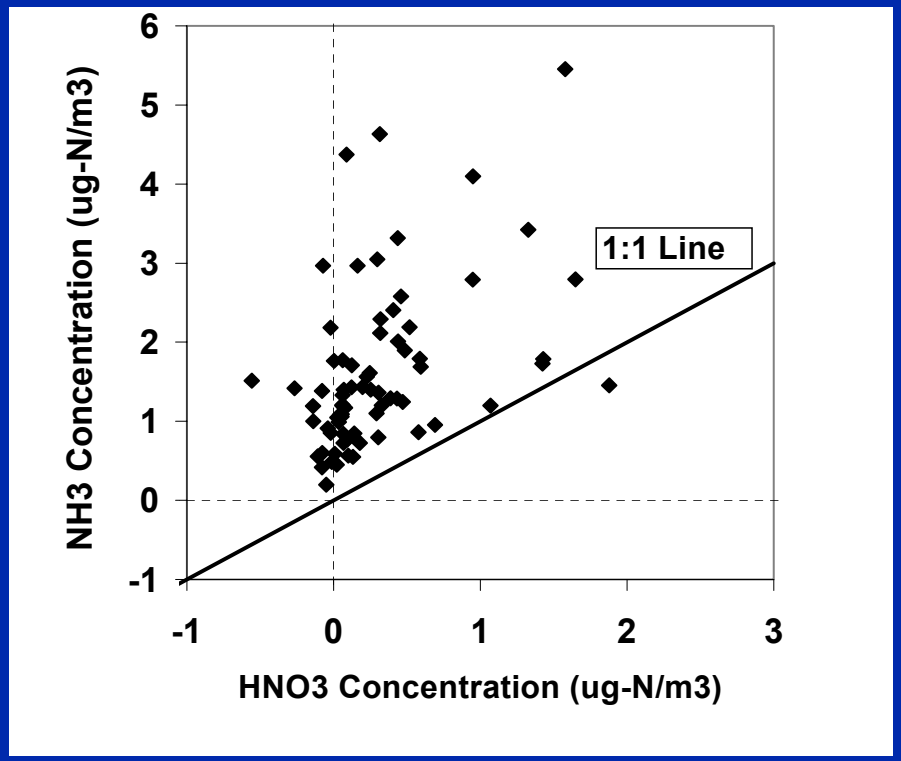




$NH_3 + HNO_3$? NH_4NO_3

HNO_3 is limiting because $HNO_3 << NH_3$

Comparison of Ammonia and Nitric Acid at a Low Ammonia Site



Sierra Nevada Foothills

HNO3 is still the limiting species

Nitric Acid Formation Pathways

Daytime Formation:

$NO_2 + OH \rightarrow HNO_3$

Nighttime Formation:

