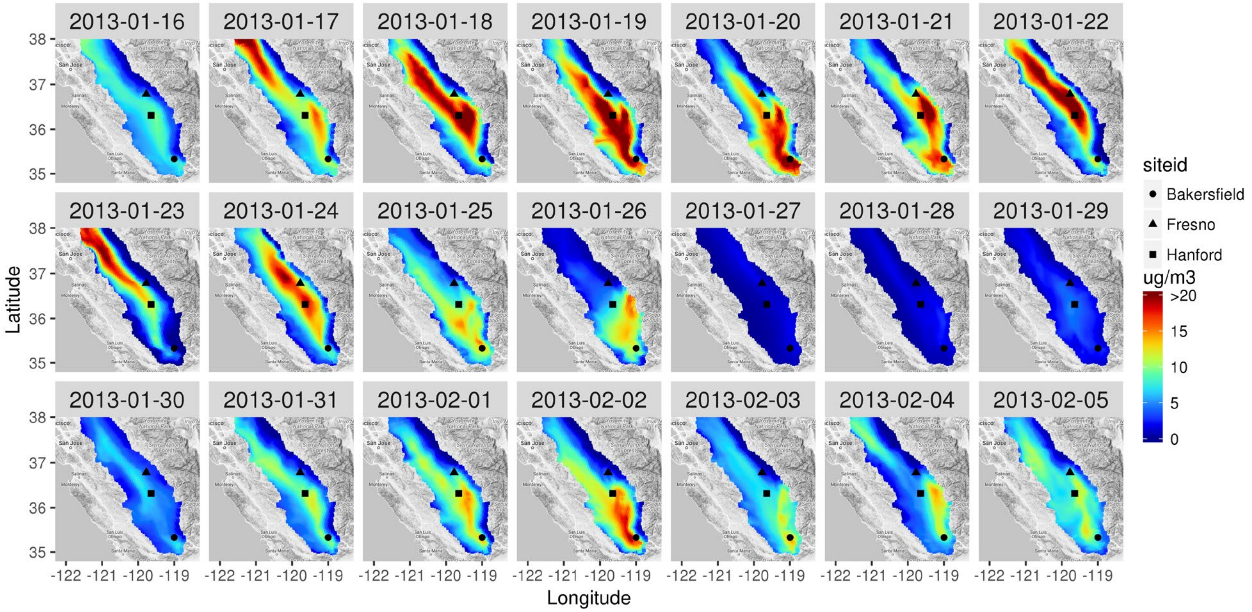
Modeling NH_4NO_3 during the 2013 SJV DISCOVER-AQ Campaign: Lessons Learned for AQUARIUS

Fine Particle Nitrate



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Particulate Matter in SJV

2017 State of the Air Report, American Lung Association

Short-Term $PM_{2.5}$ (24-hour)

Rank*	Metropolitan Statistical Area
1	Bakersfield, CA
2	Visalia-Porterville-Hanford, CA
3	Fresno-Madera, CA
4	Modesto-Merced, CA

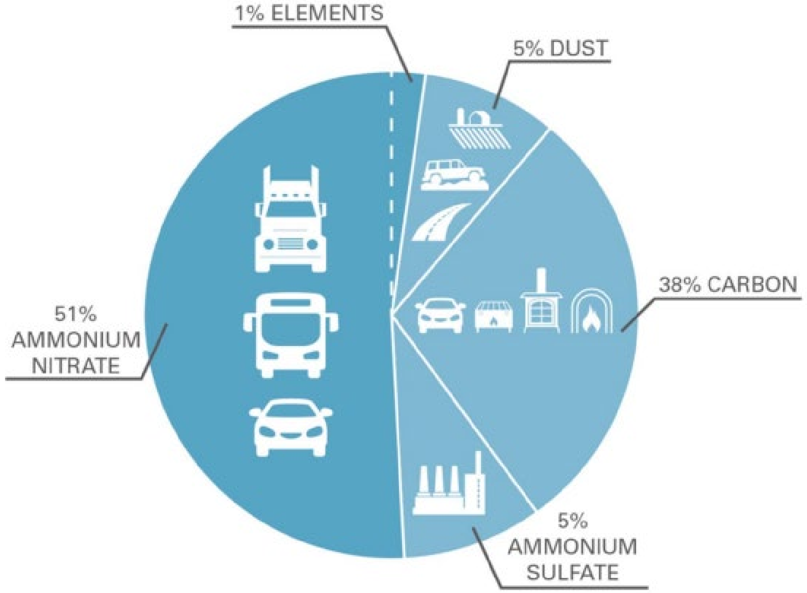
Long-Term $PM_{2.5}$ (Annual)

Rank*	Metropolitan Statistical Area
1	Visalia-Porterville-Hanford, CA
2	Bakersfield, CA
3	Fresno-Madera, CA
4	San Jose-San Francisco-Oakland, CA
5	Los Angeles-Long Beach, CA
6	Modesto-Merced, CA

*Blue: SJV

http://www.lung.org/assets/documents/healthy-air/state-of-the-air/state-of-the-air-2017.pdf

Peak $PM_{2.5}$ at Bakersfield



http://www.valleyair.org/pmplans/documents/2017/09-26-17/presentation.pdf

- SJV experiences high $PM_{2.5}$ during stagnant, cool, and humid meteorological conditions that occur episodically during winter
- NH_4NO_3 makes up about 50% of $PM_{2.5}$ during major wintertime $PM_{2.5}$ episodes

