

Photochemical Model Assessment of PM_{2.5} Ammonium Nitrate in California

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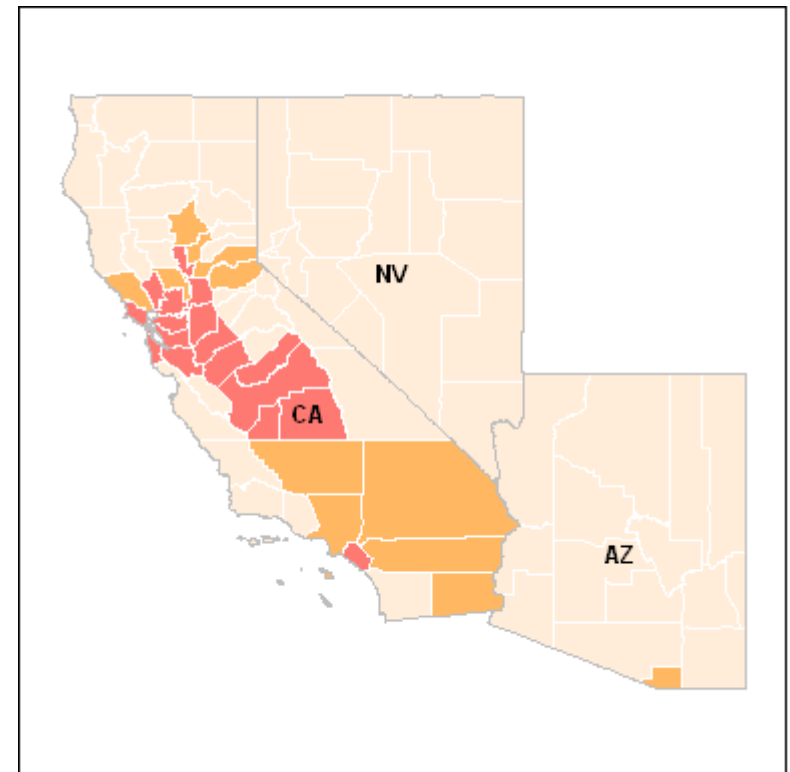
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California PM2.5

- Many nonattainment counties for the 24-hr PM2.5 NAAQS located in the central Valley of California
- Elevated 24-hr PM2.5 often composed of **ammonium nitrate** and **organic carbon** in this area



EPA Designation

- Attainment/Unclassifiable
- Nonattainment - Whole County
- Nonattainment - Partial County

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Background

MODELING SYSTEM

- Evaluate regulatory modeling system performance for PM_{2.5} in California
- MM5 meteorology
- SMOKE emissions modeling based emissions on 2005 NEI
- CMAQ v4.7 photochemical modeling
- Annual 2005 modeling of western U.S. with 12 km sized grid cells

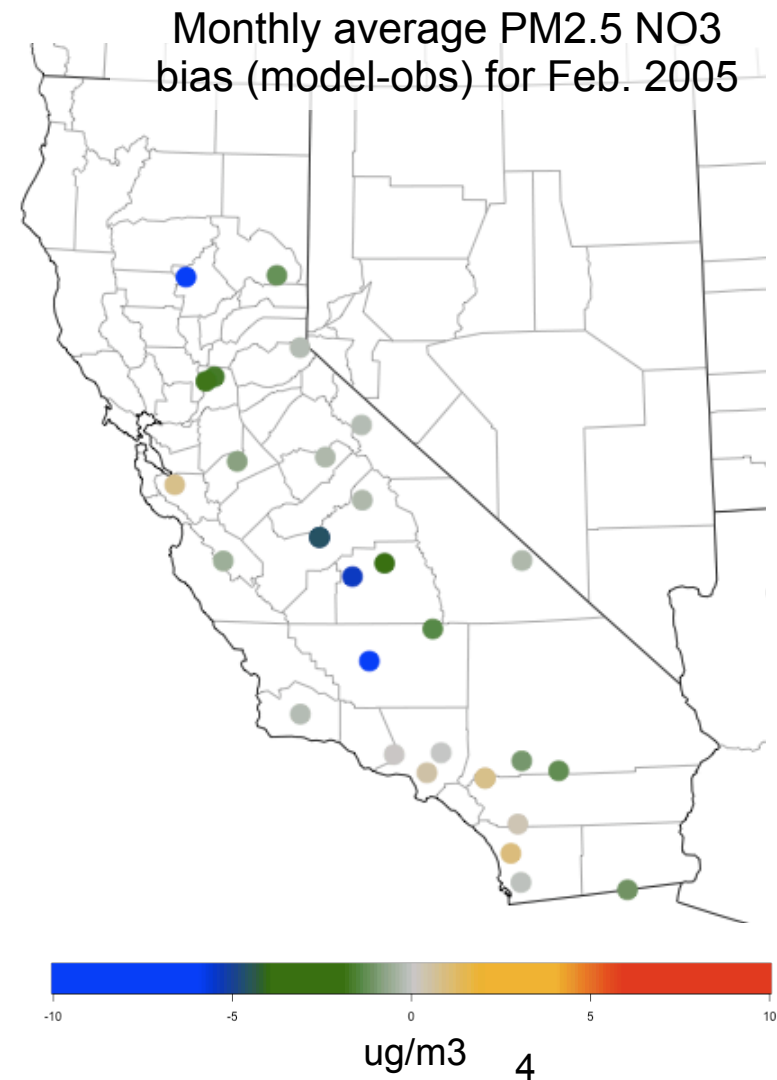
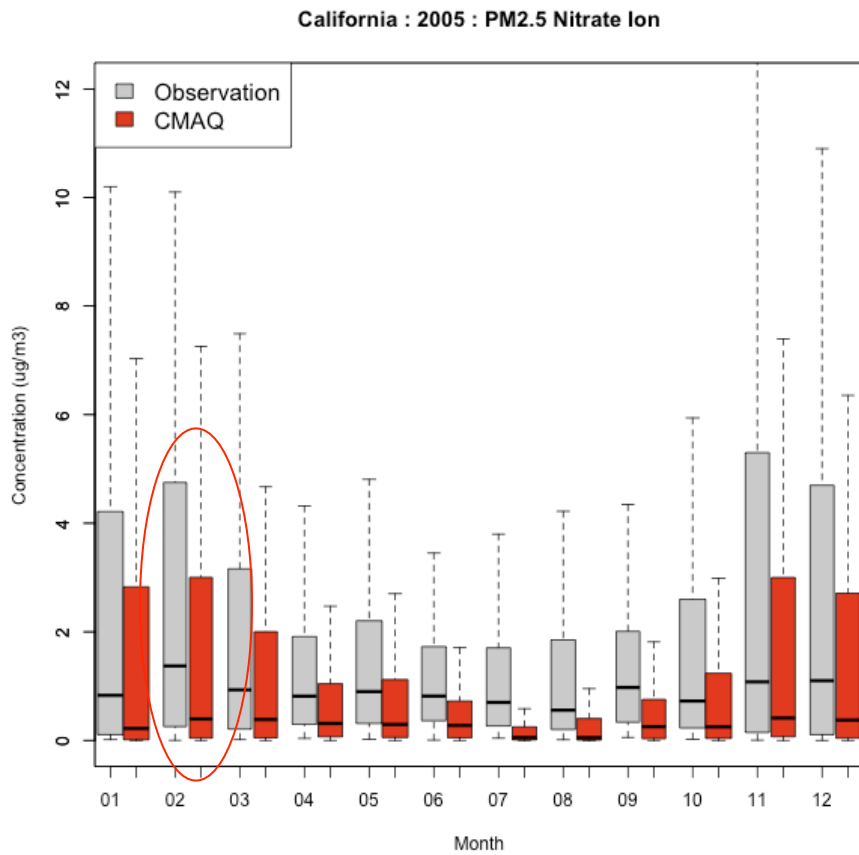
AMBIENT DATA

