Modeling PM Nitrate Formation in the San Joaquin Valley Air Basin during Recent Years

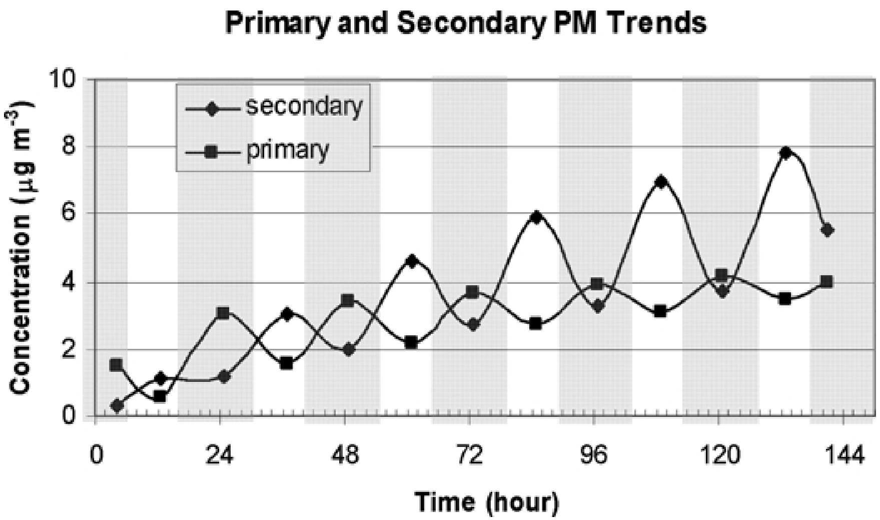
Michael J. Kleeman*, Anikender Kumar,
Abhishedk Dhiman

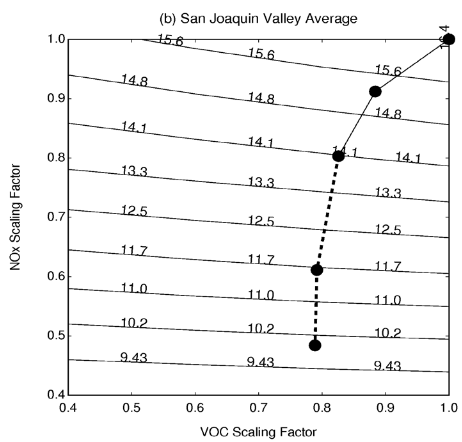
Department of Civil and Environmental
Engineering, UC Davis

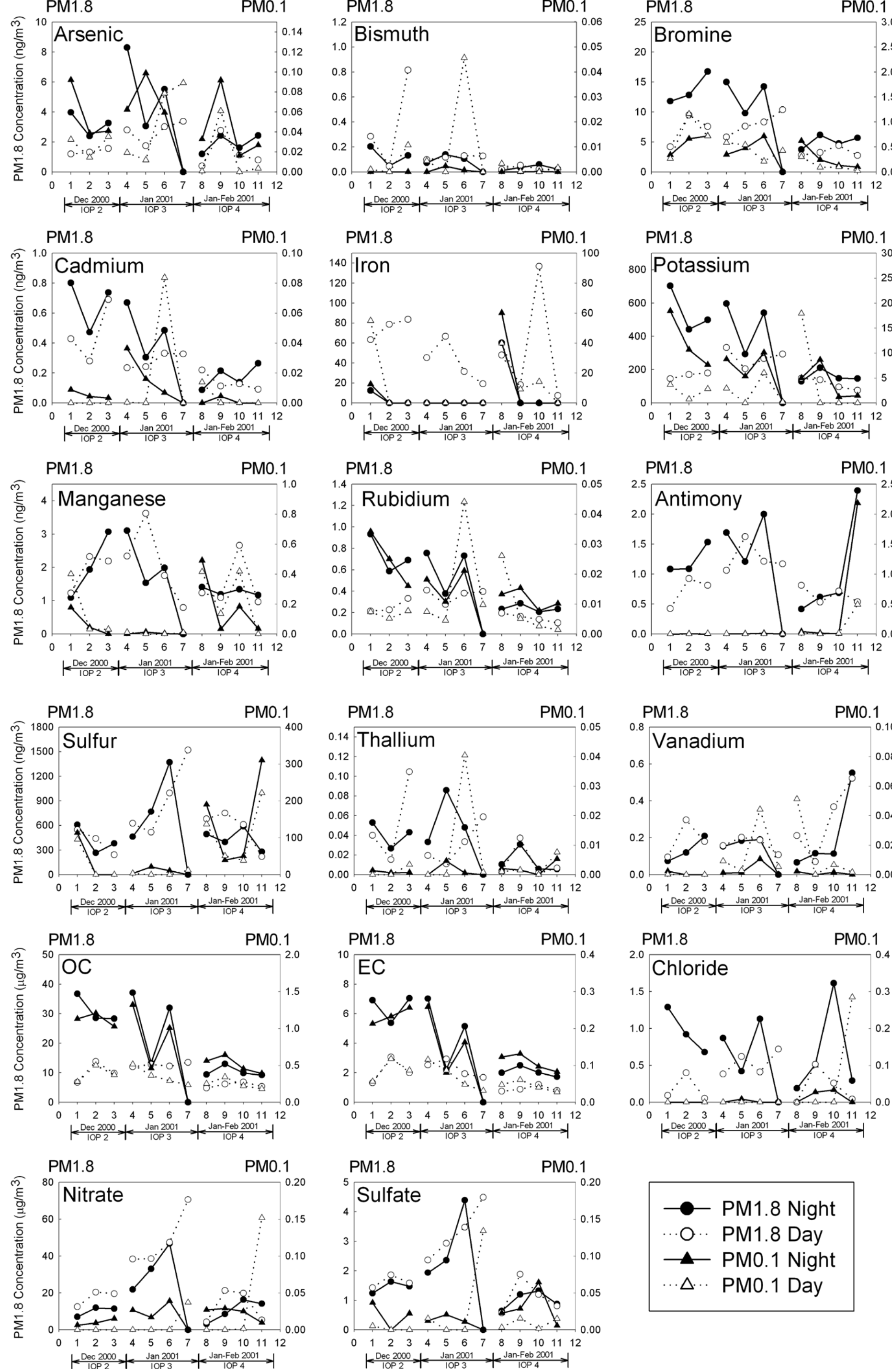
The statements and conclusions in this presentation are those of the investigators and not necessarily the California Air Resources Board.