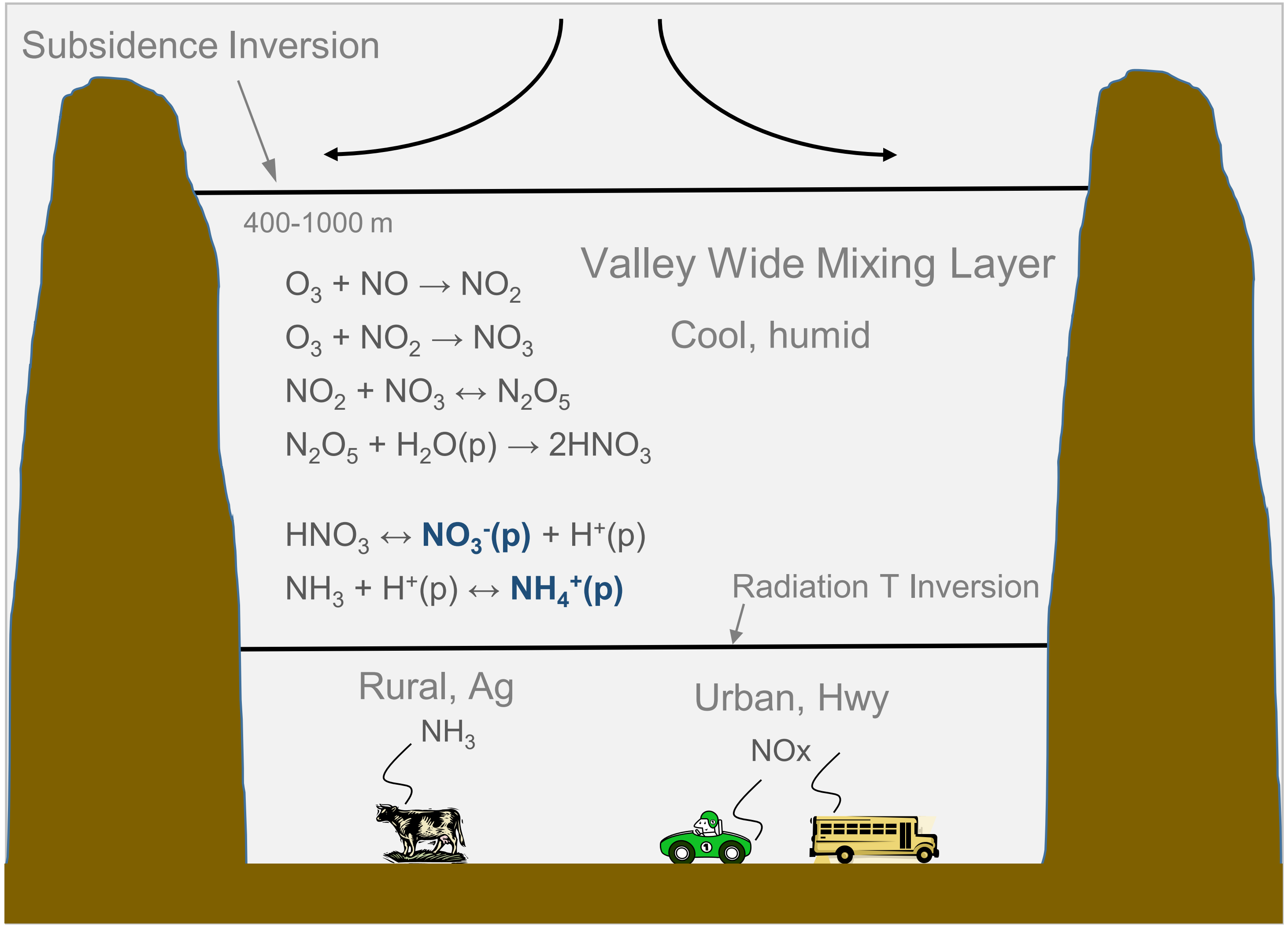
Overview

- Due to the high concentrations of $PM_{2.5}$, understanding NH_4NO_3 formation in SJV is important for NAAQS implementation, risk assessments, and cost-benefit analysis
- The NASA DISCOVER-AQ* field campaign in January and February 2013 provides a rich dataset for characterizing NH_4NO_3 during wintertime $PM_{2.5}$ episodes in SJV
- Air quality modeling (CMAQv5.1) was conducted for the DISCOVER-AQ campaign and used in combination with the field measurements to investigate NH_4NO_3 formation in SJV (Kelly et al., 2018)**
- Here, we summarize results for the SJV DISCOVER-AQ modeling study that may provide insights to inform planning for the AQUARIUS campaign

*DISCOVER-AQ: Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html

**Kelly et al. (2018) Modeling NH_4NO_3 over the San Joaquin Valley during the 2013 DISCOVER-AQ campaign. Journal of Geophysical Research: Atmospheres, 123, 4727–4745. https://doi.org/10.1029/2018JD028290

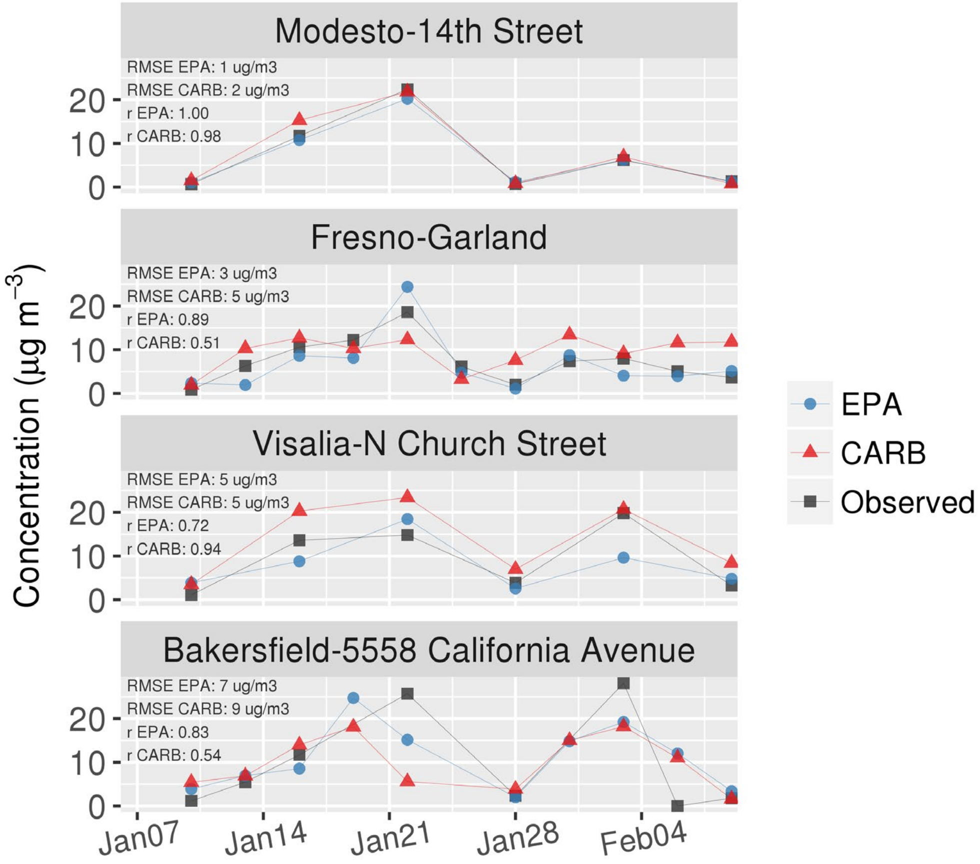
Conceptual Model for NH_4NO_3 Episode: Nighttime



- The conceptual model of nighttime nitrate formation is based on the 2000/2001California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS)*
- Roughly half of nitrate production in SJV is estimated to be from the nighttime pathway in a well-mixed residual layer
- **Do aspects of the conceptual model need to be refined (e.g., valley-wide mixing, soil NOx, effects of drought and NOx reductions)?**

*Herner, Kleeman et al. (2005 JAWMA, 2006 AS&T); Watson and Chow (2002) Atmos. Environ.

Daily Average Nitrate in SJV



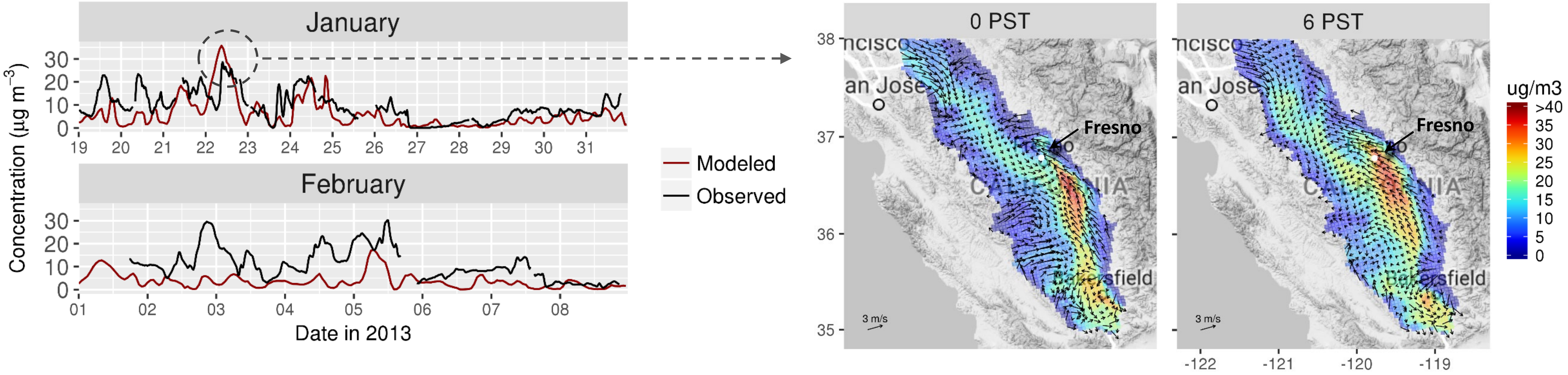
Overall, existing inventories and models capture daily average nitrate at monitoring sites reasonably well

Better model-obs agreement in the north (e.g., Modesto) than the south (e.g., Bakersfield), near convergence of mountain ranges

How do meteorological conditions vary within SJV (e.g. from north to south) and influence the distribution of nitrate throughout the valley?