- 24-hr avg speciated PM_{2.5}: IMPROVE and CSN (STN,ESPN)
- Hourly PM_{2.5} nitrate ion & black carbon at Fresno
- Hourly surface meteorology: T, WS, WD, MR, Fog, Haze
- Upper air soundings at Hanford, CA

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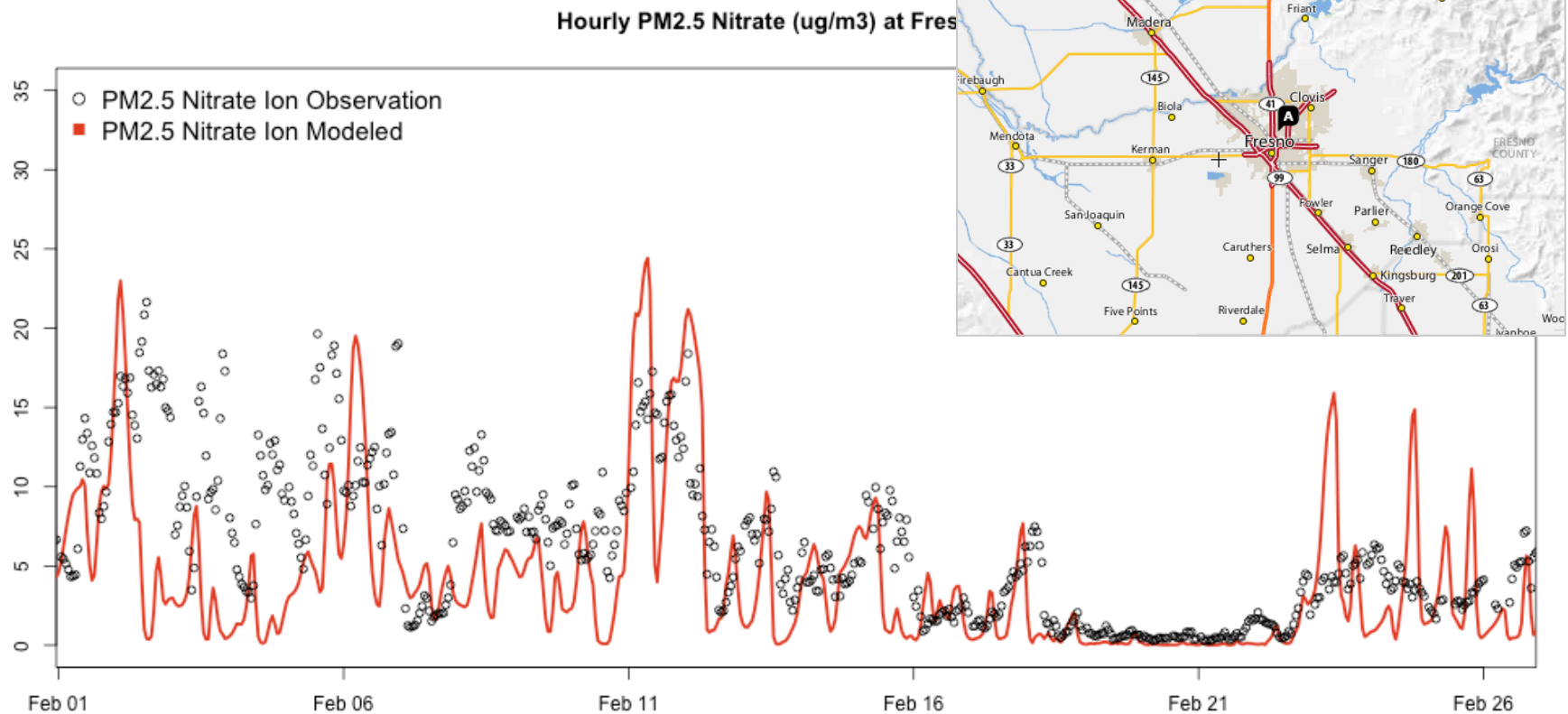
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Modeling system underpredicting PM2.5 nitrate ion in the winter in central California



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Hourly PM2.5 Nitrate at Fresno



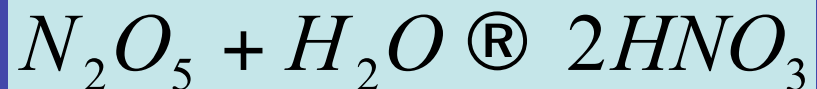
Possible Causes of Nitrate Bias

- Chemistry related issues
 - Formation of HNO_3 : chemistry(gas-phase, heterogeneous, cloud/fog) or NO_x emissions
 - Gas/particle partitioning: NH_4 emissions or met
- How well is the hourly meteorology characterized at Fresno
 - Temperature and relative humidity important for nitrate partitioning
 - Any clear connection between performance issues in meteorological variables and $\text{PM}_{2.5}$ performance problems?
- Transport/Dilution

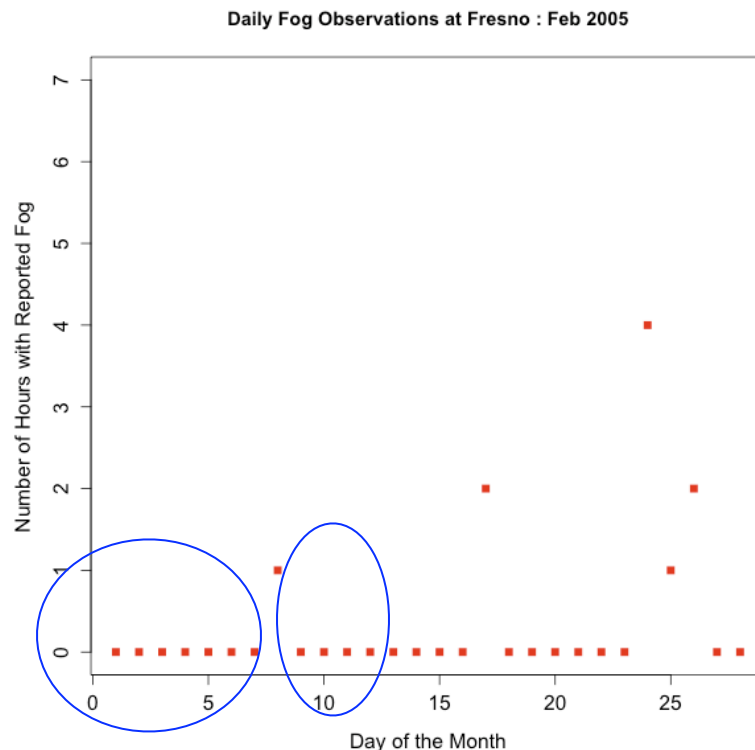
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HNO₃ Formation: chemistry



- CMAQ gas and heterogeneous chemistry already over-predict this chemistry
- This process also occurs in clouds/fog
 - Does model under-predict fog occurrences in SJV?
- Days with highest nitrate bias for this Fresno episode (Feb 1-5, 2005) did not have any reported fog