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

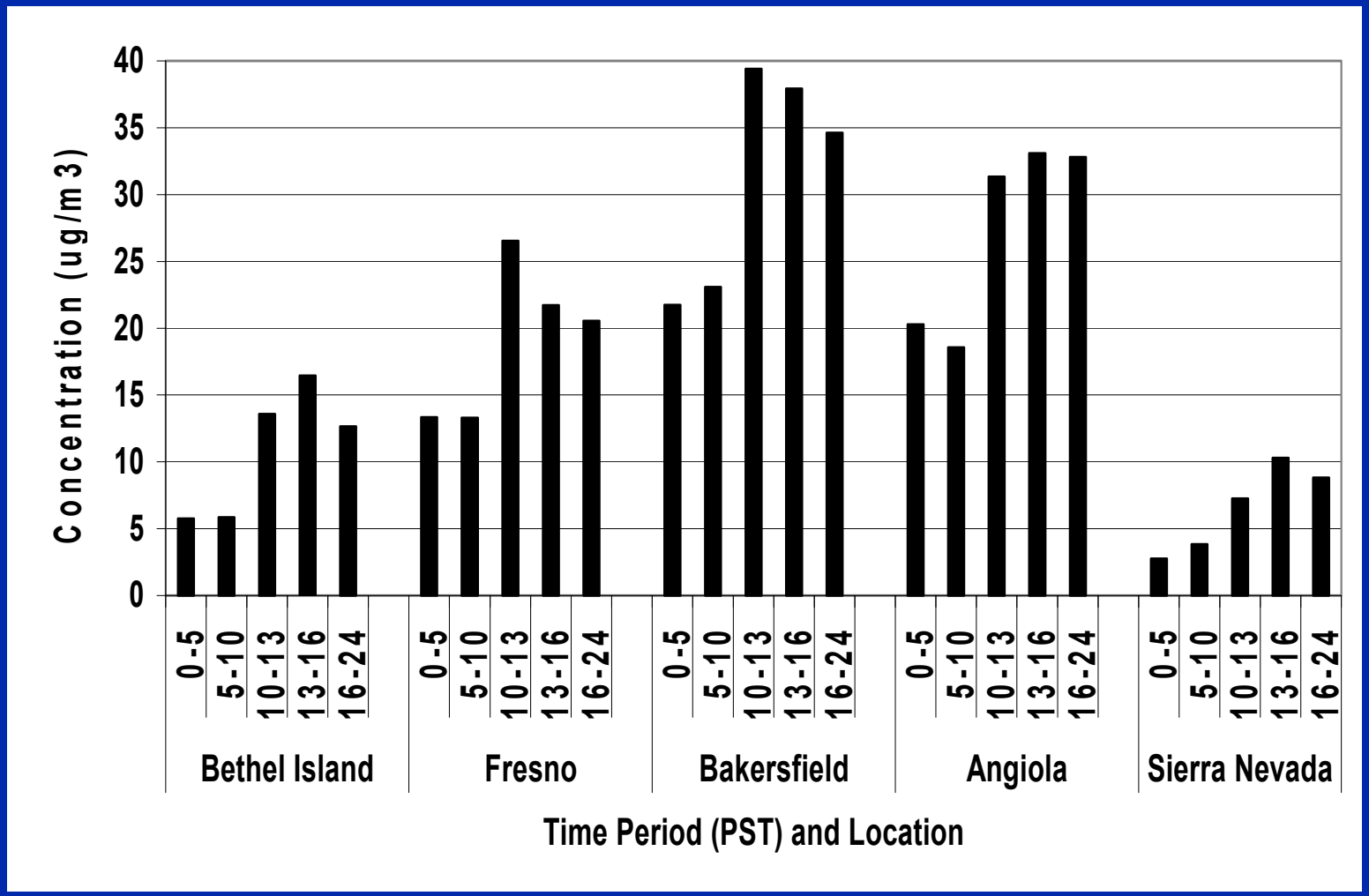
$N_2O_5 + H_2O \rightarrow 2\ HNO_3$

$NO_3 + R \rightarrow HNO_3 +$ organic products

Inhibiting Reactions:

$NO_3 + h\nu \rightarrow NO + O_2$		Sunlight
$NO_3 + h\nu \rightarrow NO_2 + O$		
$NO_3 + NO \rightarrow 2\ NO_2$		Fresh Emissions
$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$		
$N_2O_5 \rightarrow NO_2 + NO_3$		Warm Temperature
$NO_3 + R \rightarrow NO_2$ or RNO_3		Certain Organics

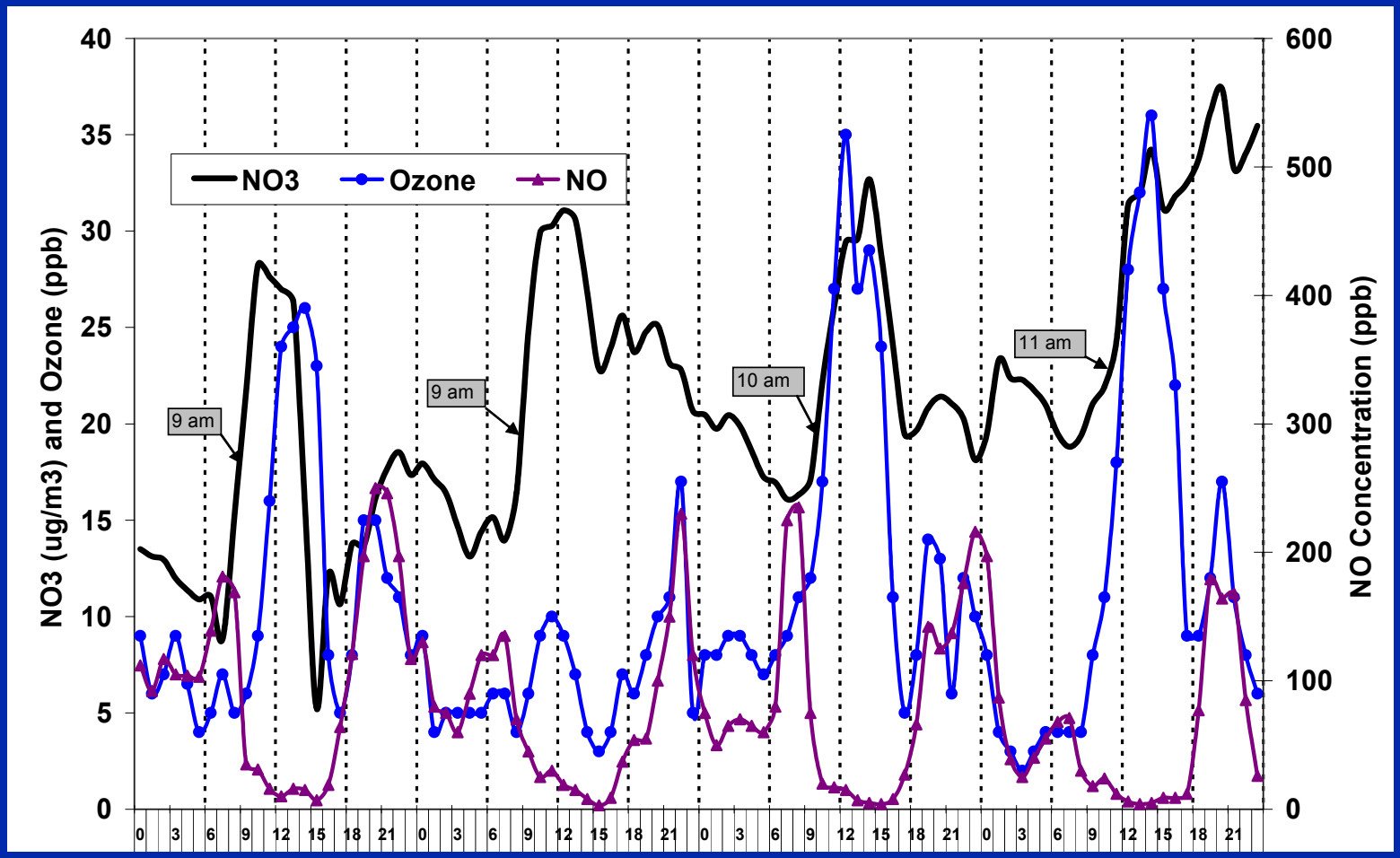
15-day Average PM2.5 Nitrate Concentrations by Sampling Period