UCDAVIS
CIVIL AND ENVIRONMENTAL
ENGINEERING & AQRC

Modesto PM Composition



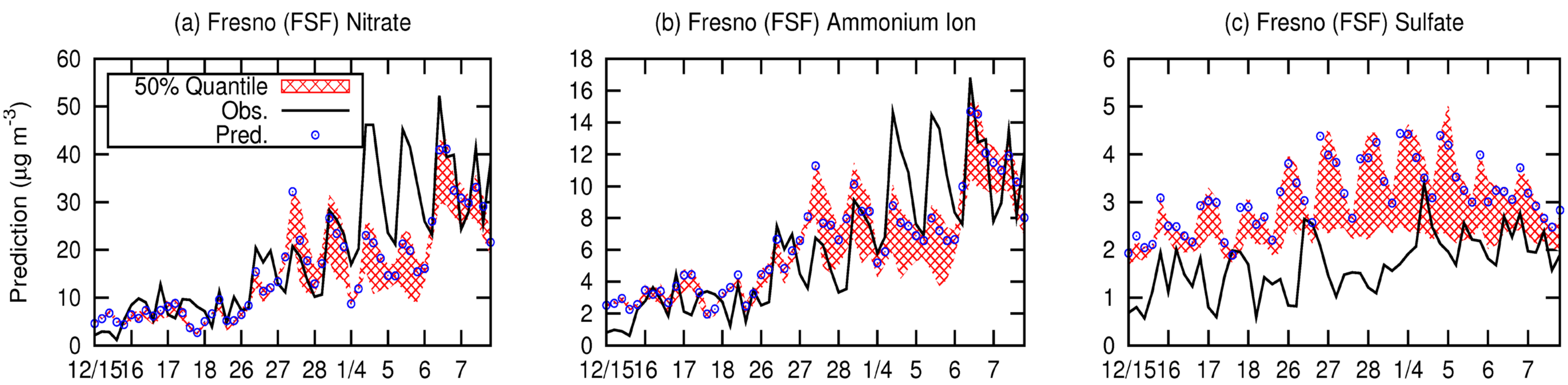


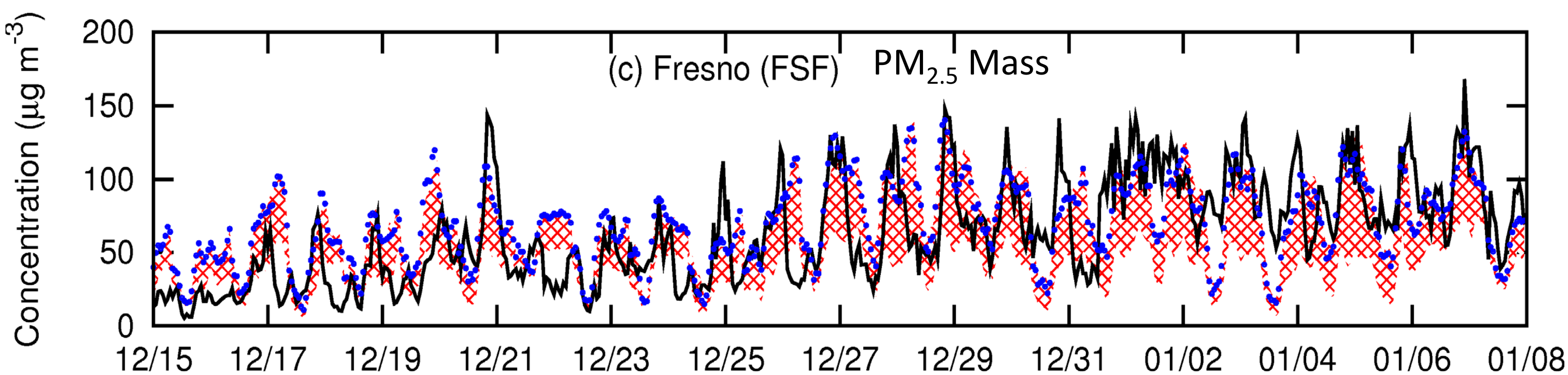


Source: W. Ham et al., Size Distribution of Health Relevant Trace Elements in Airborne Particulate Matter During a Severe Winter Stagnation Event: Implications for Epidemiology and Inhalation Exposure Studies, Aerosol Science and Technology, 4, 753-765, 2010.

Background – Particulate Nitrate Simulations in the San Joaquin Valley for the Years 2000-2001

- Particulate nitrate (NO_3^-) contributes significantly to winter $PM_{2.5}$ concentrations in California's San Joaquin Valley (SJV)





Source: 2008 Ying, Q., J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M.J. Kleeman. Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results. Atmospheric Environment, 42, pp 8954-8966.

UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Objective 1: Investigate Possible Emissions Bias in Recent Inventories

- Total reactive nitrogen (NOy) includes all oxidized forms of nitrogen in the atmosphere

- NOy = **NO** + **NO_2** + NO_3 + $2N_2O_5$ + HNO_2 + HNO_3 + HNO_4 + PAN + PPN + **particulate nitrate**

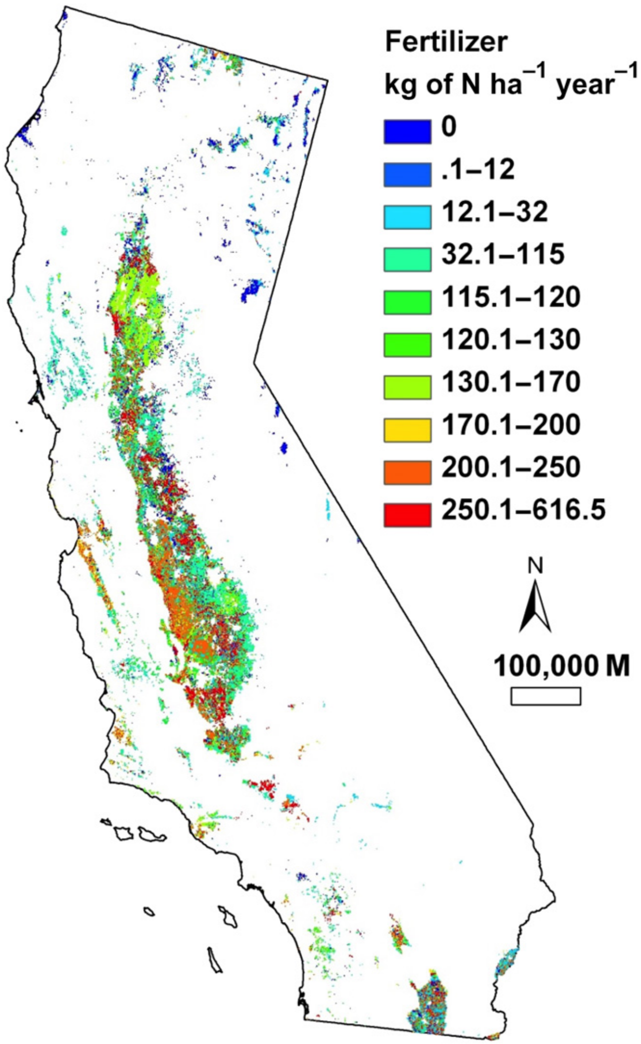
- Conservation of total NOy is easier to check than conservation of individual NOy species
  - Balance between emissions, deposition, and transport with lesser impacts from chemistry