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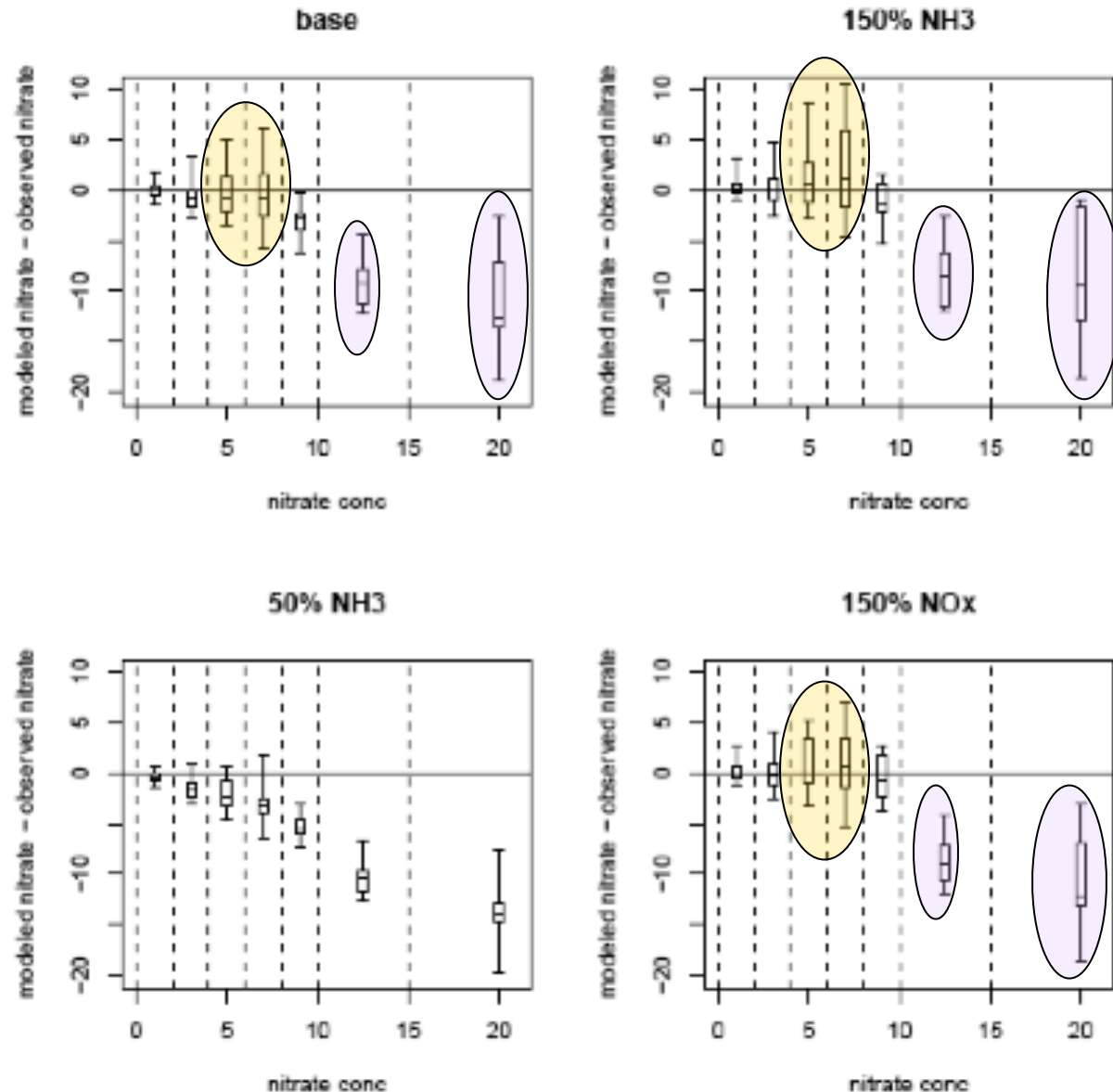
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Emissions: NH₃ and NO_x

- Can emissions inaccuracies explain these nitrate under-predictions?
- Modeling system currently applies a national ammonia emissions profile to California by month and hour of the day

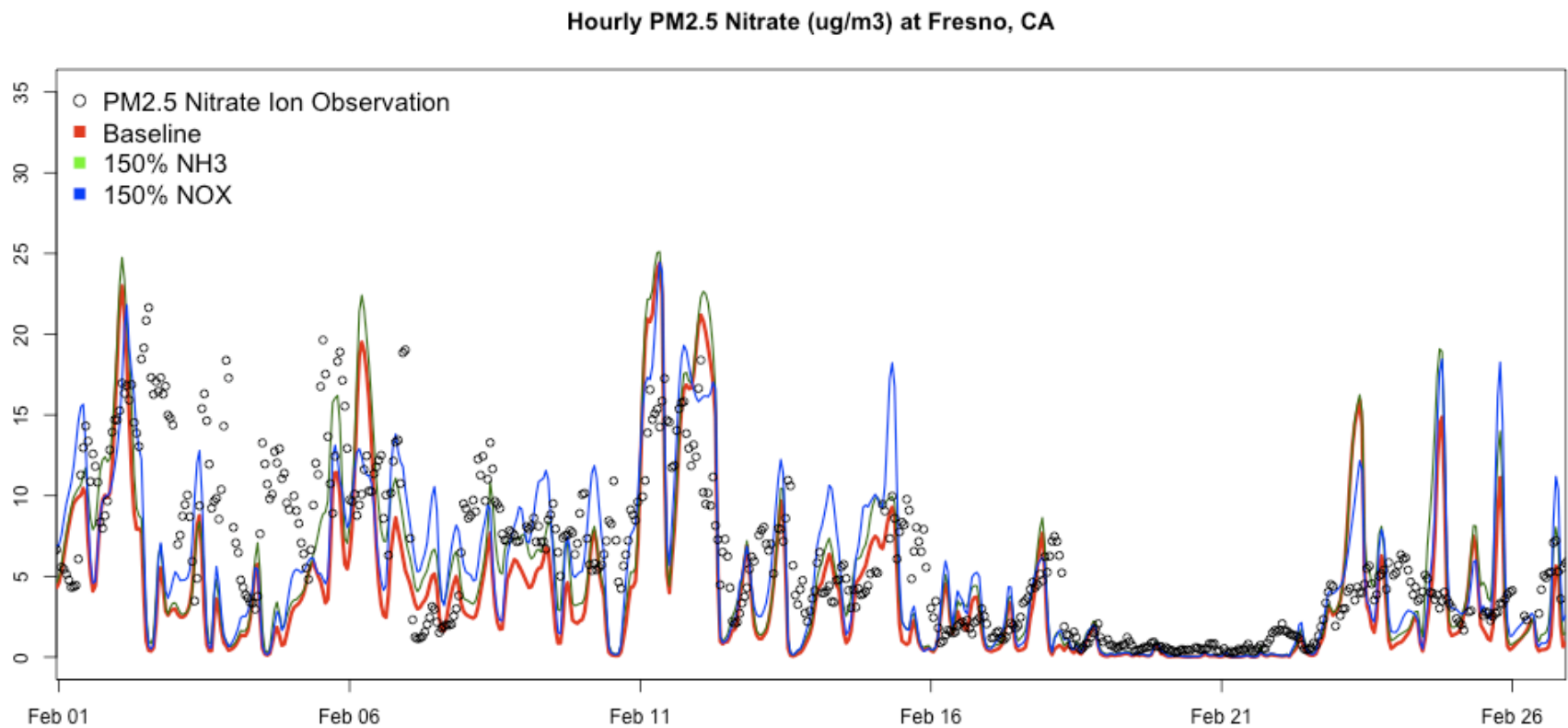
Emissions Sensitivities

- Sensitivity runs were performed in which NO_x and NH_3 emissions were increased by 50% across the board
- Increasing NH_3 and NO_x emissions does not significantly affect nitrate levels below $\sim 4 \text{ ug/m}^3$, but causes **over-predictions** in nitrate when concentrations are between 4-8 ug/m^3
- Increasing NH_3 and NO_x emissions by 50% is not enough to correct for **under-predictions** of high nitrate concentrations