Daytime HNO3 Production

- Within the 5 diurnal sampling periods, the highest PM2.5 nitrate levels occurred at
  - 1000-1300 PST in Fresno and Bakersfield
  - 1300-1600 PST in Angiola, Sierra Nevada Foothills, and Bethel Island
- The peaks in ozone concentrations, the key indicator of photochemical activity, occur from 1200-1500 PST at most SJV sites in winter
- The diurnal pattern of aerosol nitrate concentrations in the SJV suggests the daytime nitric acid formation is occurring in the region

Fresno
Hourly Concentrations of NO, O3, and PM2.5 NO3



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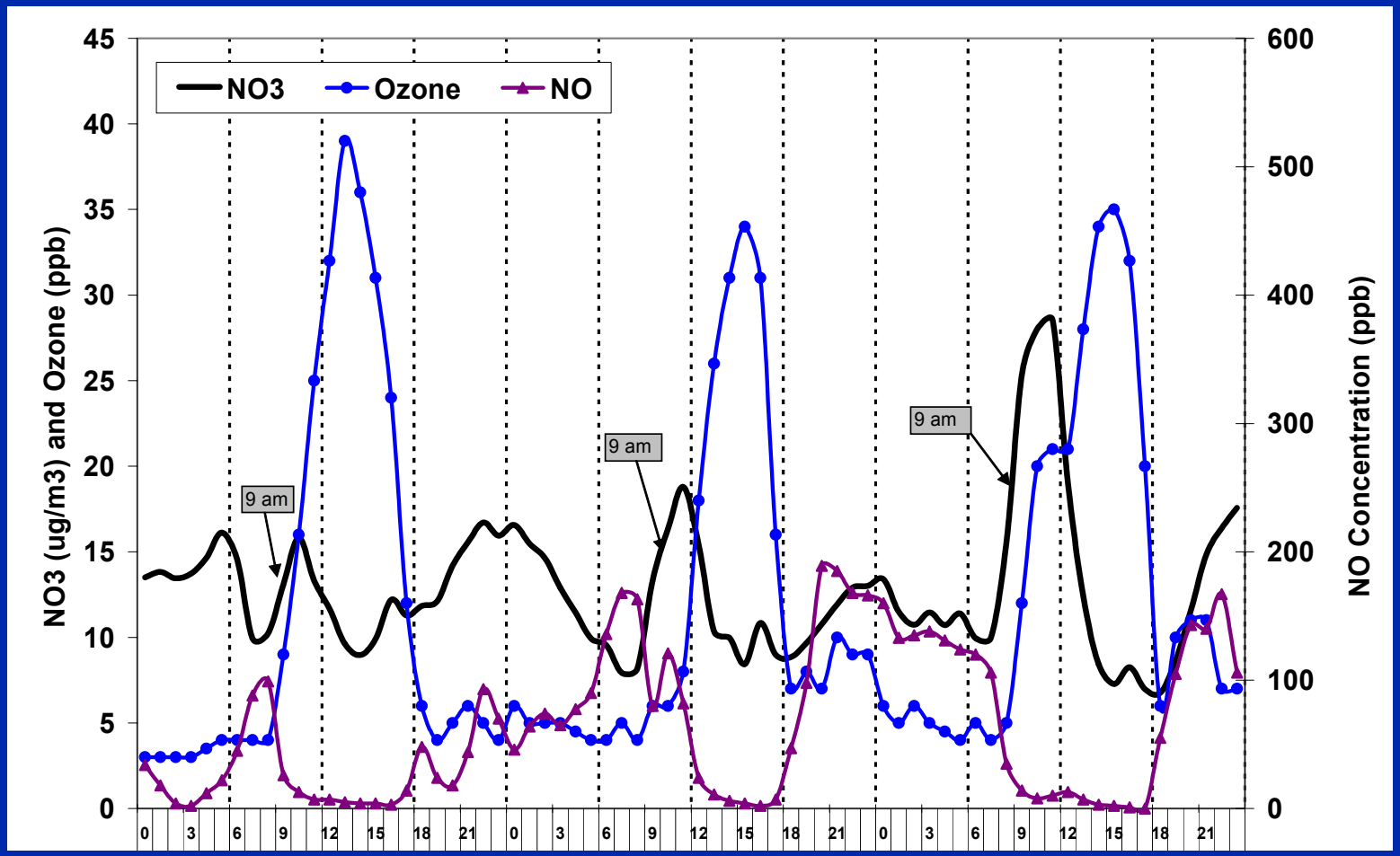
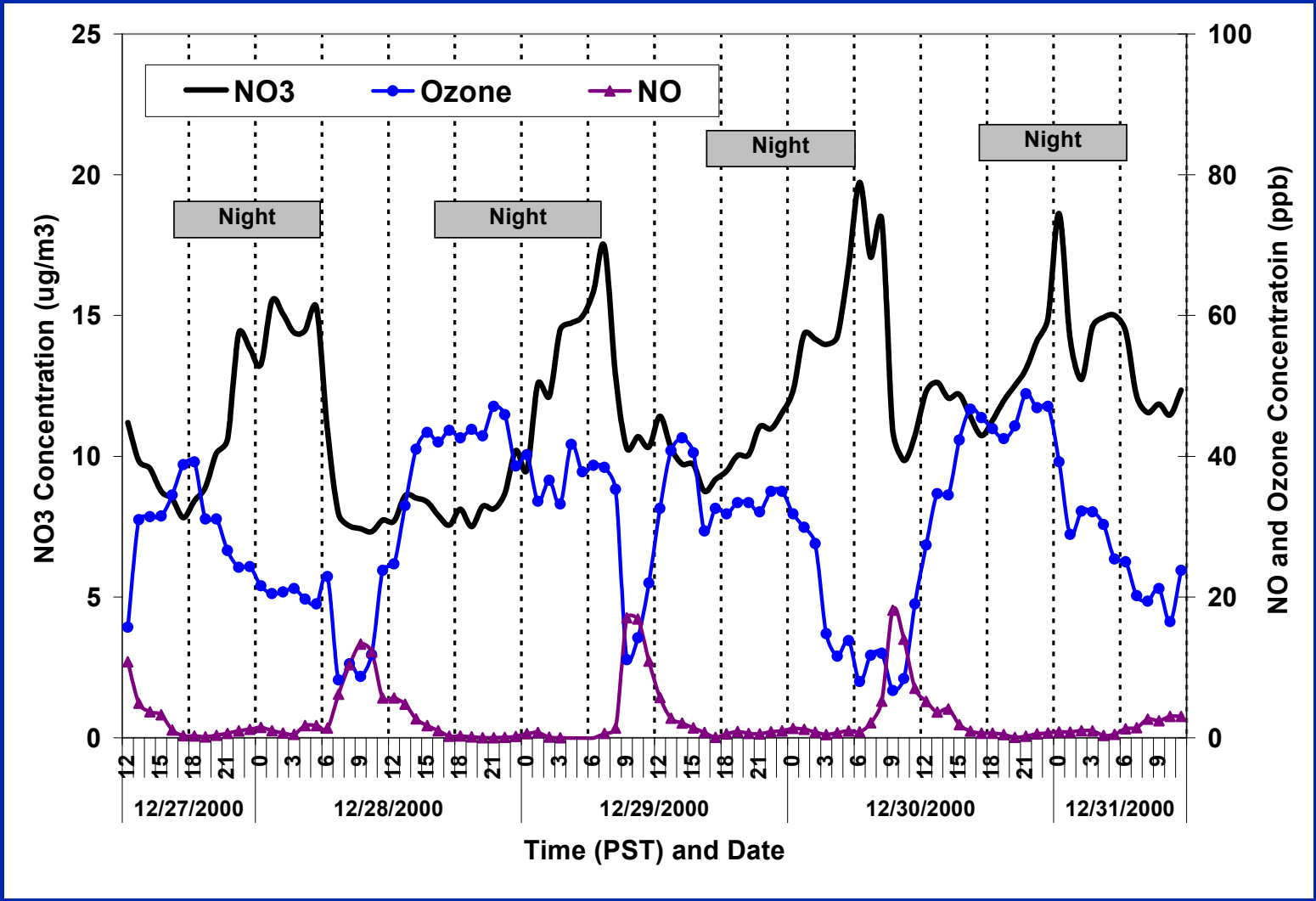


Angiola Tower - 90 m above ground
Hourly concentrations of NO, O3, and PM2.5 nitrate