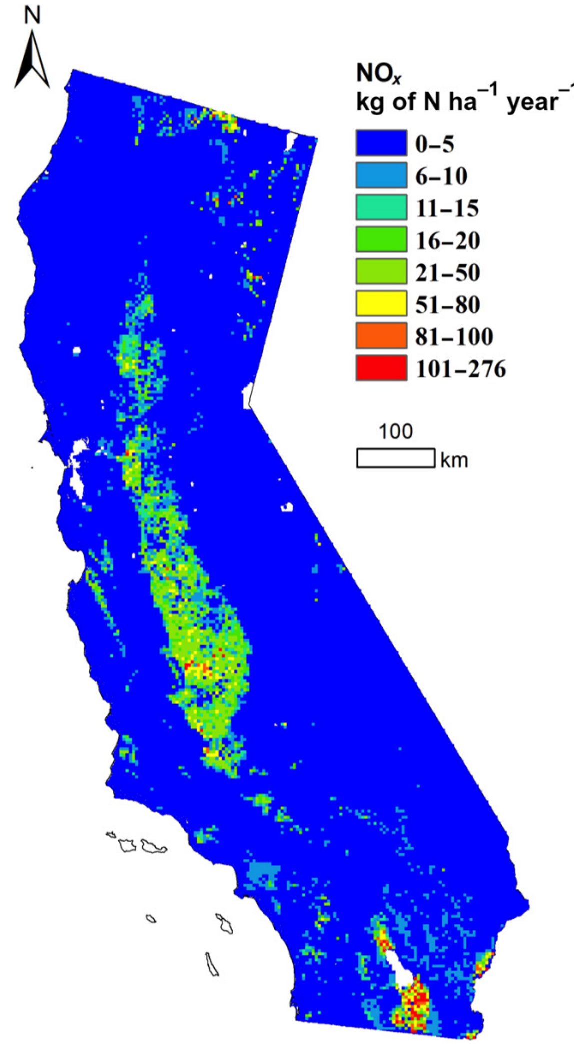
- Predict NOy concentrations during winter months in the years 2010, 2013, and 2015 and compare to measured values
  - Is there evidence of an emissions bias?

UCDAVIS CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Objective 1: Investigate Possible Emissions Bias

- Candidate soil NOx emissions predicted by the IMAGE model





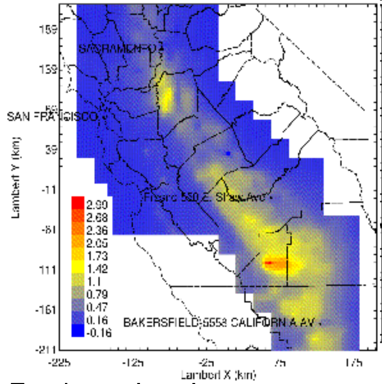
Source: Maya Almaraz et al. Sci Adv 2018;4:eaao3477

UC DAVIS CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

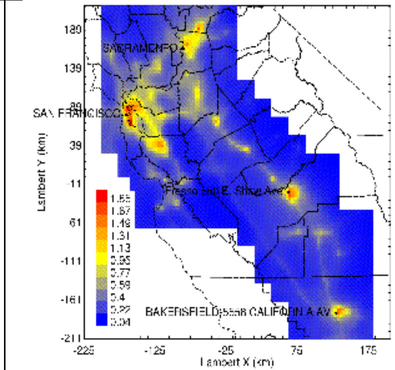
NOy Spatial Distribution in Jan 2010, 2013, 2015

Candidate soil NOx emissions contribute significantly to NOy in rural locations of the SJV

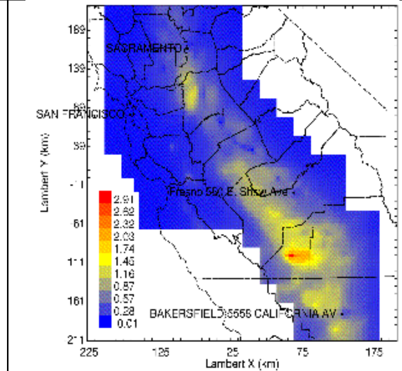
Candidate soil NOx emissions contribute ~20% to NOy in urban locations of Fresno and Bakersfield



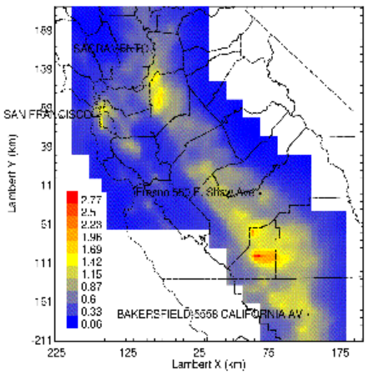
Total reactive nitrogen (µmoles/m^3) in Jan 2010 with soil NOx case



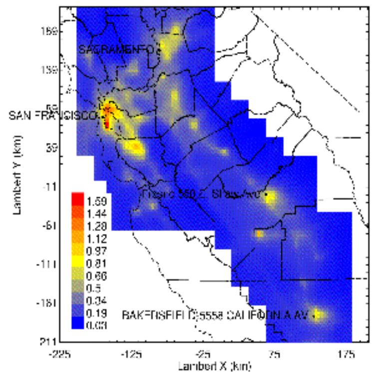
Total reactive nitrogen (µmoles/m^3) in Jan 2010 without soil NOx (base) case



