Investigation of Wintertime Nitrate at Mammoth Cave and Great Smoky Mountains National Parks

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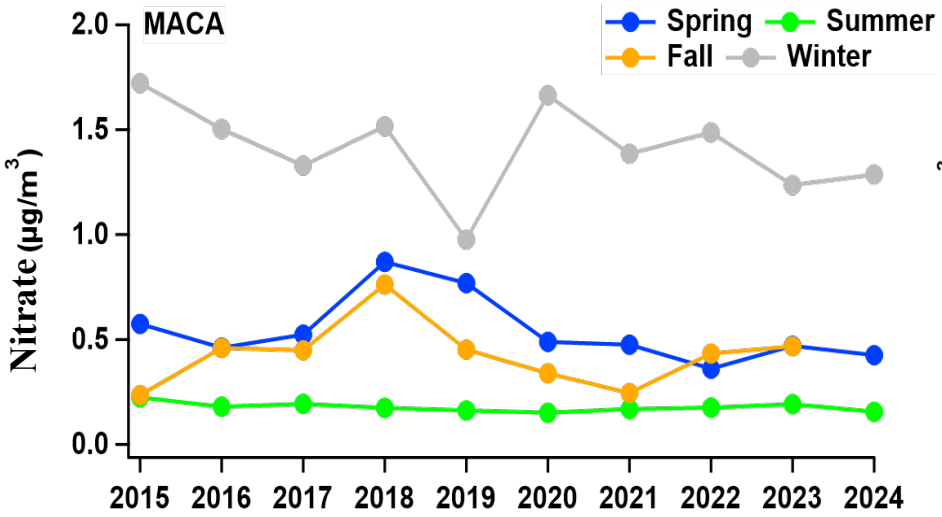
National Park Service

Outline

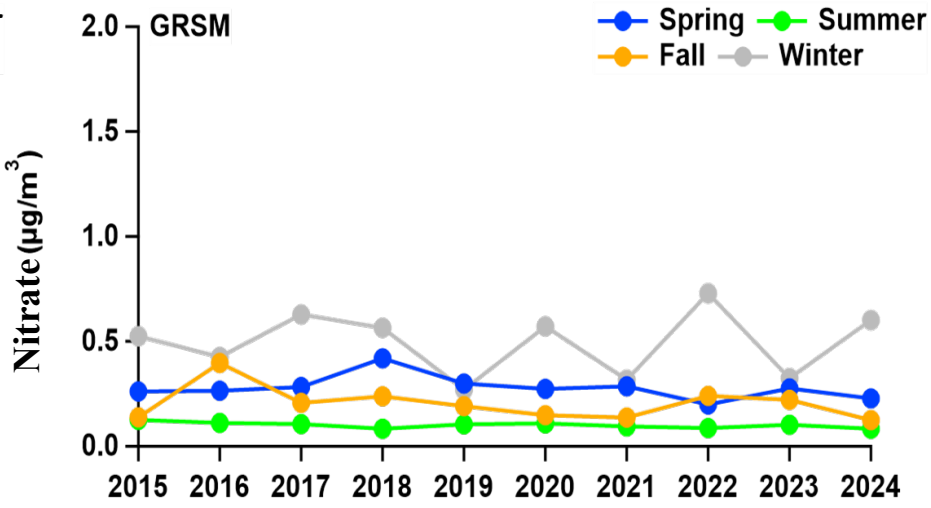
- Motivation
- Overview of measurements
- Results
  - Time series
  - Role of temperature and transport
  - Thermodynamic modeling
- Summary