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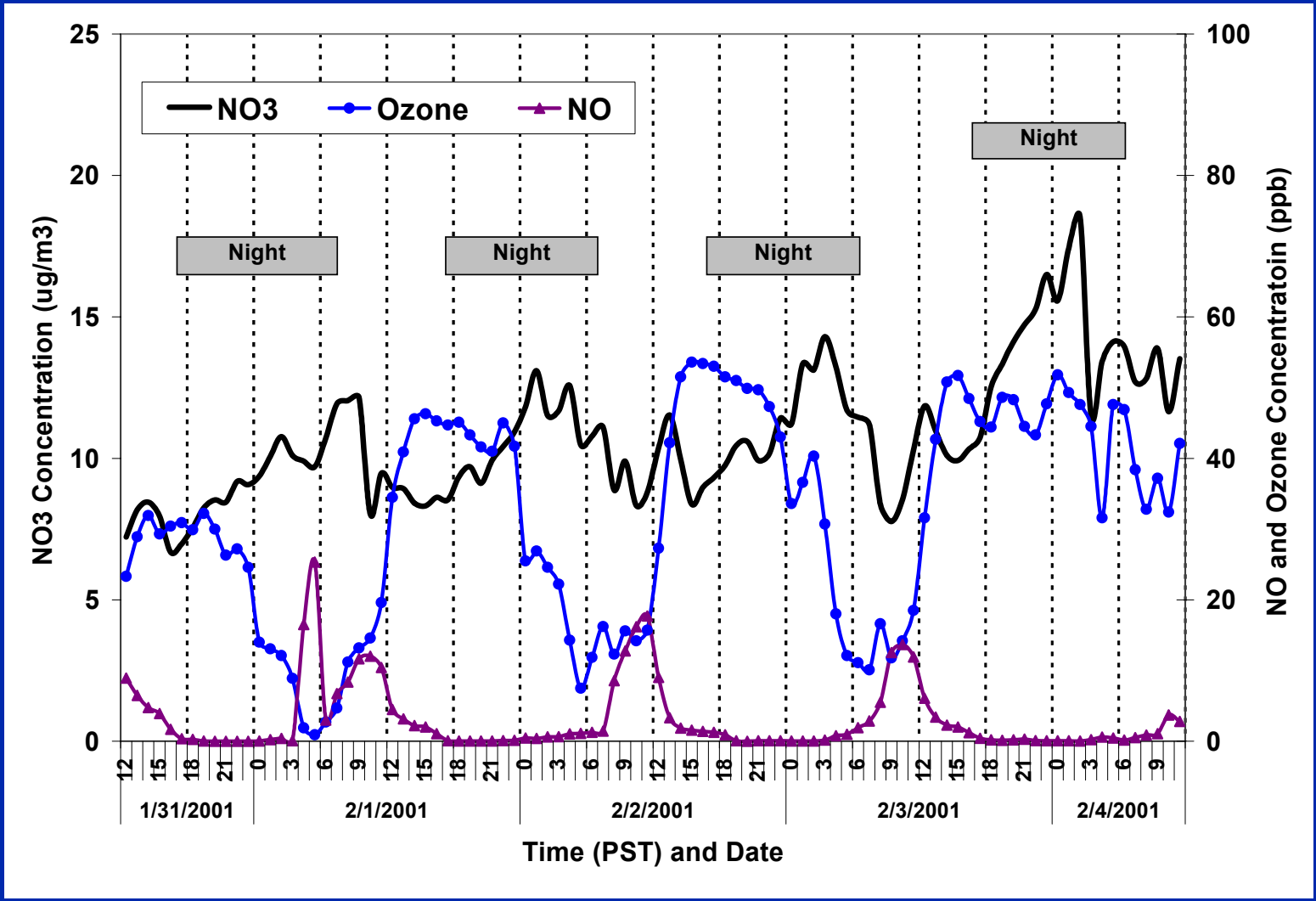
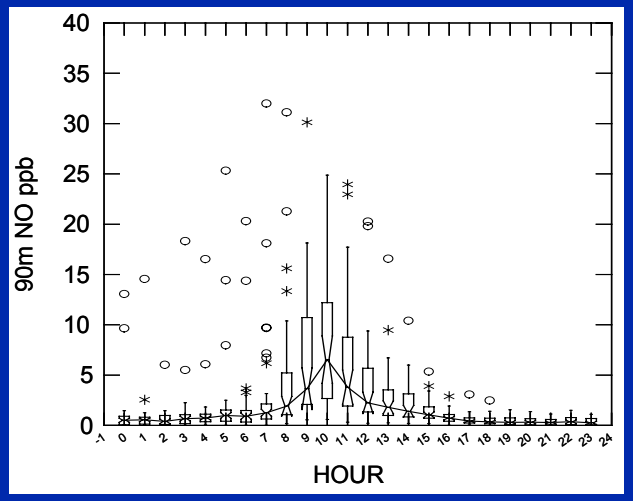


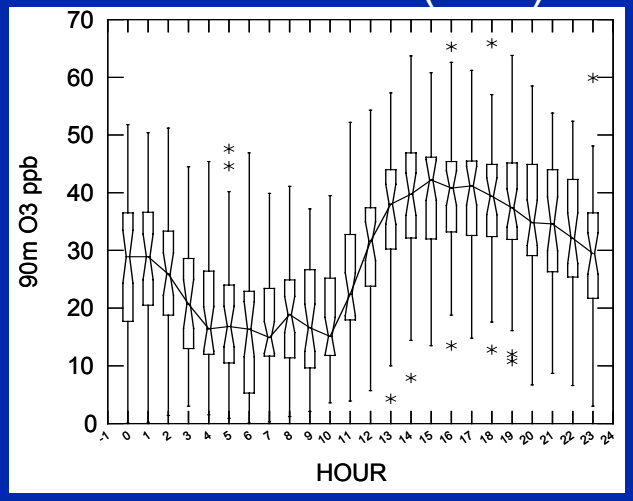
Angiola Tower NO and Ozone – Dec & Jan

NO is low aloft at night

NO Aloft (90m)