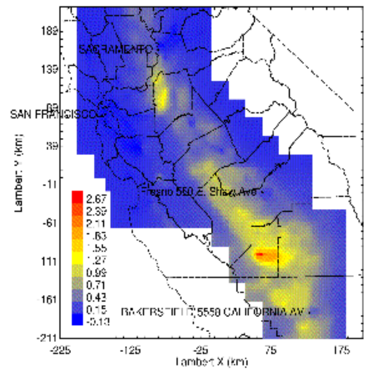
Diff of total reactive nitrogen (µmoles/m^3) in Jan 2010 with - without soil NOx case



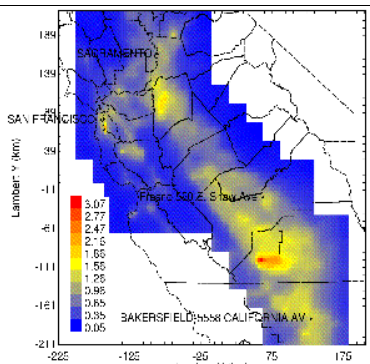
Total reactive nitrogen (µmoles/m^3) in Jan 2013 with soil NOx case



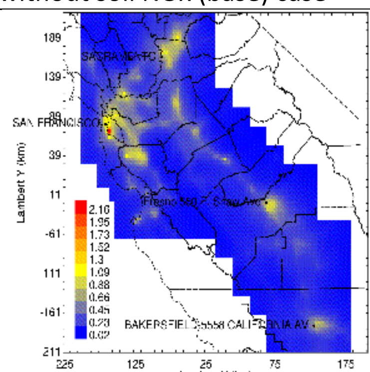
Total reactive nitrogen (µmoles/m^3) in Jan 2013 without soil NOx (base) case



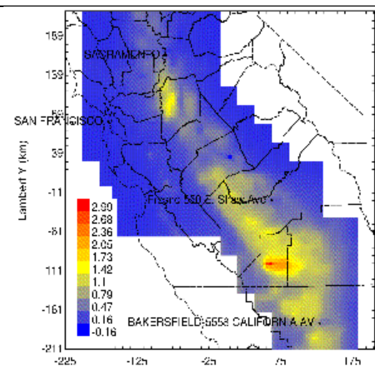
Diff of total reactive nitrogen (µmoles/m^3) in Jan 2013 with - without soil NOx case



Total reactive nitrogen (µmoles/m^3) in Jan 2015 with soil NOx case



Total reactive nitrogen (µmoles/m^3) in Jan 2015 without soil NOx (base) case

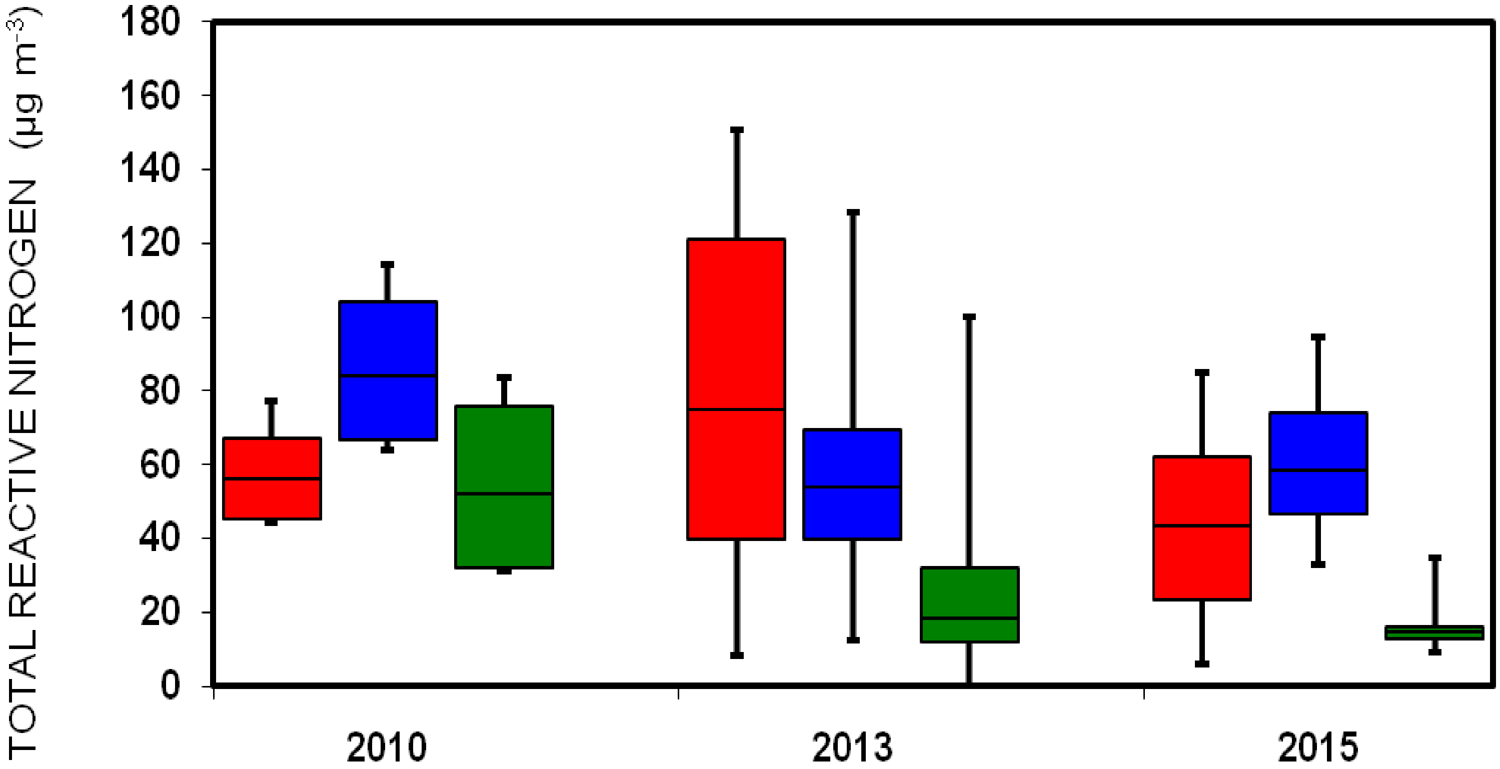


Diff of total reactive nitrogen (µmoles/m^3) in Jan 2015 with - without soil NOx case

UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

NOy Trends in January at Fresno, Bakersfield, and Visalia

- Measurements of NO+NO_2+particulate nitrate
- Predictions with candidate soil NOx emissions
- Predictions without candidate soil NOx emissions



UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Objective 2: Investigate Vertical Profiles