PM2.5 Nitrate – Emissions Sensitivities

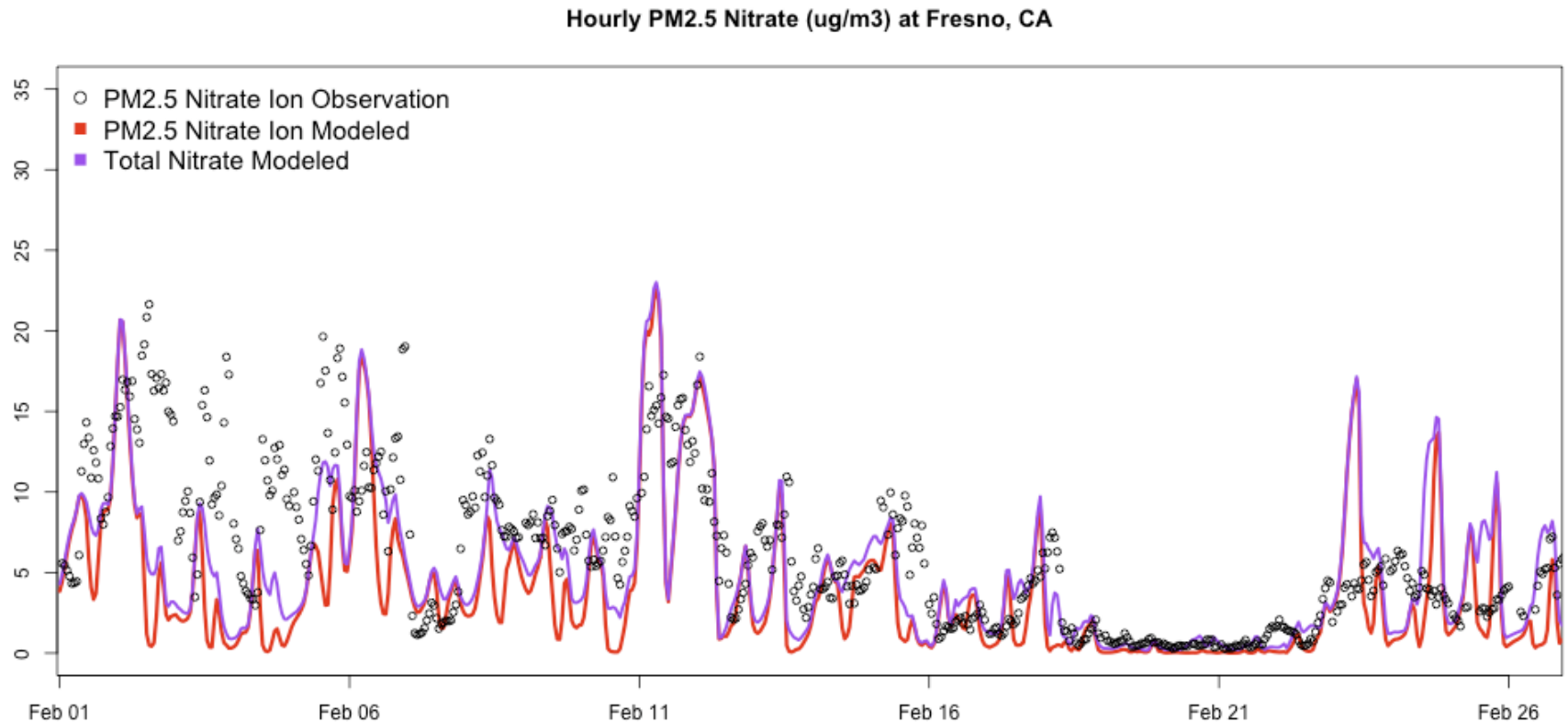
- Emissions adjustments do not substantively “improve” model performance of hourly PM2.5 nitrate ion



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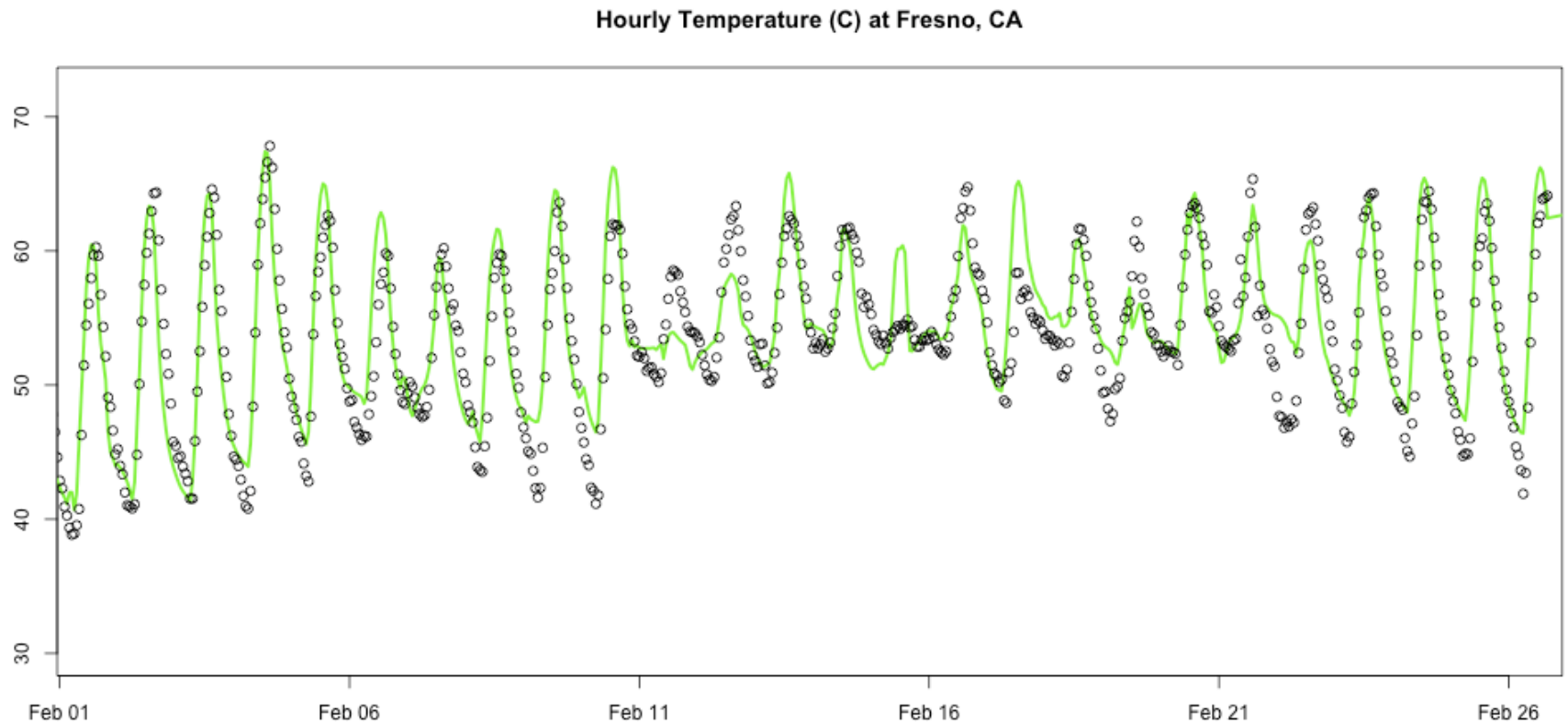
Hourly PM2.5 Nitrate at Fresno