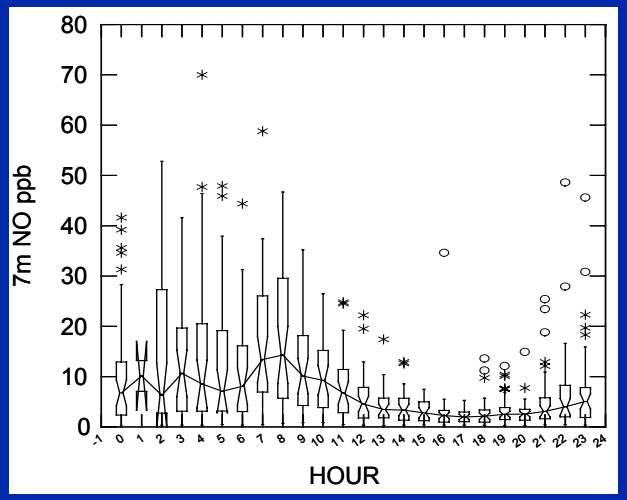


Ozone Aloft (90m)



O3 is plentiful aloft at night

NO Surface (7m)



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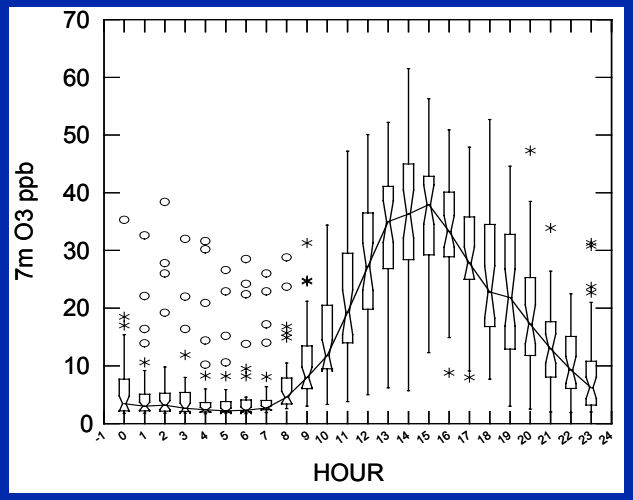
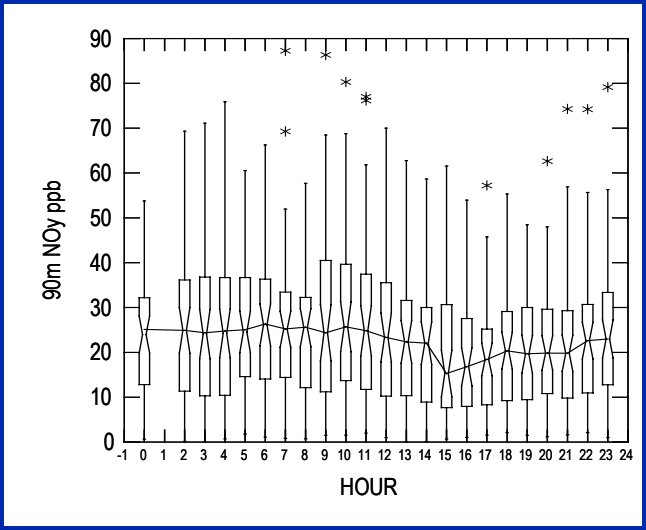