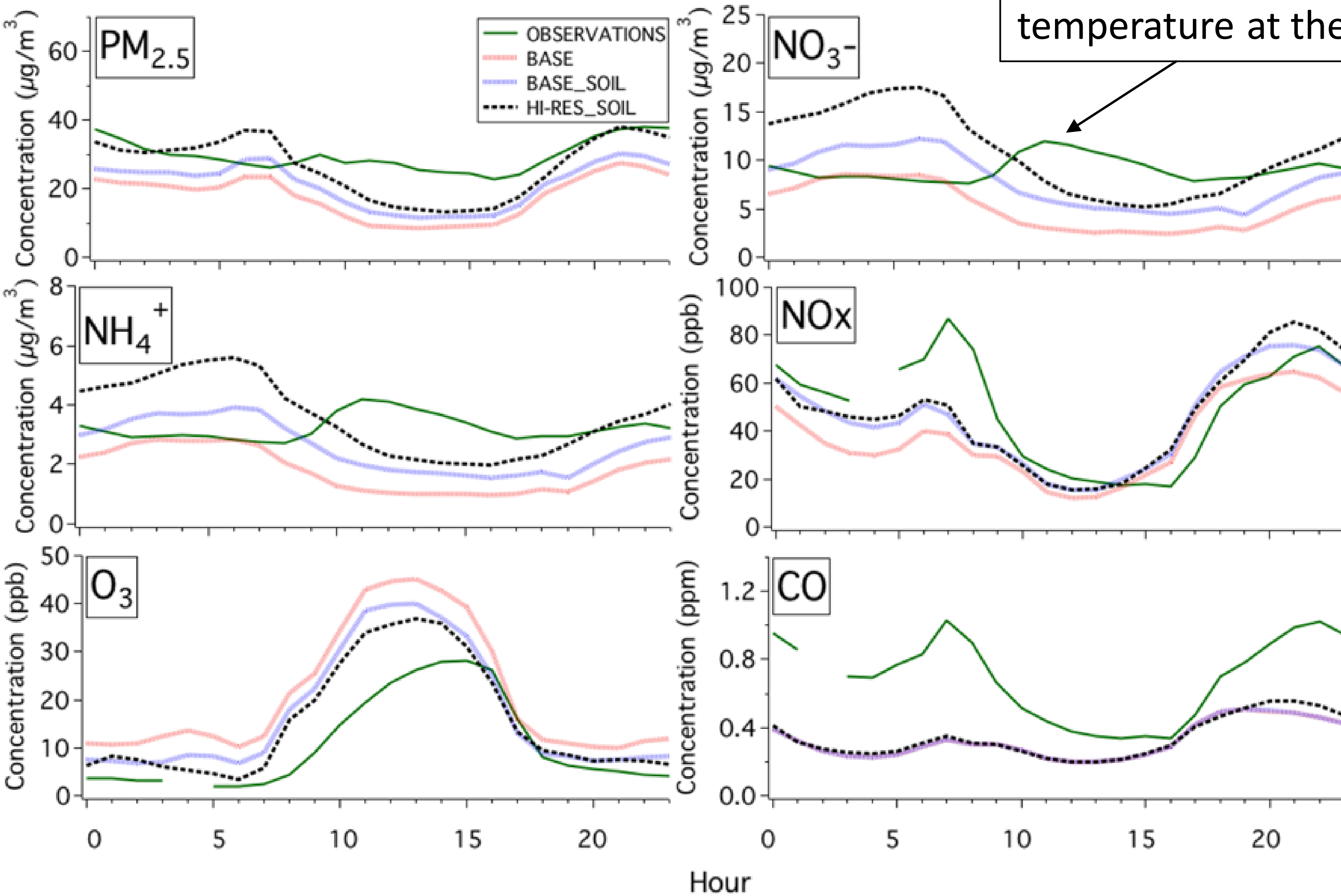
- DISCOVER-AQ Field and Aircraft Observations
  - Jan 16 – Feb 10, 2013
  - HR-ToF-AMS, GCMS, TDILF-MS measurements above Fresno

- UCD/CIT air quality model vertical profile predictions
  - 16 levels up to 5km (standard resolution)
  - 42 levels up to 5km (high resolution)
  - Reduced nighttime Kzz minimum values from 0.5 $m^2 s^{-1}$ to 0.01 $m^2 s^{-1}$
  - Set Kzz values to 0.04 $m^2 s^{-1}$ above the mixing depth under neutral stability conditions

- Emissions
  - Candidate soil NOx emissions from the IMAGE model included as part of the sensitivity analysis

Objective 2: Average Diurnal Profiles at Surface

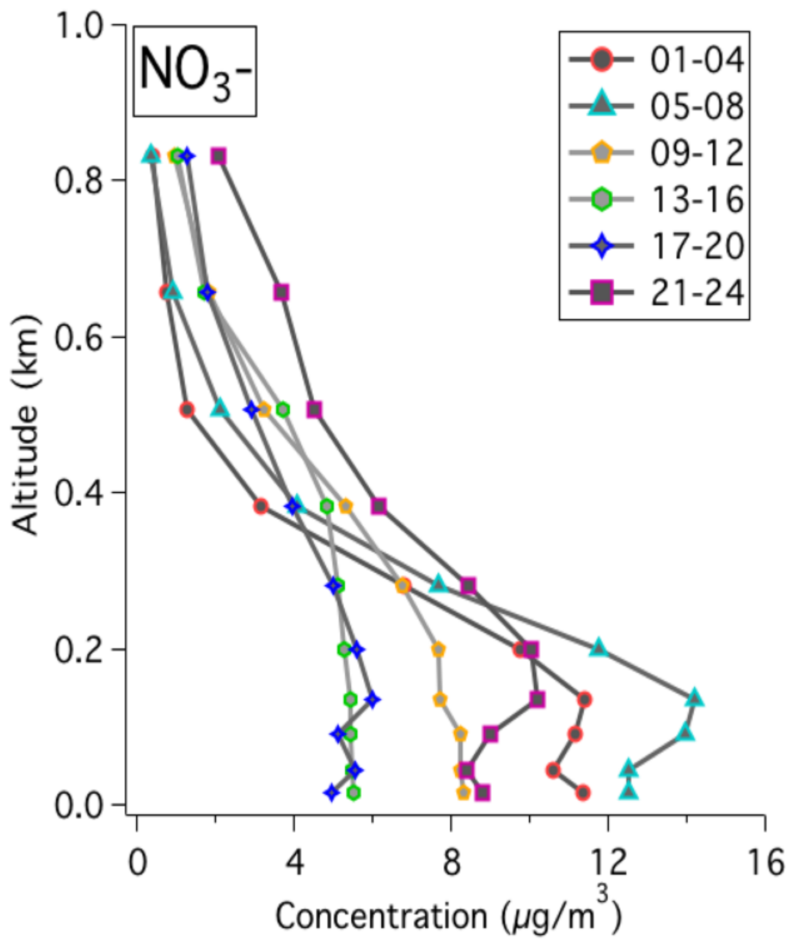
Late morning maximum consistent with nocturnal layer that is mixed into the surface layer as temperature at the surfaces rises