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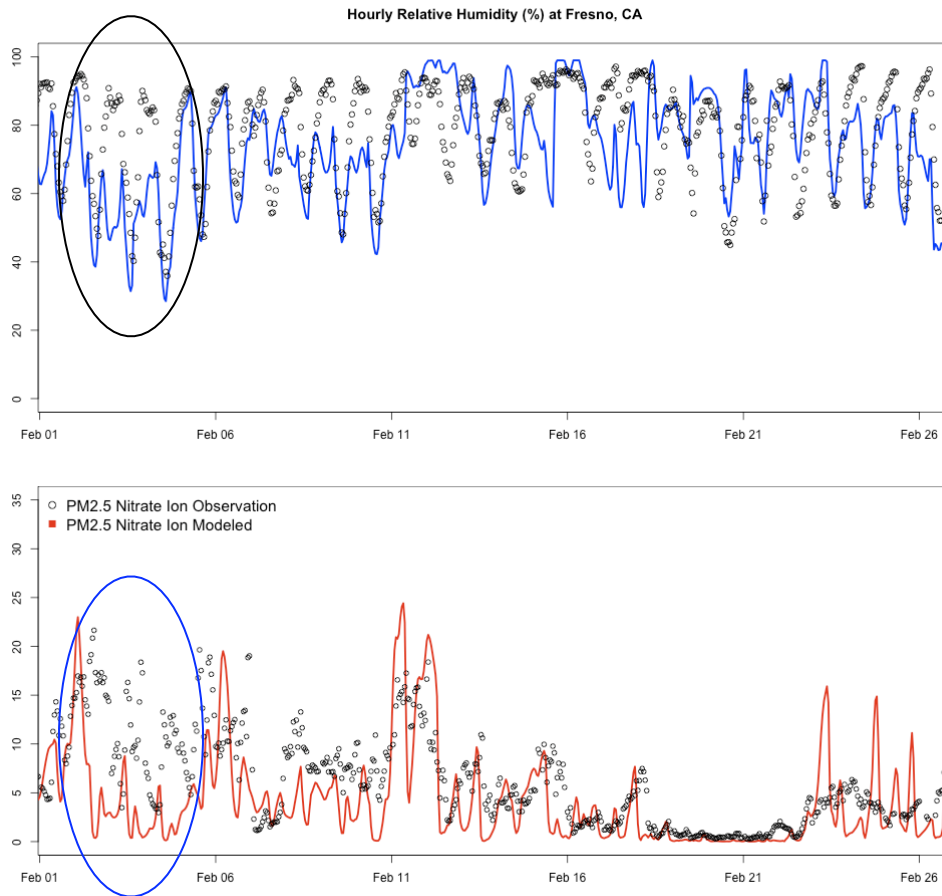
Temperature



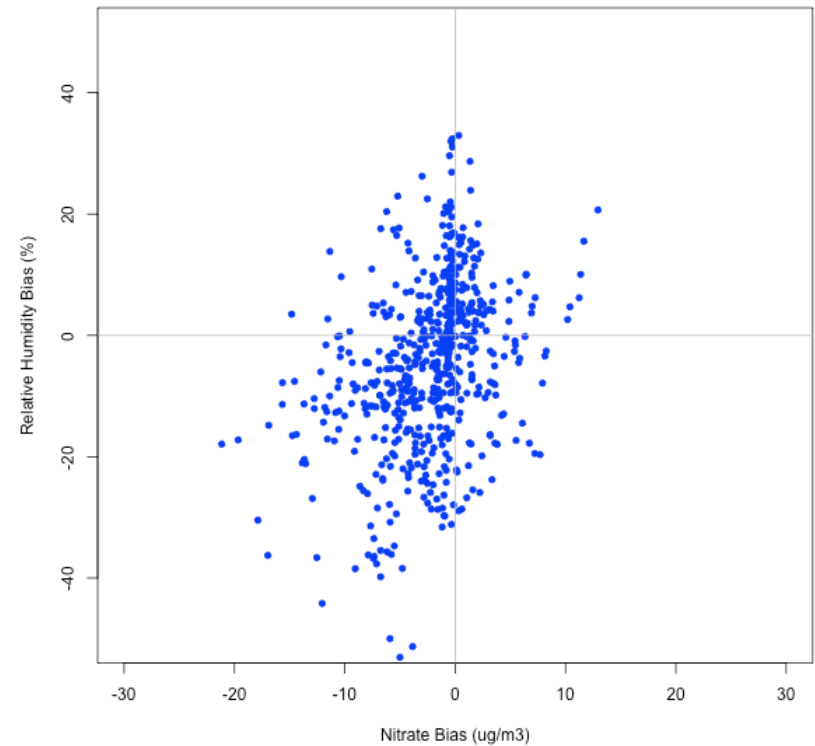
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Relative Humidity



PM2.5 Nitrate ion bias compared to relative humidity bias

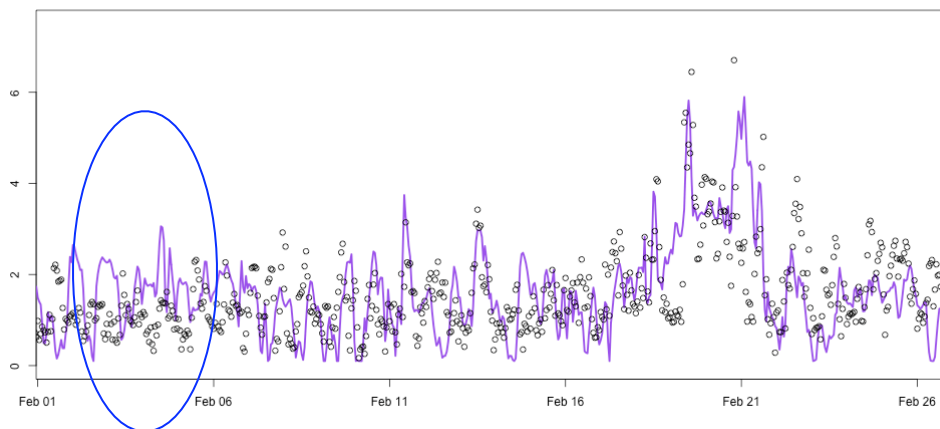


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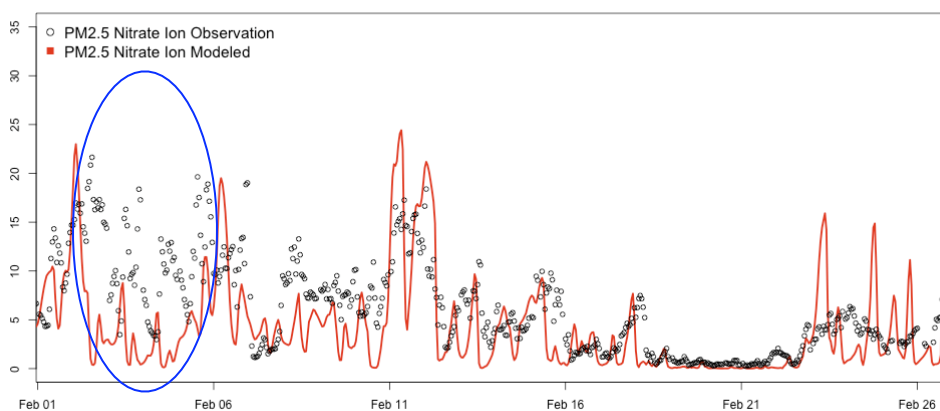
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Wind Speed