CARB Modeling: James Chen, Jeremy Avise, Ajith Kaduwela

Hourly Nitrate in Fresno

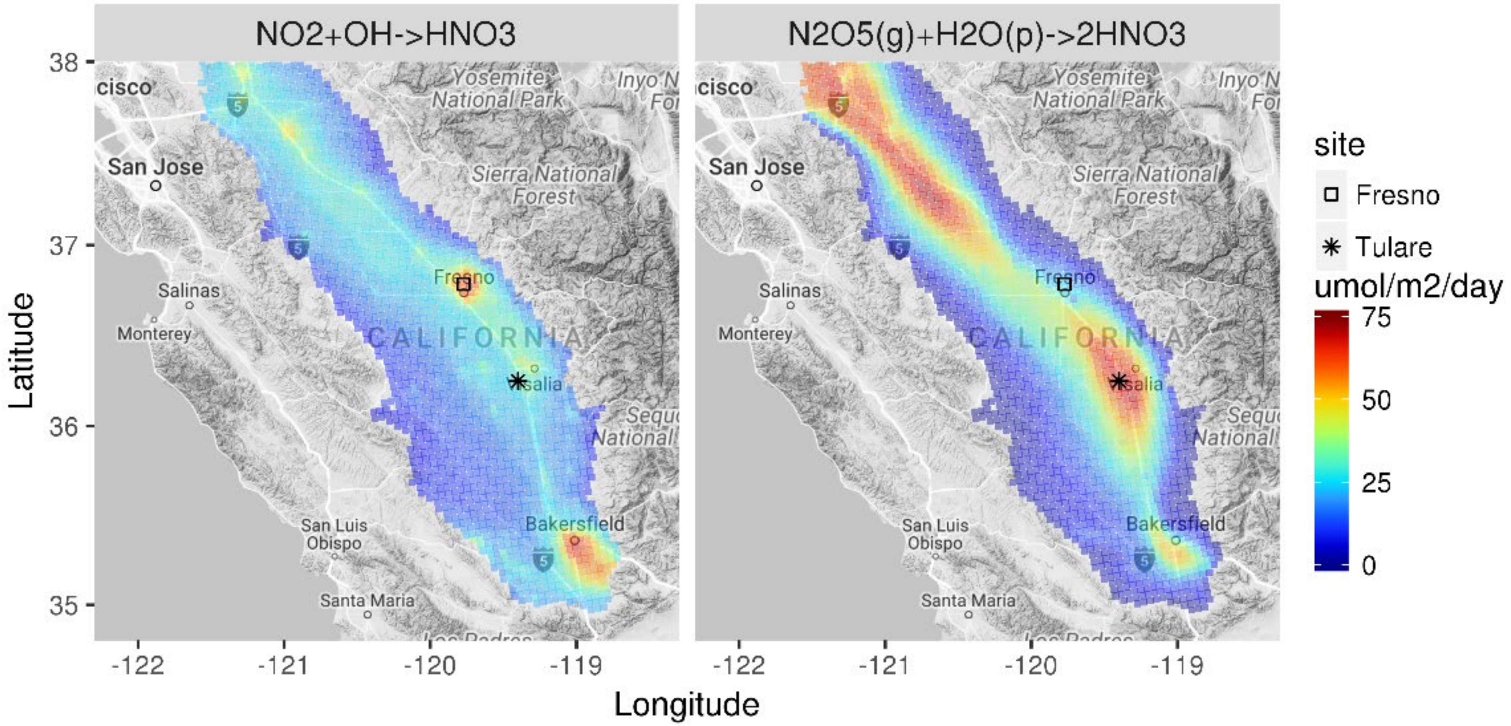


- The model captures observed nitrate episodes reasonably well in late January
- The peak in modeled nitrate on 22 January is due to transport of nitrate from the south, but observation-based studies suggest that elevated nitrate in Fresno is due to mixing of nitrate formed aloft to the surface in the morning
- **An improved understanding of the influence of rural-urban transport of nitrate (and other pollutants) would be valuable**

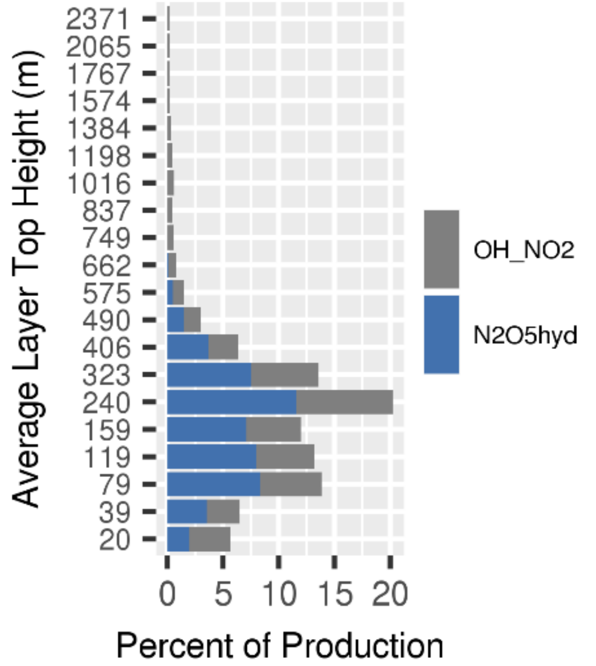
PILS measurements: Caroline Parworth, Qi Zhang (UC-Davis)