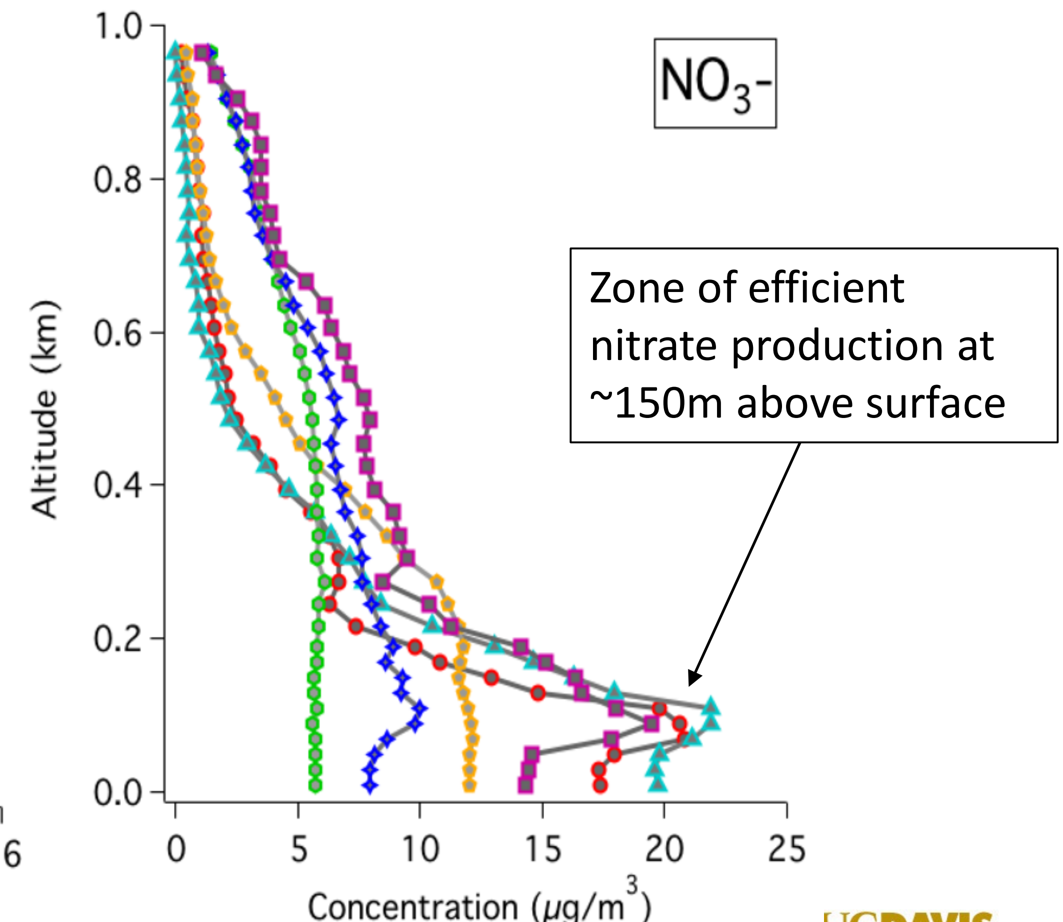
UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Objective 2: Investigate Vertical Profiles
Predicted Episode-average Profiles at Fresno