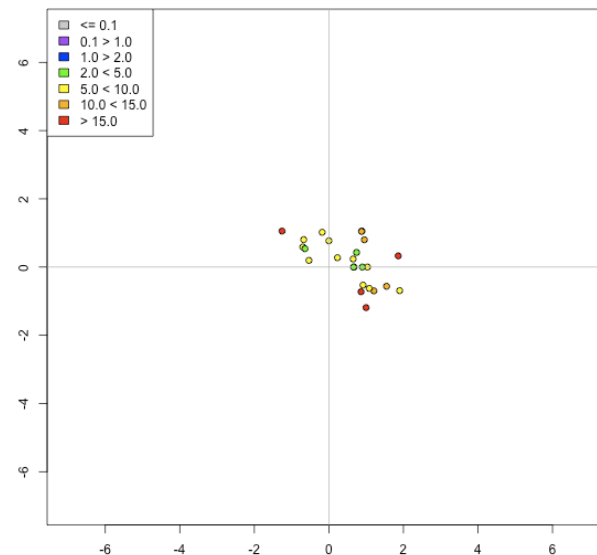
Hourly Wind Speed (mps) at Fresno, CA



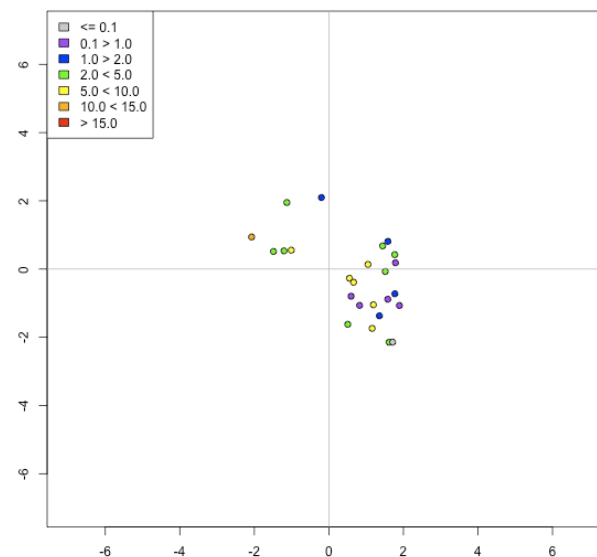
Hourly PM2.5 Nitrate (ug/m3) at Fresno, CA



Observed PM2.5 Nitrate Ion (ug/m3) Feb 2005



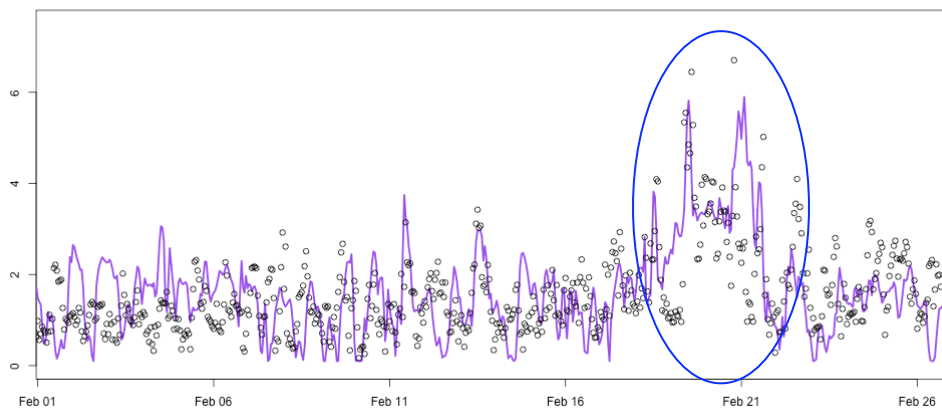
Predicted PM2.5 Nitrate Ion (ug/m3) Feb 2005



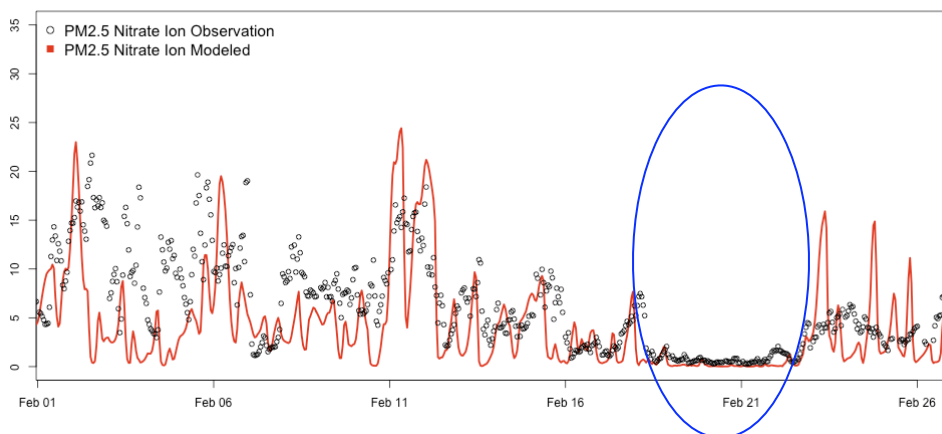
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Wind Speed

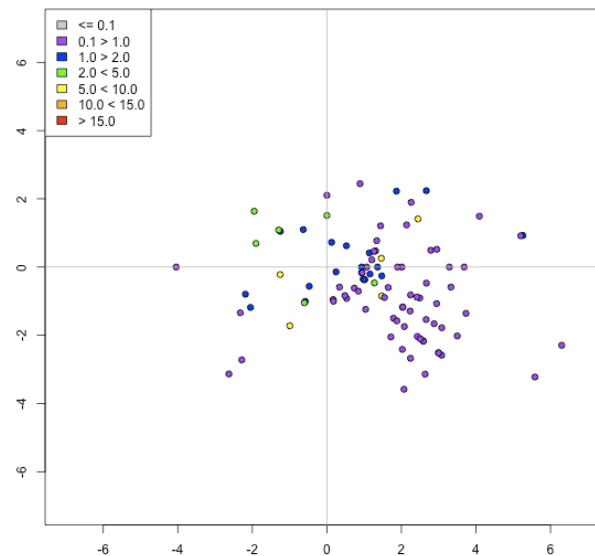
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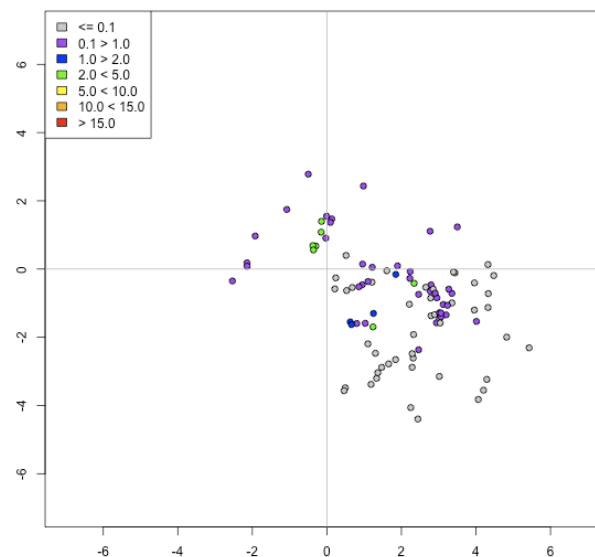
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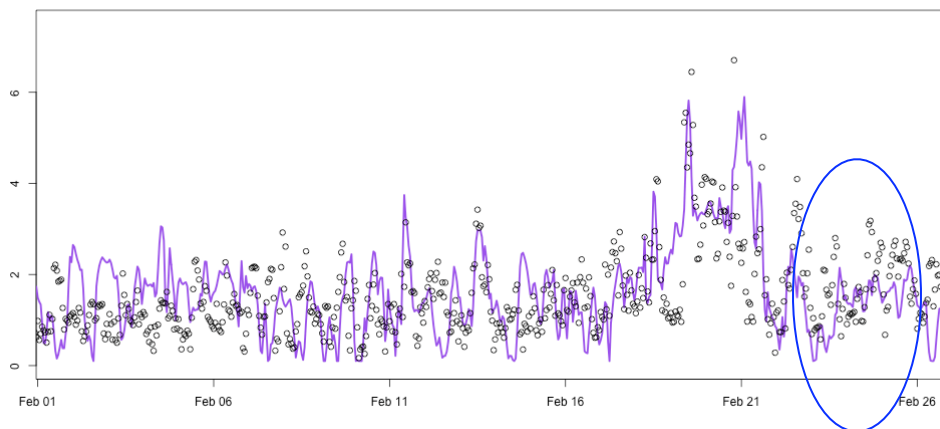
Predicted PM2.5 Nitrate Ion (ug/m3) Feb 2005