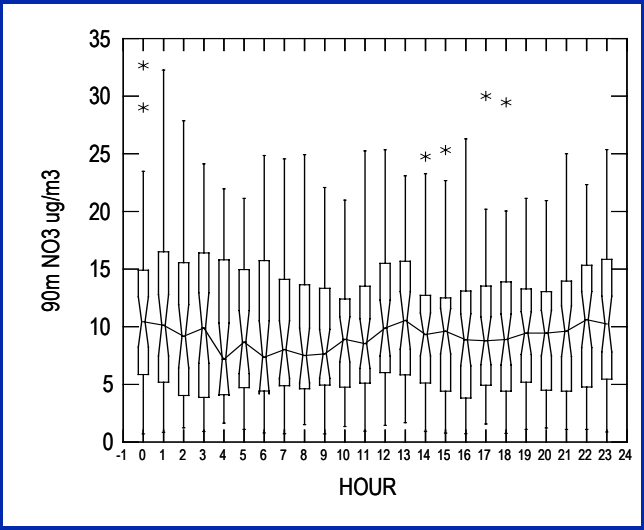
Angiola Tower NOy and PM2.5 NO3

NOy is plentiful aloft at night

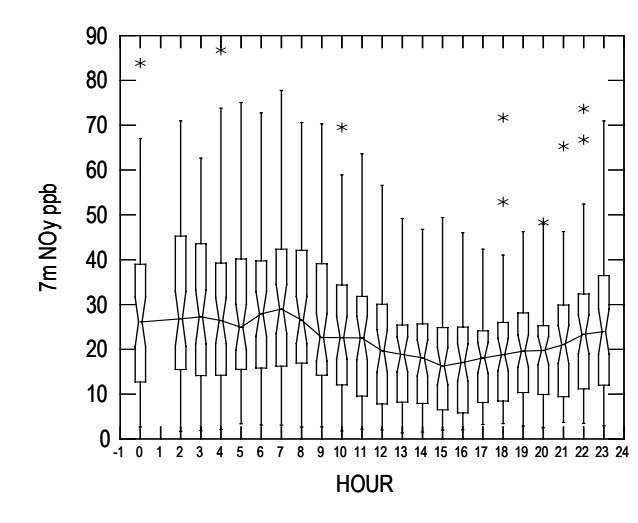
NOy Aloft (90m)



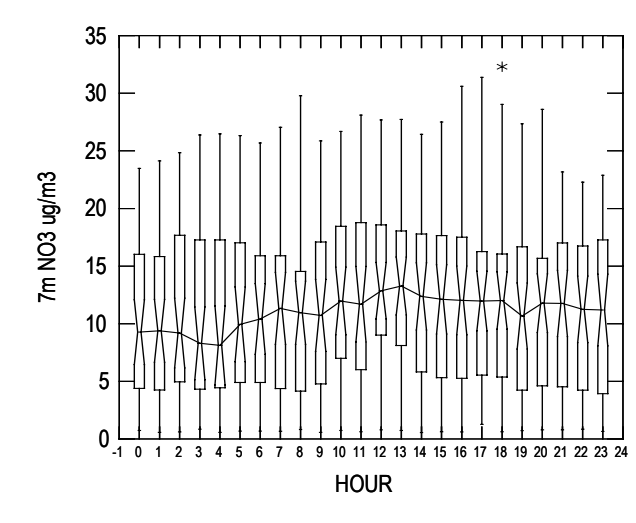
PM2.5 NO3 Aloft (90m)



NOy Surface (7m)



PM2.5 NO3 Surface (7m)



Rate Limiting Factors

- NOx is abundant in SJV in winter
- Daytime HNO3 production rates are limited by sunlight, VOCs, and background ozone
- Nighttime HNO3 production is limited by background ozone which is abundant aloft but not at the surface