BASE_SOIL



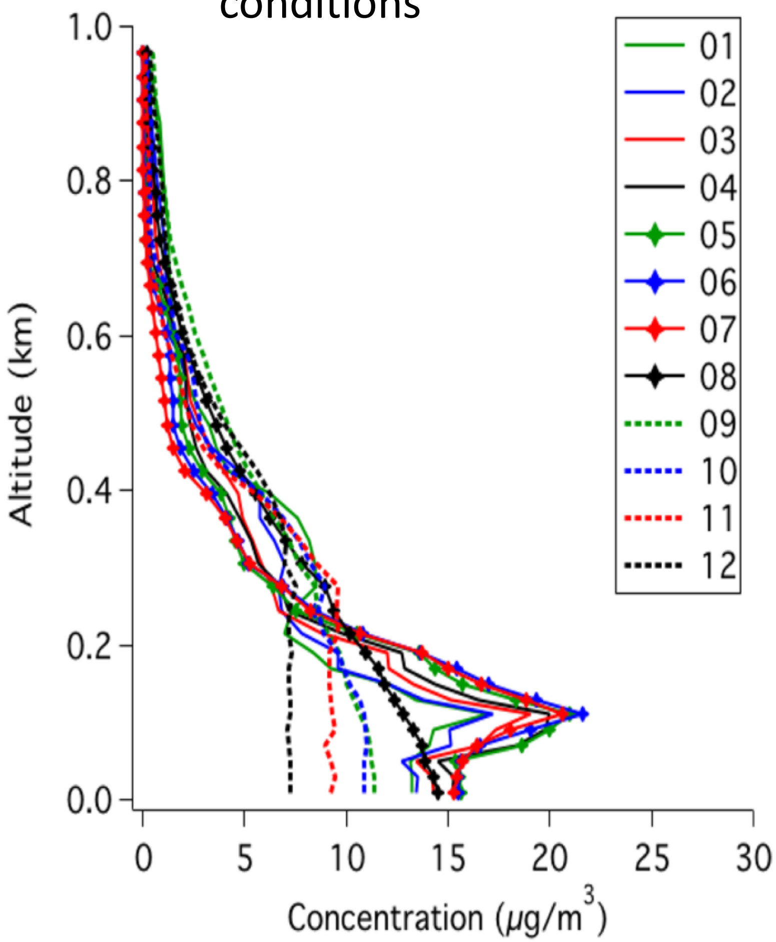
HI-RES_SOIL



UC DAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

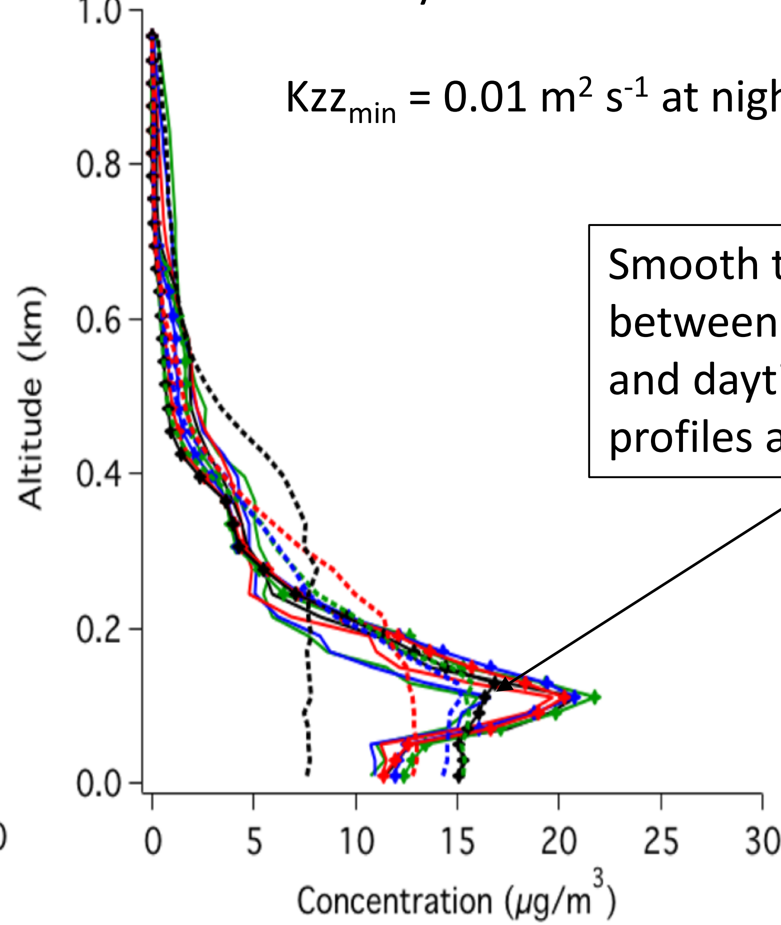
Objective 2: Investigate Vertical Profiles Predicted Profiles at Fresno on Jan 16-21, 2013