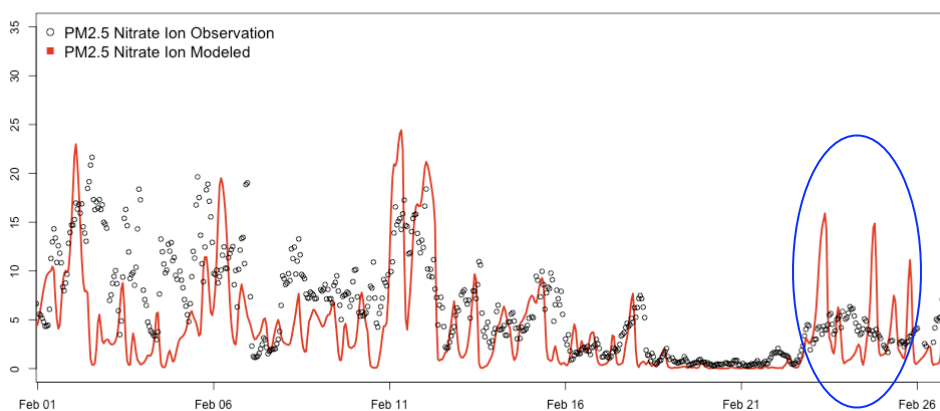
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Wind Speed

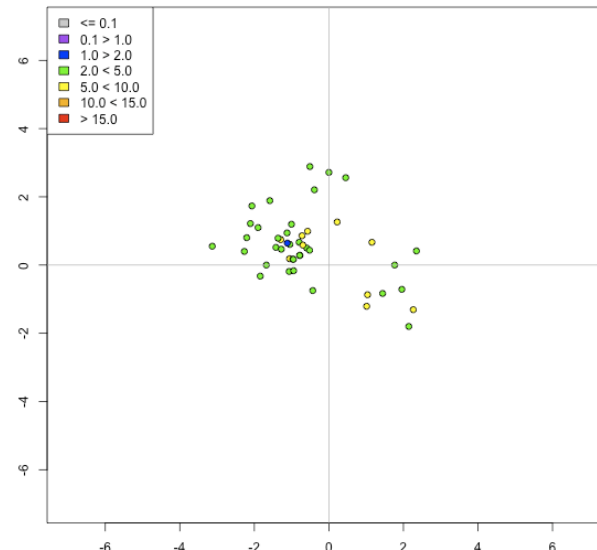
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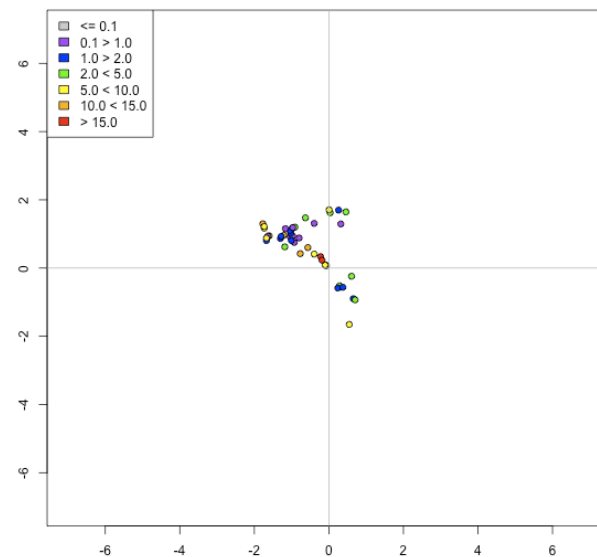
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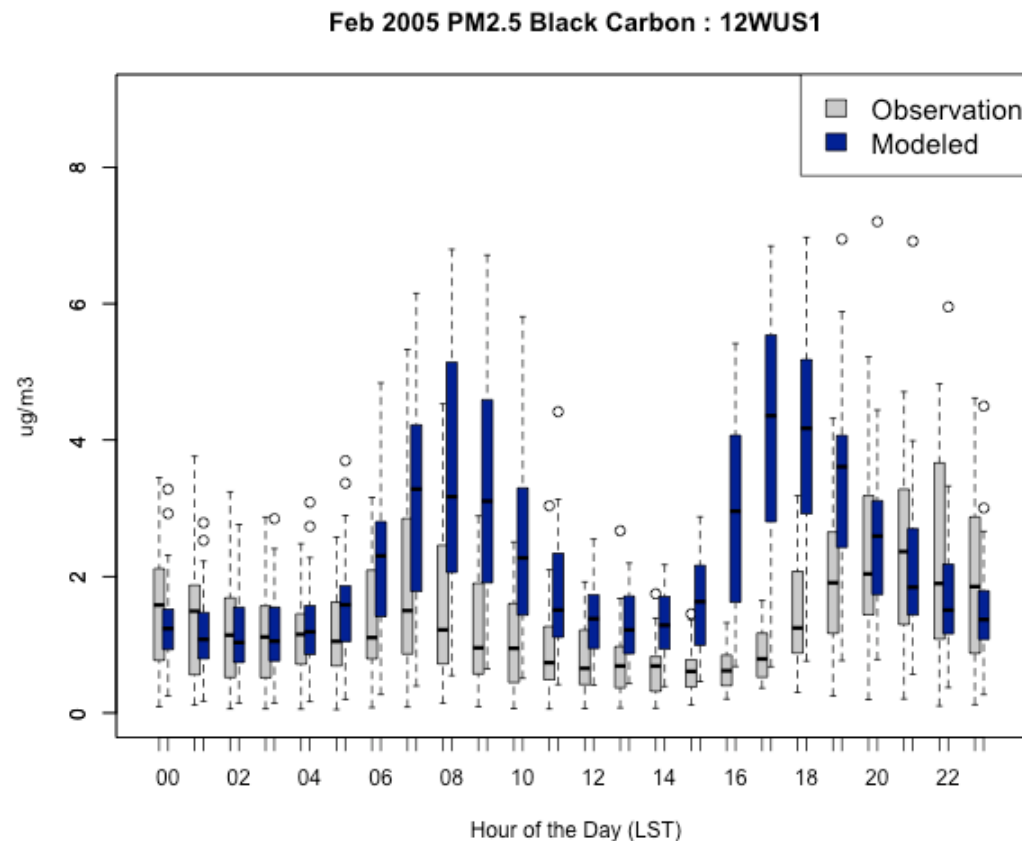
Predicted PM2.5 Nitrate Ion (ug/m3) Feb 2005