HNO_3 Production in SJV: 17-22 January

Vertically Integrated HNO_3 Production

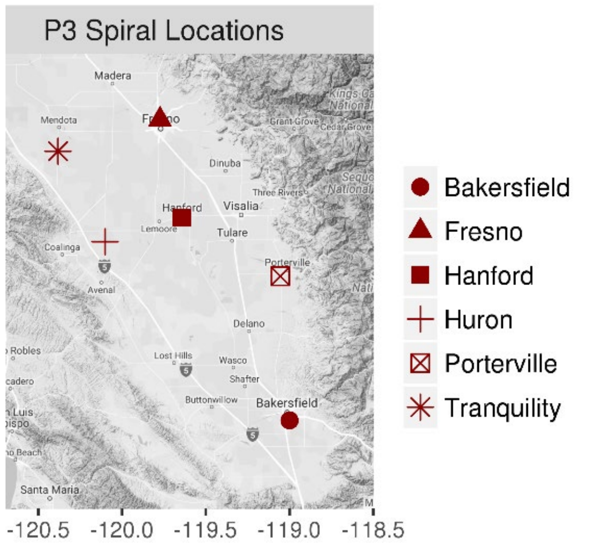


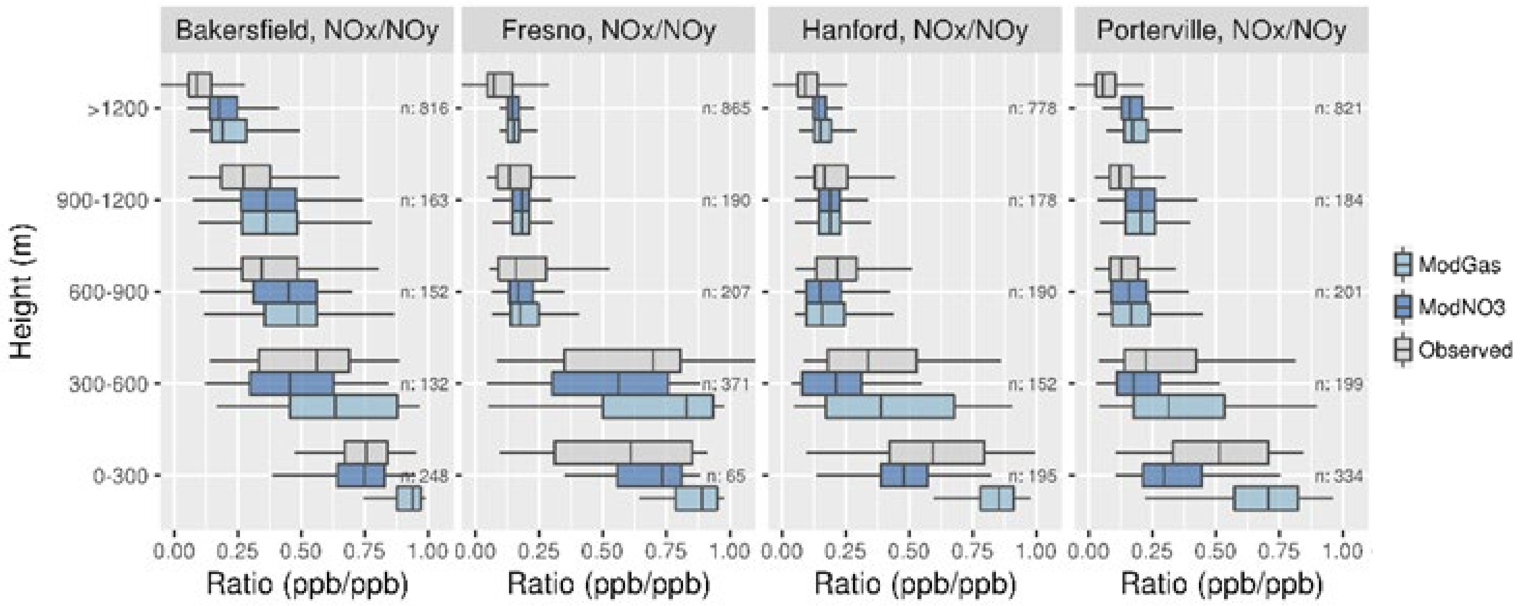
Spatially Integrated HNO_3 Production



- The daytime HNO_3 production pathway contributes about 46% to total production and the nighttime pathway 54%
- The daytime pathway is projected to become more important as NOx concentrations decrease
- **New measurements (e.g, NO_2, O_3, NO_3, N_2O_5) in the nighttime residual layer are needed to constrain spatial patterns and magnitudes of nitrate production (no nighttime flights during D-AQ)**

Oxidation in SJV

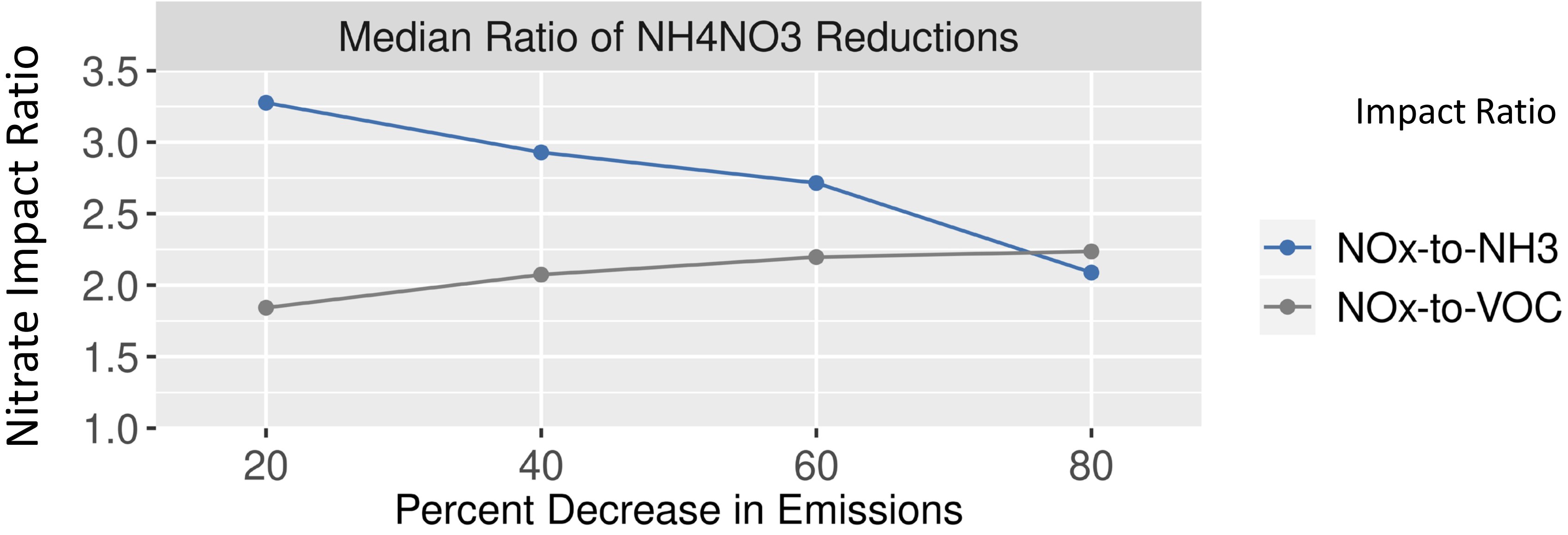




- Uncertainty in the NOx/NOy ratio due to uncertainty in the fraction of particle nitrate sampled by the instrument hampered our evaluation of modeled NOx oxidation
- HCHO and O_3 are underestimated by the model (appendix)
- **Measurements/analyses are needed to better constrain NOy speciation, oxidant abundance (local O_x production and transported O_3), and radical budgets**

NCAR NOy measurements: Andrew Weinheimer

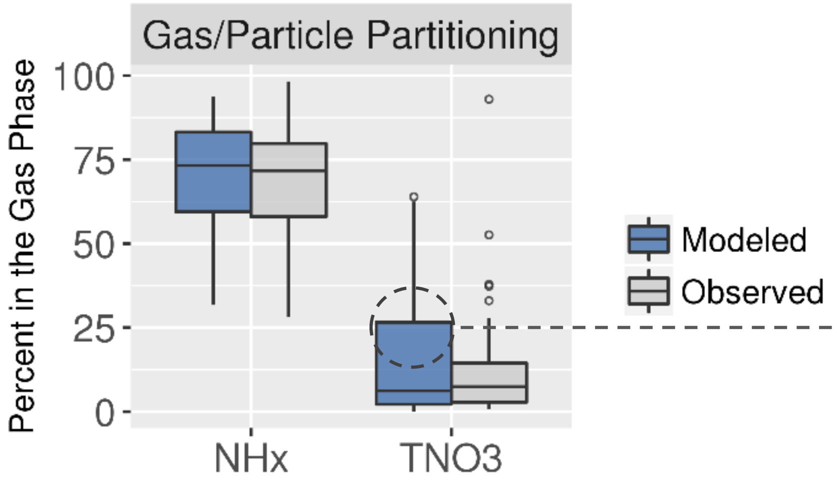
Relative Response of NH_4NO_3 to Precursor Reductions



$$\text{Impact Ratio} = \frac{(\Delta NH_4NO_3)_{NO_x}}{(\Delta NH_4NO_3)_{NH_3\ or\ VOC}}$$

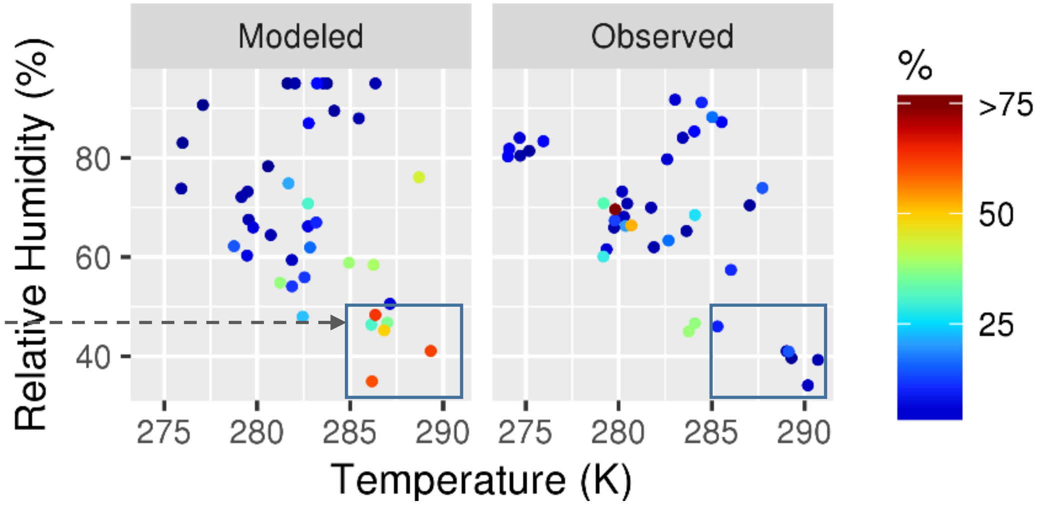
- Sensitivity simulations were performed with reductions in NOx, NH_3, and VOC emissions
- NH_4NO_3 concentrations are most responsive to NOx emissions in the model
- **Additional characterization of precursor levels, oxidant abundance, and radical budgets would be valuable for interpreting results on NH_4NO_3 responsiveness to emissions**