Original Kzz above mixing depth for neutral stability conditions



Kzz = 0.04 $m^2\ s^{-1}$ above mixing depth for neutral stability conditions

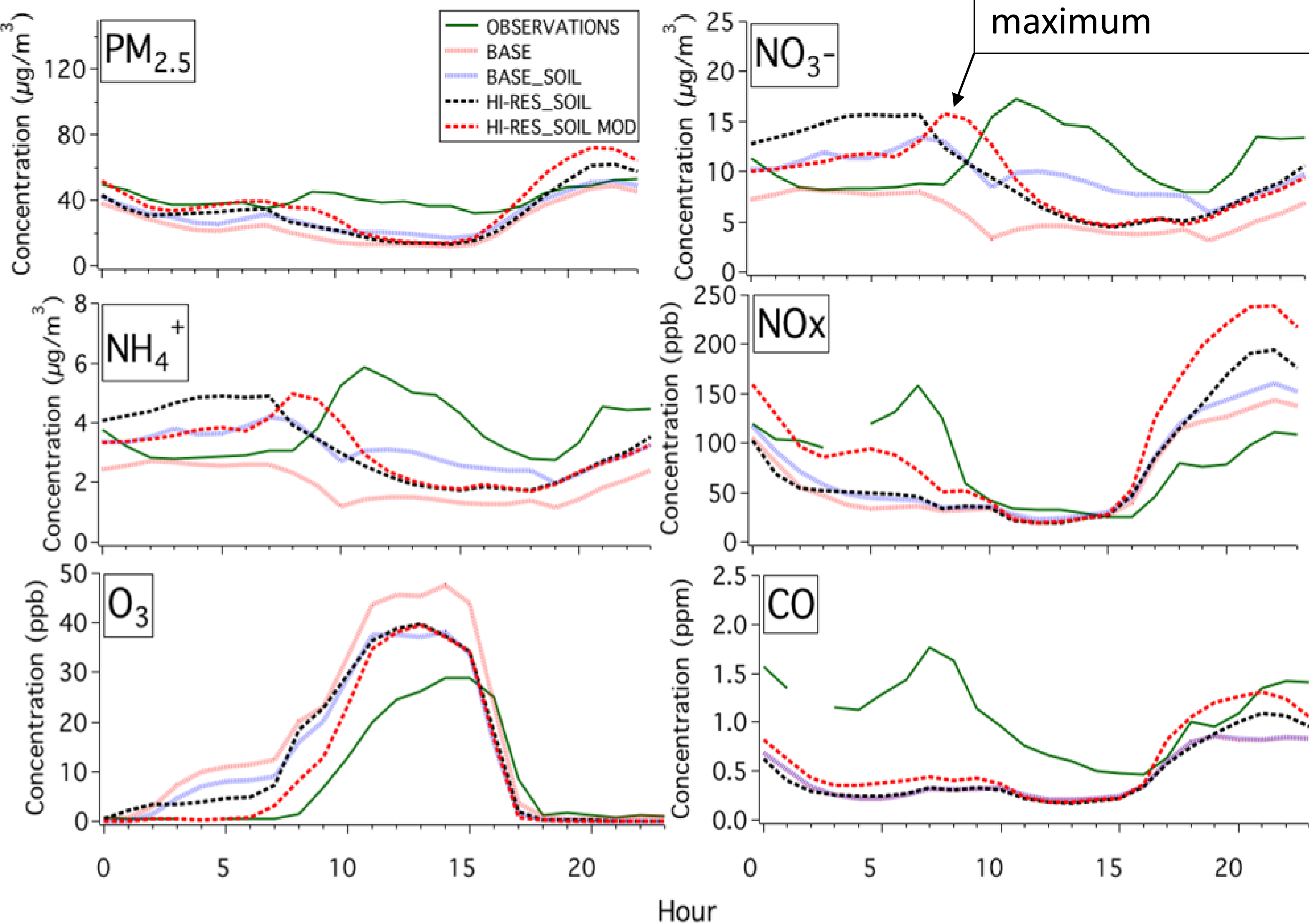
Kzz_{min} = 0.01 $m^2\ s^{-1}$ at night



Smooth transition between nighttime and daytime vertical profiles at hour 8am

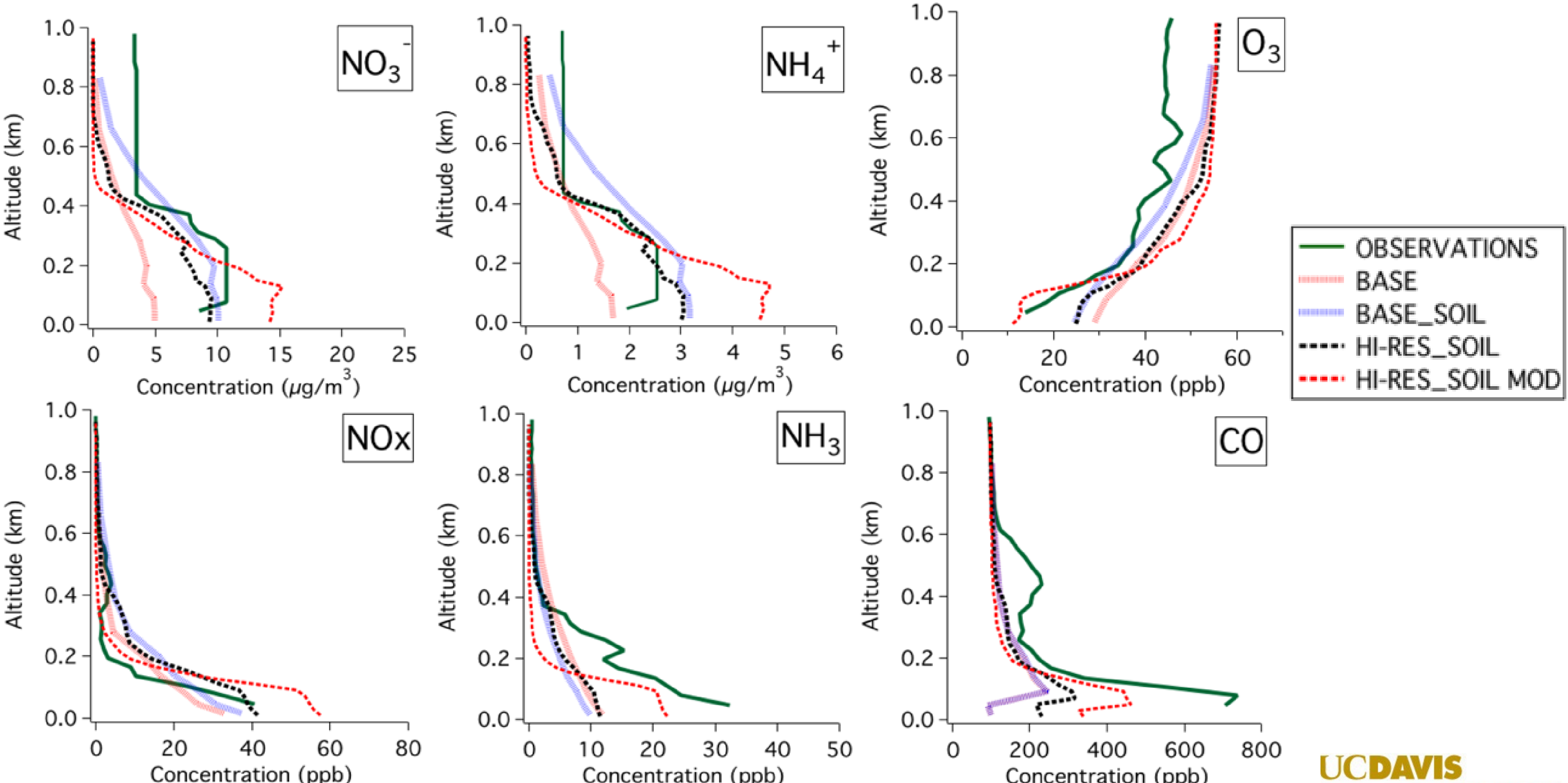
Objective 2: Investigate Vertical Profiles Predicted Time Series at Fresno on Jan 16-21, 2013

Model begins to capture morning maximum



UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Objective 2: Investigate Vertical Profiles Predicted Profiles at Fresno on Jan 18, 20-21, 2013 (10am)



UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC

Conclusions

- Total NOy concentrations are under-predicted in the SJV
  - Bias becomes more severe with years past 2010
  - Trends suggest a missing emissions source that becomes more important as NOx emissions from mobile sources decrease

- Candidate soil NOx emissions in the SJV
  - Strongly increase predicted NOy concentrations in rural areas
  - Contribute to ~20% of predicted NOy concentrations in urban locations of Fresno and Bakersfield

- Candidate soil NOx emissions in Jan 2010, 2013, and 2015 were efficiently converted to particulate nitrate due to favorable mixing ratios with background O_3
  - Future evaluations of NOx emissions sources should account for nitrate conversion efficiency

Conclusions Continued

- Candidate soil NOx emissions in Jul 2010, 2013, and 2015 improved overall predictions of O_3 and NOx
  - O_3 concentrations decreased in rural locations and slightly increased in urban locations at the edges of the SJV
- Candidate soil NOx emissions in Jan-Feb 2013 improved the prediction of vertical profiles for NOx, particulate nitrate, particulate ammonium ion, and O_3
  - High vertical resolution calculations can start to resolve nocturnal residual layers leading to improved predictions for diurnal profiles at the surface
- Candidate soil NOx emissions in Jan 2010, 2013, and 2015 help correct an under-prediction in particulate nitrate, but do not explain year-to-year variation
- Currently tested candidate soil NOx emissions did not account for year-to-year variations in temperature, precipitation, and fertilizer application rates

UCDAVIS
CIVIL AND ENVIRONMENTAL
ENGINEERING & AQRC

Future Measurements Needed

- Long term measurements needed in the rural portions of the SJV to evaluate the plausibility of candidate soil NOx emissions
- Seasonal and diurnal measurements needed to better characterize candidate soil NOx emissions
- Vertical profiles needed over urban and rural areas between 50-300 m in elevation from 4am-8am in order to better understand nitrate formation in nocturnal layers
  - NOy species, oxidants
  - SOA and SOA precursors

Acknowledgements

- California Air Resources Board Research Division # 15-301
- California Air Resources Board Air Quality Planning and Science Division # 14-753
- William Vance (CARB Project Manager)
- Jeremy Avise, James Chen, Dazhong Yin (CARB AQPSD)

UCDAVIS
CIVIL AND ENVIRONMENTAL ENGINEERING & AQRC