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Speciated PM_{2.5} by Hour of the Day

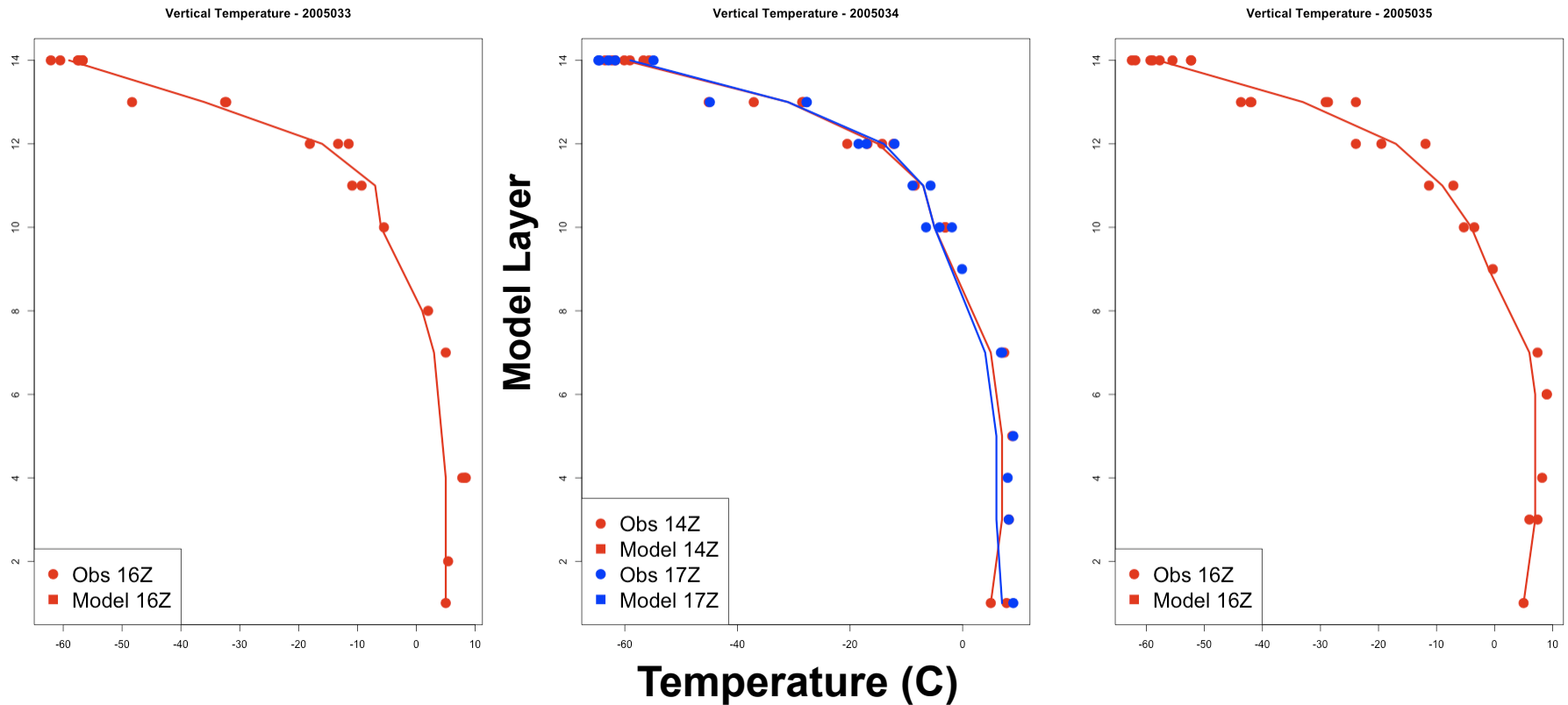
- No direct measurements of PBL in the central valley
- Hourly elemental carbon measurements provide an indirect characterization of the tendency of the modeling system to capture diurnal variability in mixing height



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Vertical Temperature Performance at Hanford, CA (near Fresno)

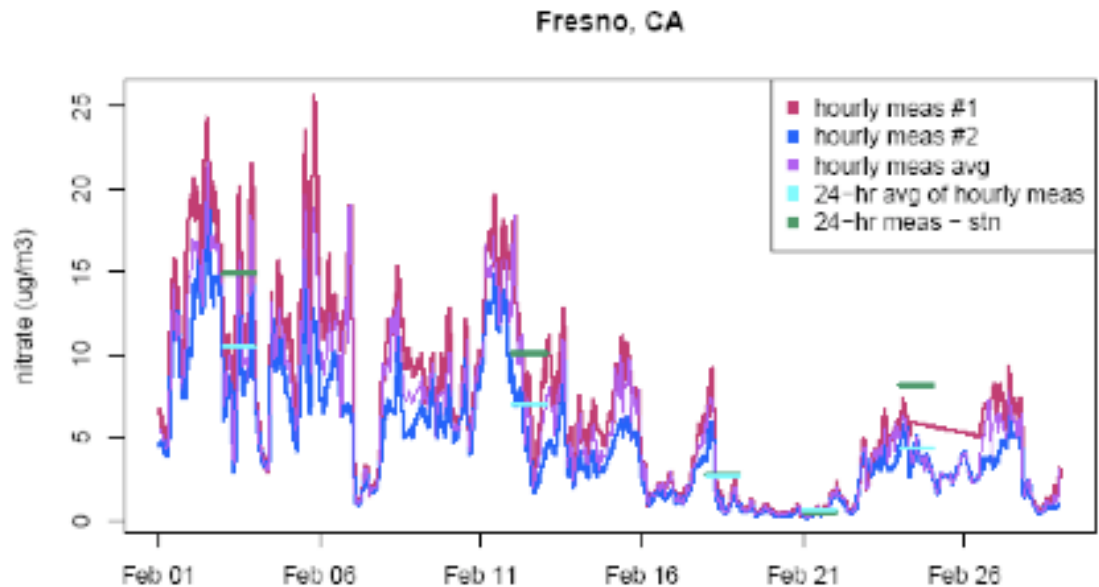


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Measurements

- **How accurate are measurements of PM2.5 nitrate ion at Fresno?**
- Multiple methods making hourly PM2.5 nitrate ion measurements
- Additional 24-hr measurements from CSN network site
- Large variability between measurement methods



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Conclusions

- RH and wind speed influence model estimates of PM2.5 nitrate ion in central California during the winter
- Increased NOX did not improve performance during these episodes
- Increases in ammonia emissions do not help with PM2.5 nitrate under estimation events and actually degrade model performance
- EC temporal profiles compare well but model tends to overestimate EC which suggests PBL may not be contributing to under estimation events
- Quite a bit of variability in PM2.5 measurements at Fresno
- Next steps of investigation: deposition (may be affected by phase of nitrate)