Inorganic Aerosol Partitioning at Fresno



NHx: $NH_3 + NH_4^+$ and TNO3: $HNO_3 + NO_3^-$

Percent of TNO3 in Gas Phase



- Most of NHx is in the gas phase and most of TNO3 is in the particle phase in the model and ambient suggesting that HNO_3 is the limiting NH_4NO_3 precursor
- However, partitioning of TNO3 to the gas phase is overestimated at high temperature and low relative humidity conditions in afternoon

Ground sites with comprehensive datasets for thermodynamic and other analyses are important complements to "snapshots" provided by flights

Obs: Caroline Parworth, Qi Zhang (UC-Davis)

Summary of Future Needs for NH_4NO_3 in SJV

- Measurements of spatial patterns of species concentrations relevant to nitrate production in the nighttime residual layer (e.g., NO_2, O_3, NO_3, N_2O_5)
- Characterization of chemical indicators, oxidant abundance (local O_x production and transported O_3), and radical budgets to inform model evaluation and understanding of nitrate response to precursor reductions
- Characterization of variations in meteorology throughout the basin (e.g., north-to-south) and within-basin transport of nitrate and other pollutants
- Continuous comprehensive ground measurements to complement "snapshots" from flights
- Synthesis of new information to refine, if necessary, the conceptual model of winter nitrate formation in SJV

Disclaimer

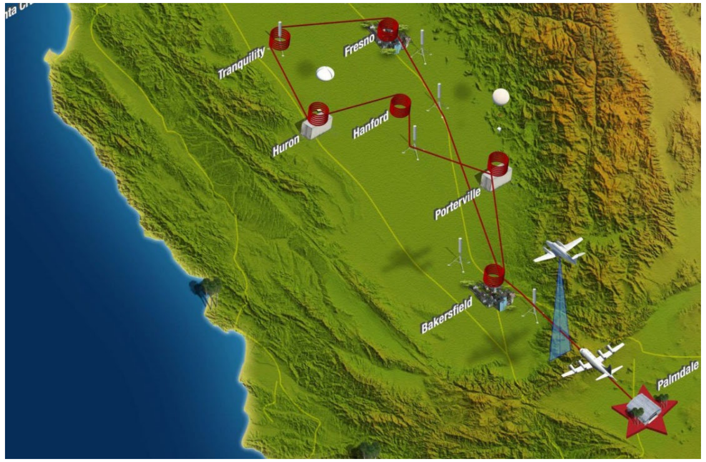
- The views in this presentation are those of the authors alone and do not necessarily reflect the policy of the U.S. Environmental Protection Agency.

Additional Slides

Methods

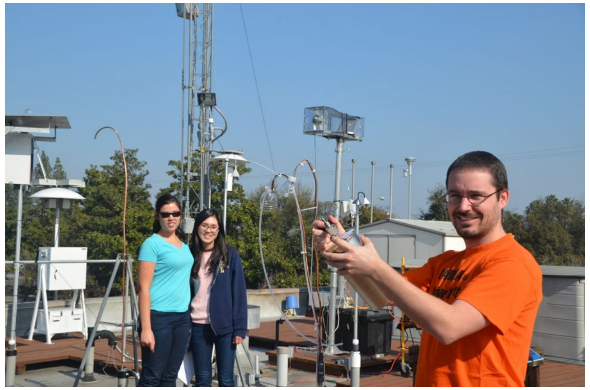
- Air Quality Modeling: Community Multiscale Air Quality (CMAQ) model version 5.1 (4-km resolution, 10 January – 15 February 2013)
- Measurements: NASA P-3B aircraft, Fresno ground site, and Princeton mobile laboratory

NASA P-3B Aircraft



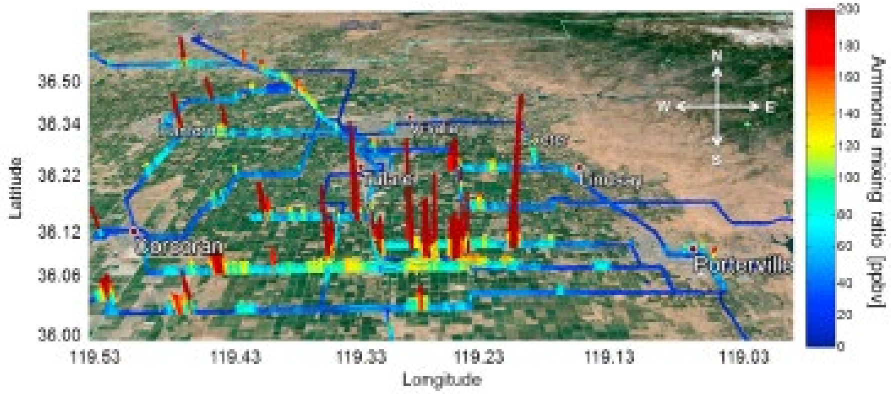
CMAQ Domain

Fresno Site (Qi Zhang)

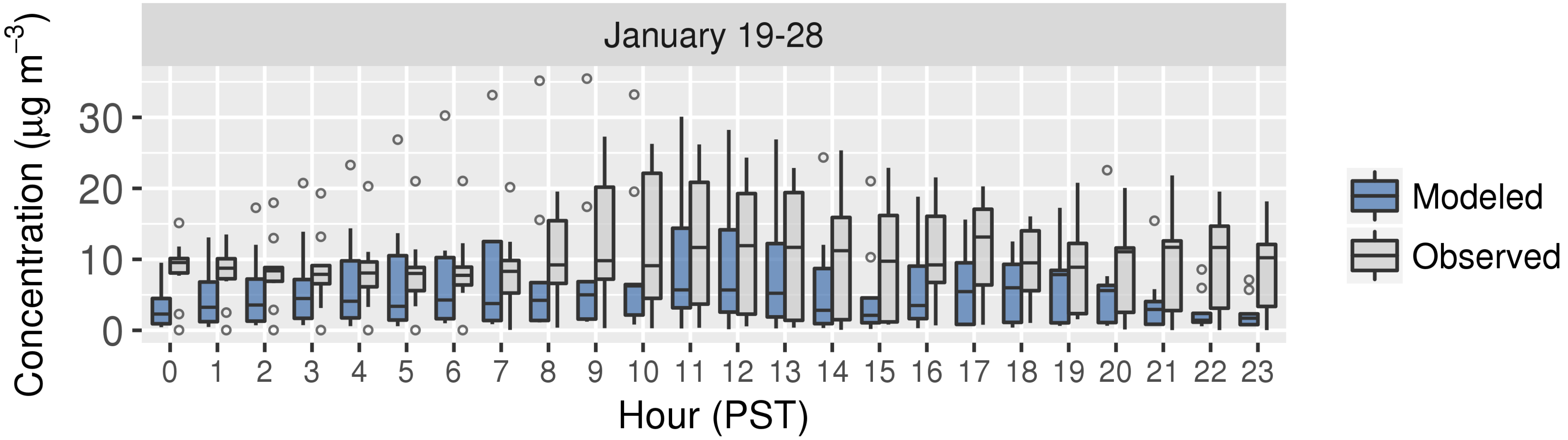


https://climate.nasa.gov/news/870/campaign-to-diagnose-air-quality-concludes-in-california/

Princeton Mobile Lab (Mark Zondlo)