Conclusions

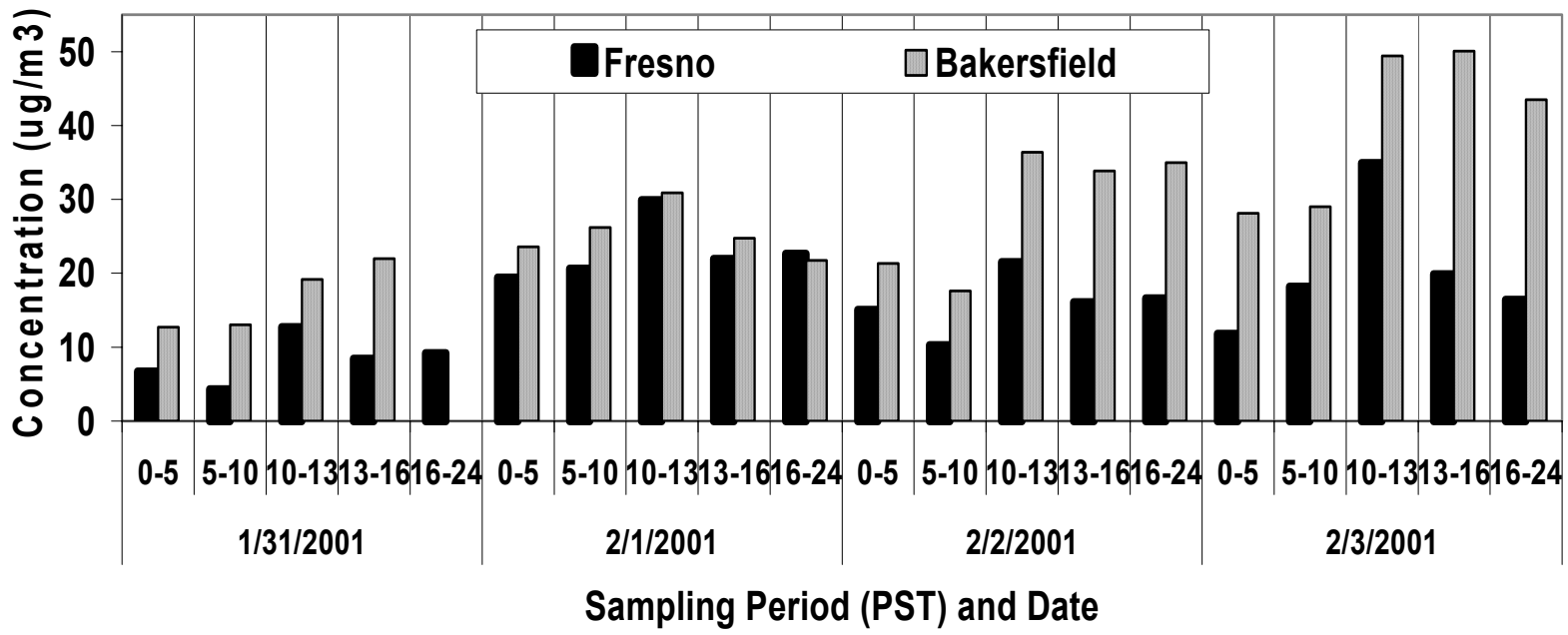
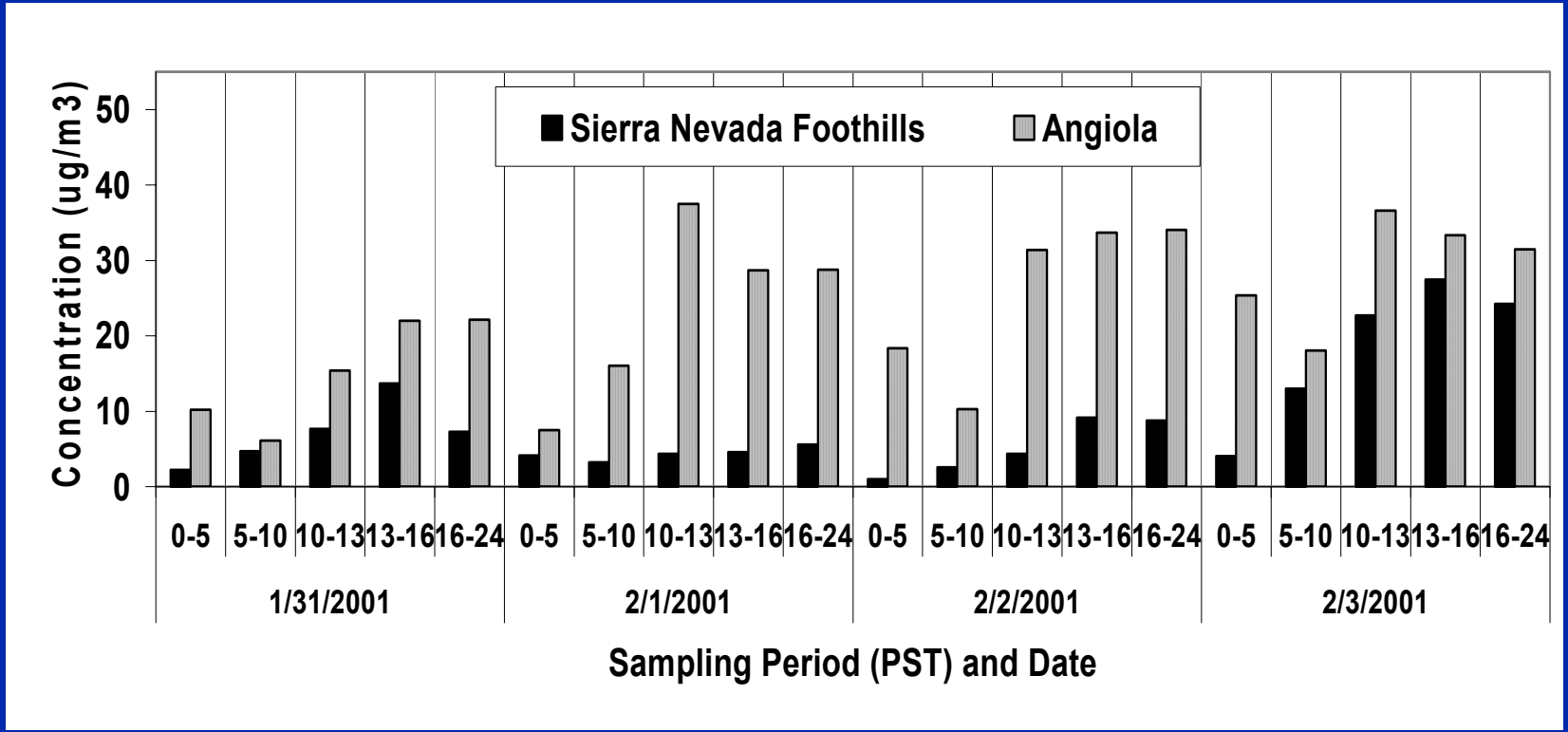
- Particulate NO_3 concentrations are small relative to gaseous NO_y precursor concentrations
- Ammonium nitrate concentrations are limited by the rate of HNO_3 formation, rather than by the availability of NH_3
- HNO_3 is formed via both daytime photochemistry and aloft nighttime chemistry
- Nighttime chemistry aloft may significantly contribute to the regional nature of ammonium nitrate in winter in the SJV

Acknowledgement

- Sponsored by San Joaquin Valley Air Pollution Study Agency
- Managed by California Air Resources Board staff

The End

PM2.5 nitrate concentrations in Fresno and Bakersfield from January 31 to February 3, 2001



PM2.5 nitrate concentrations in Sierra Nevada Foothills and Angiola from January 31 to February 3, 2001