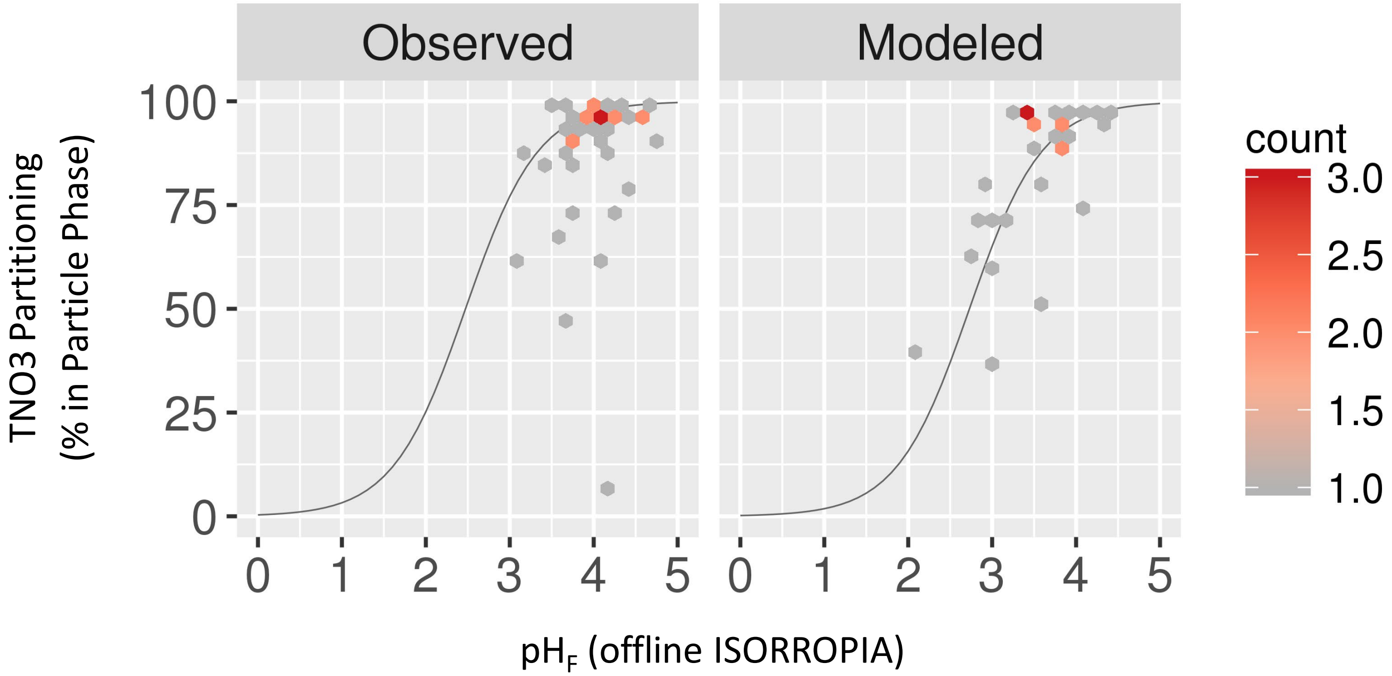


Hourly Distributions of Modeled and Measured NO_3^-



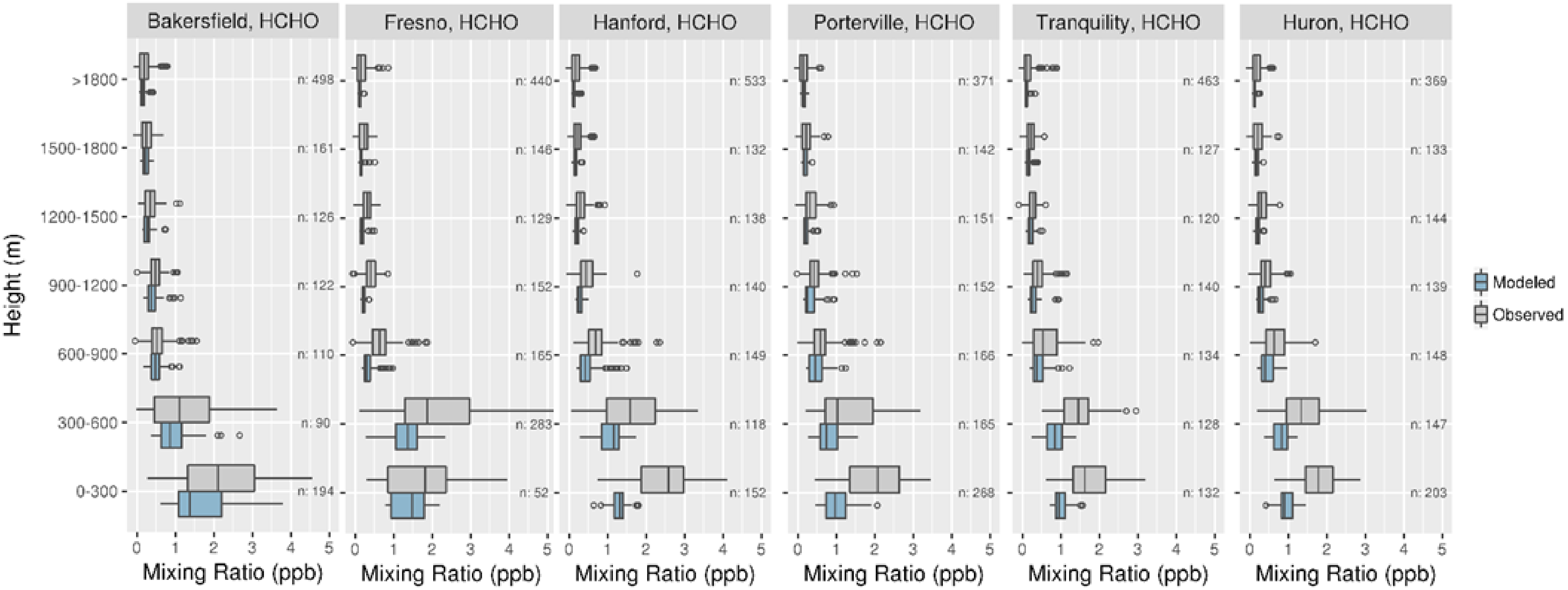
- Modeled NO_3^- concentrations decrease during afternoon (possibly due to gas-particle partitioning issues) whereas observations are relatively flat
- The measured NO_3^- increase in the morning (due to mixing of residual layer to the surface) is underestimated by the model, possibly due to issues with meteorological factors and/or vertical distributions of HNO_3 production

Gas-Particle Partitioning and pH_F at Fresno, SJV

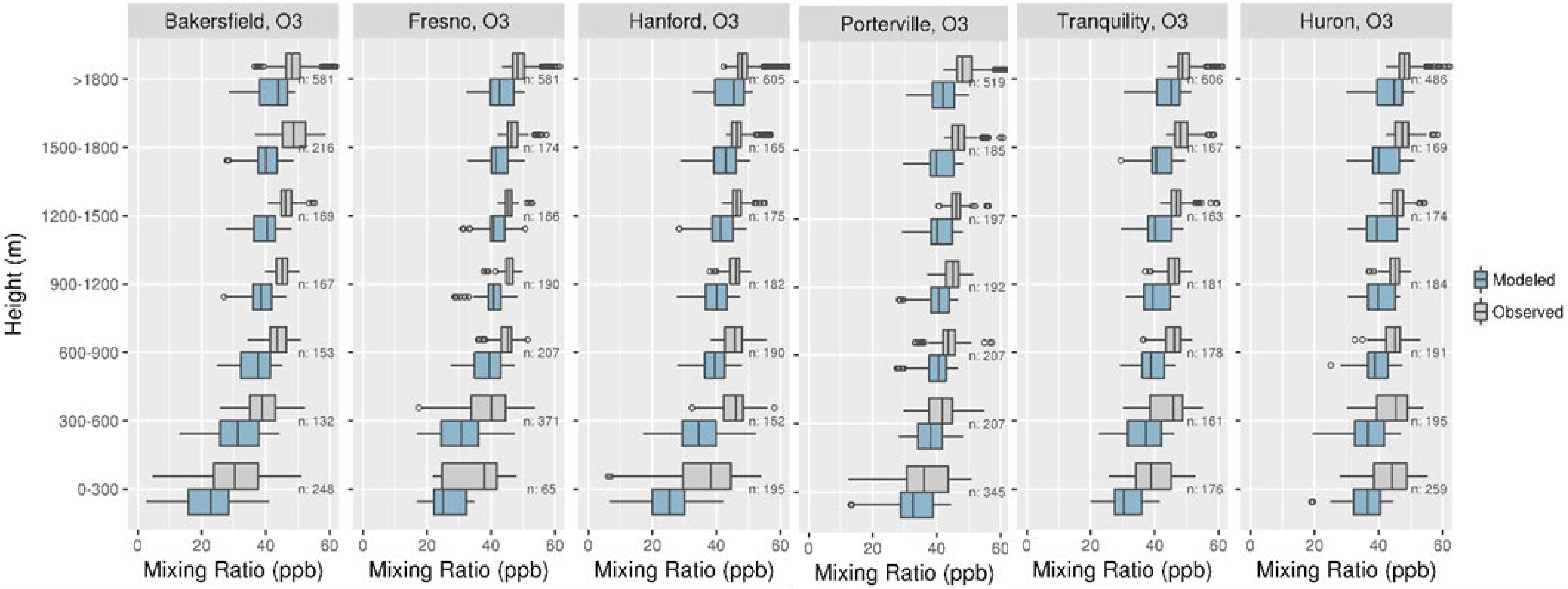


- Estimated median pH_F is 4.0 based on observations and 3.7 based on modeling
- Total nitrate partitioning is not very sensitive to pH_F (i.e., data are at the top of the S-curve)

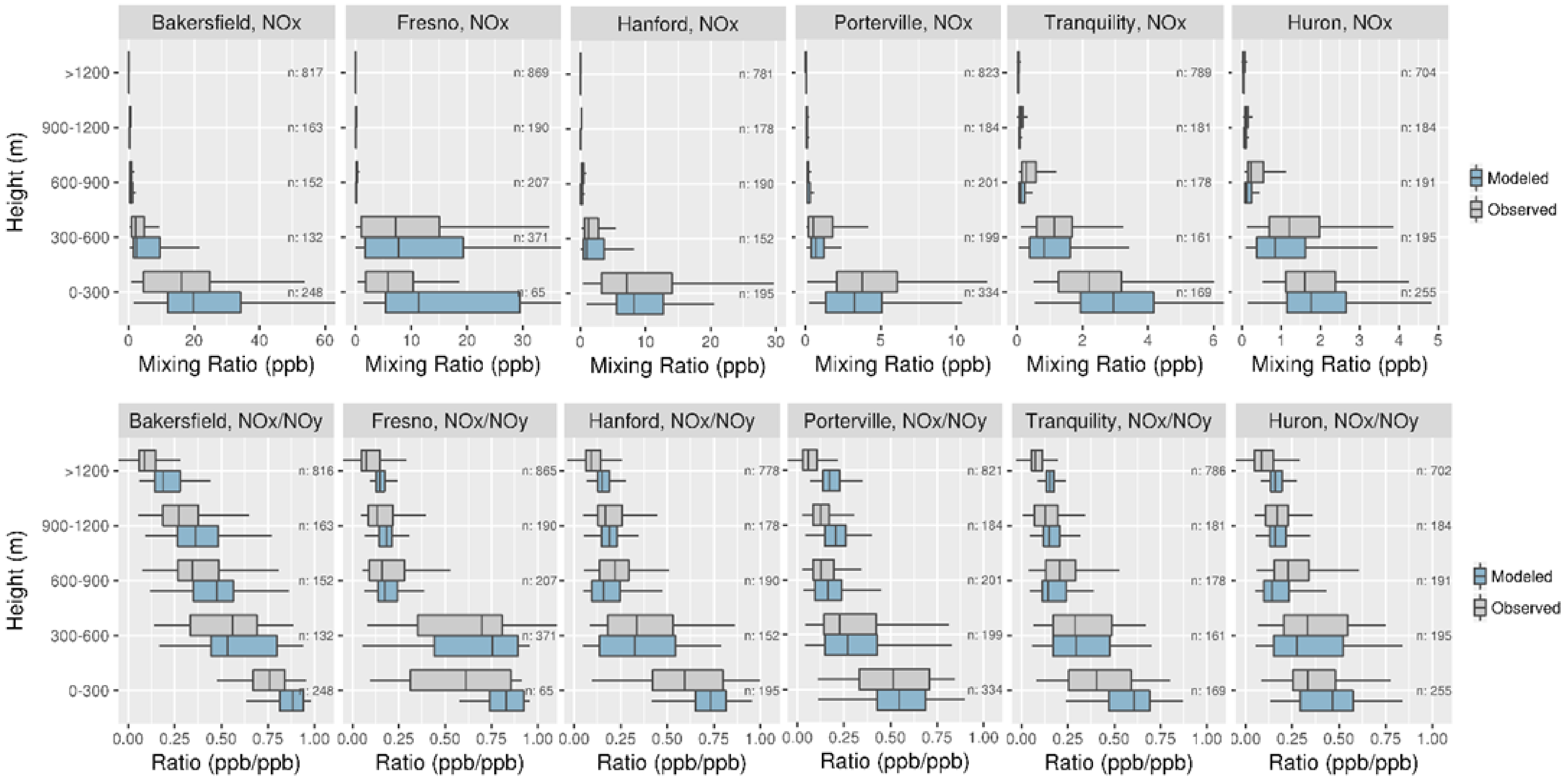
HCHO Along Aircraft Spirals



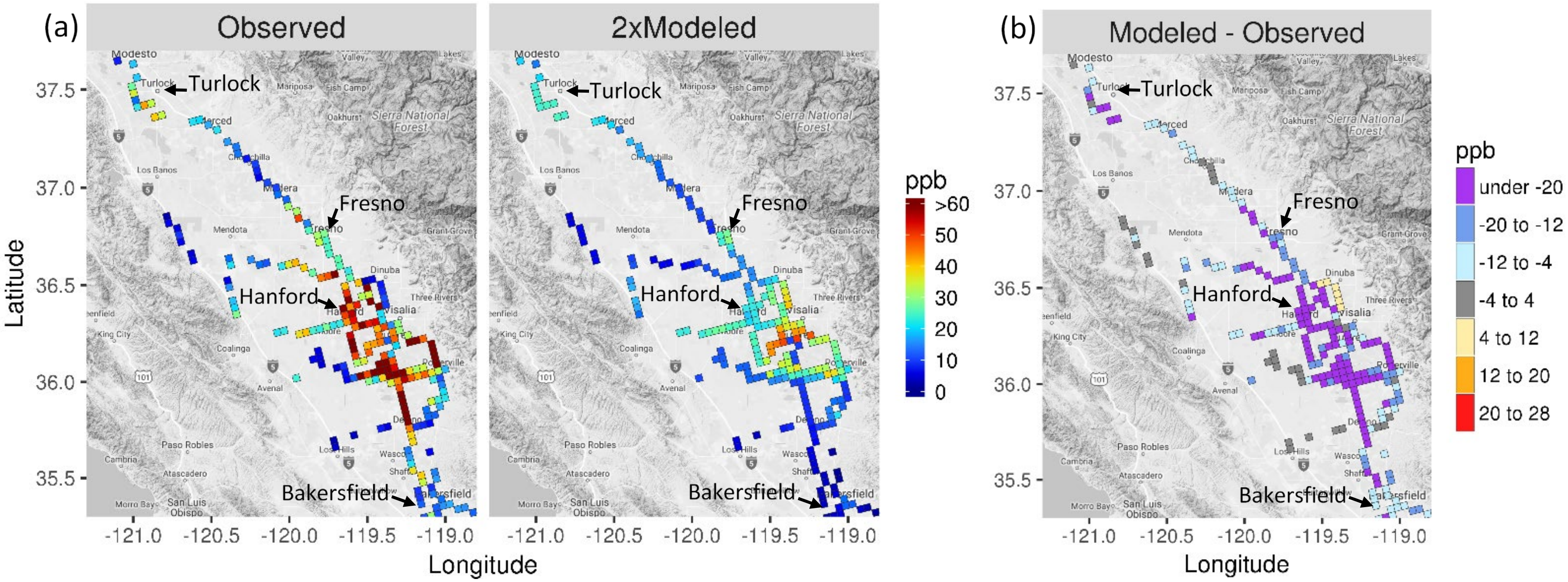
Ozone Along Aircraft Spirals



NOx and NOx/NOy Along Aircraft Spirals

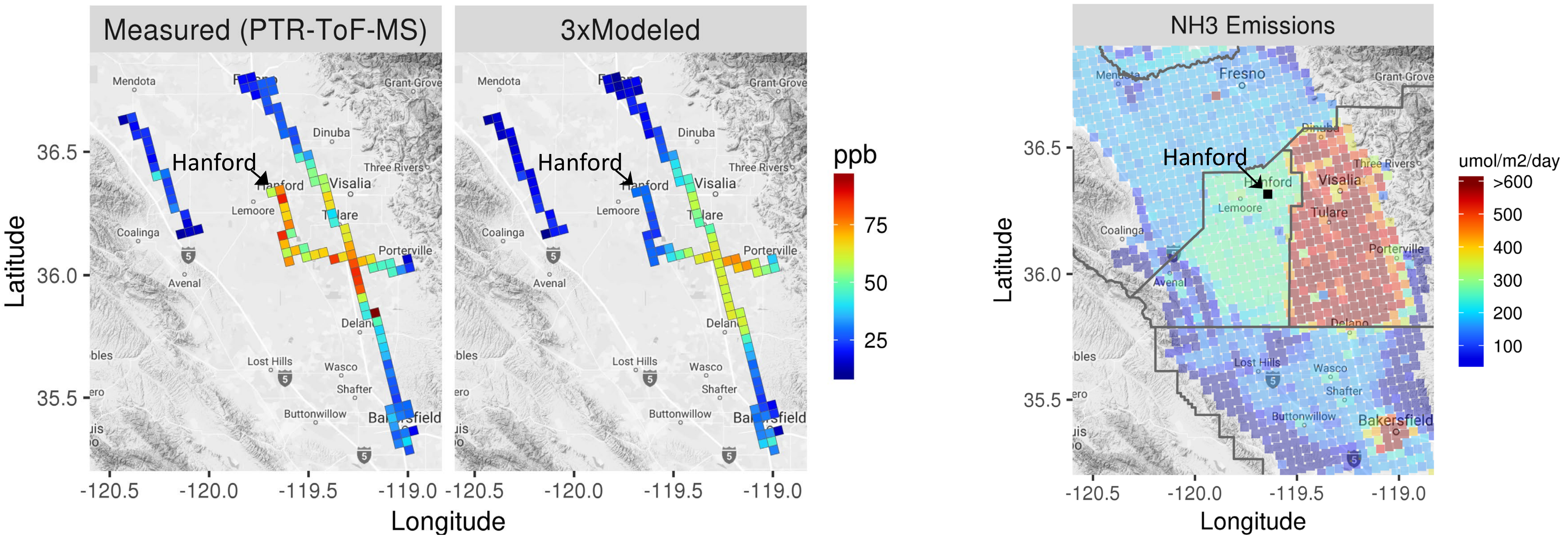


Spatial Evaluation of Ammonia Predictions: Model vs. Princeton Mobile Lab Measurements



NH_3 measurements: Mark Zondlo, David Miller, and Kang Sun (Princeton)

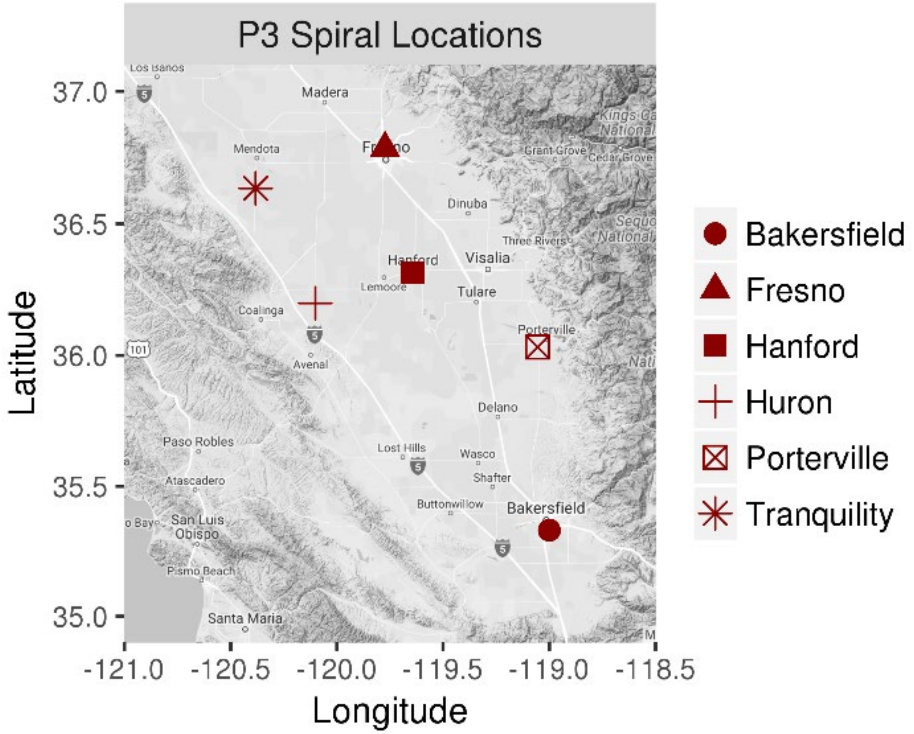
Spatial Evaluation of Ammonia Predictions: Model vs. NASA P-3B Measurements

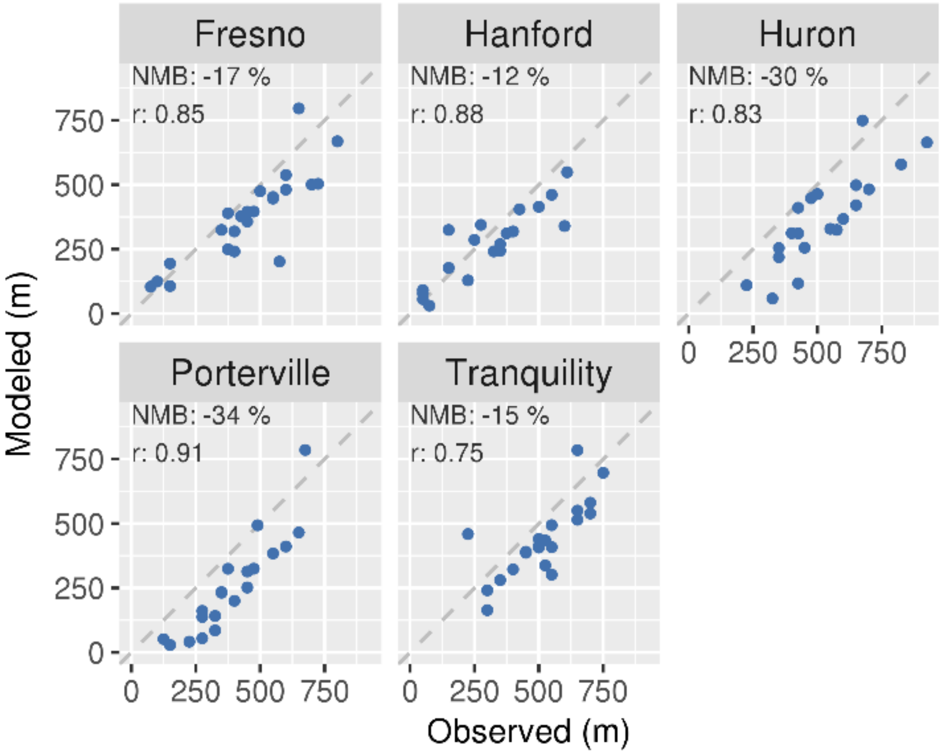


- The model generally predicts elevated NH_3 in the region with high measured NH_3, but predicted mixing ratios are too low
- Predictions are especially low near Hanford, which is just outside of the major emission region in Tulare County in the model (above, right)
- Note: nitrate is not very sensitive to NH_3 in the model (HNO_3-limited formation)

NH_3 measurements: Armin Wisthaler (University of Innsbruck)

P-3B Spiral Locations and PBL Height Estimates





- Daytime PBL heights may be slightly biased low during daytime (consistent with HSRL evaluation)

Observation-based PBL Heights from Jim Crawford (NASA)