Motivation

Mammoth Cave



Great Smoky Mountains

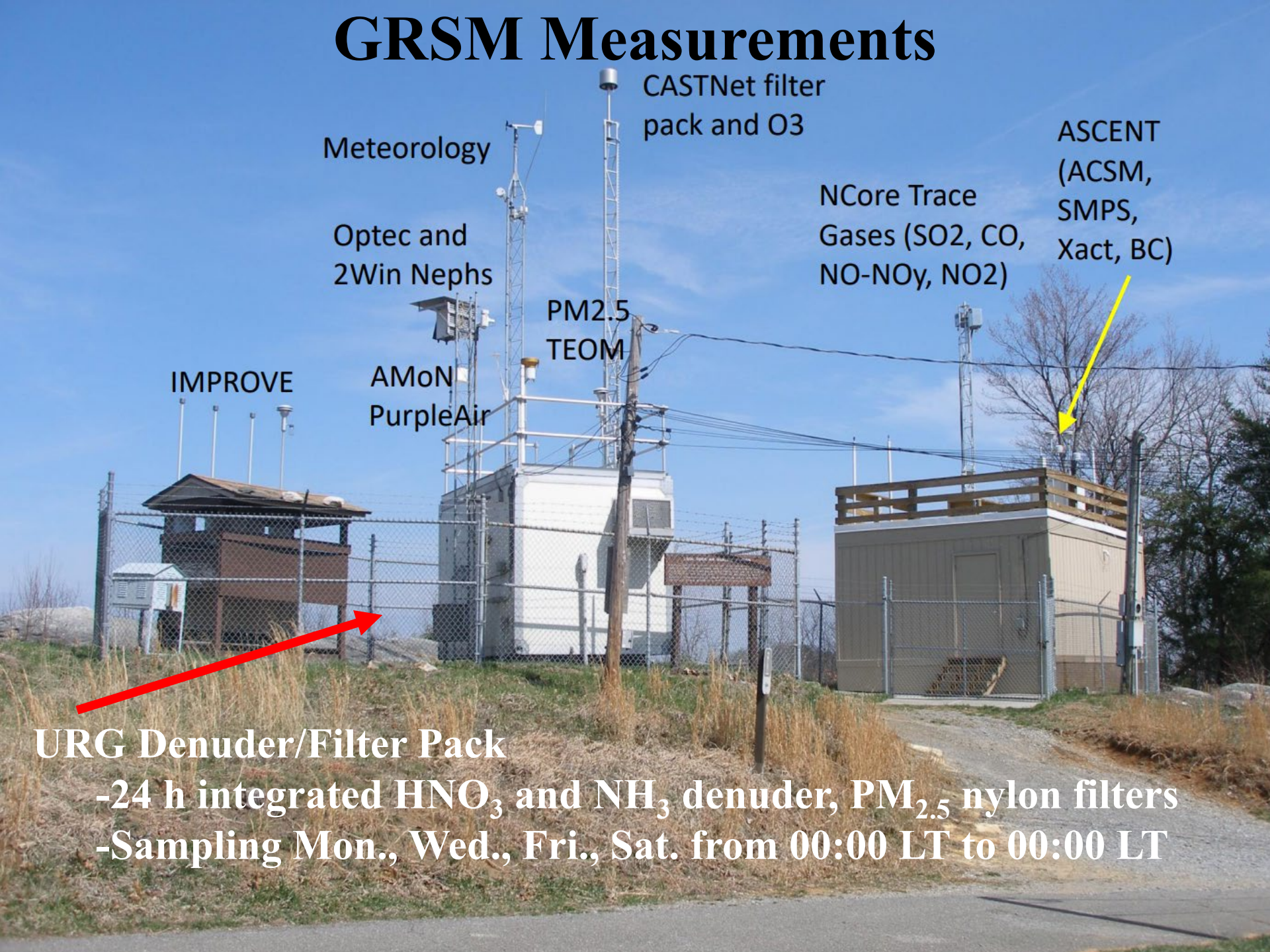


- IMPROVE filters show winter nitrate concentrations have consistently been higher over the past 10 years
- Nitrate formation/evaporation function of precursors, meteorological conditions, existing particle composition that determine particle liquid water content and pH
- Therefore, it is important to identify the factors leading to and main sources of nitrate to understand how to control its emissions

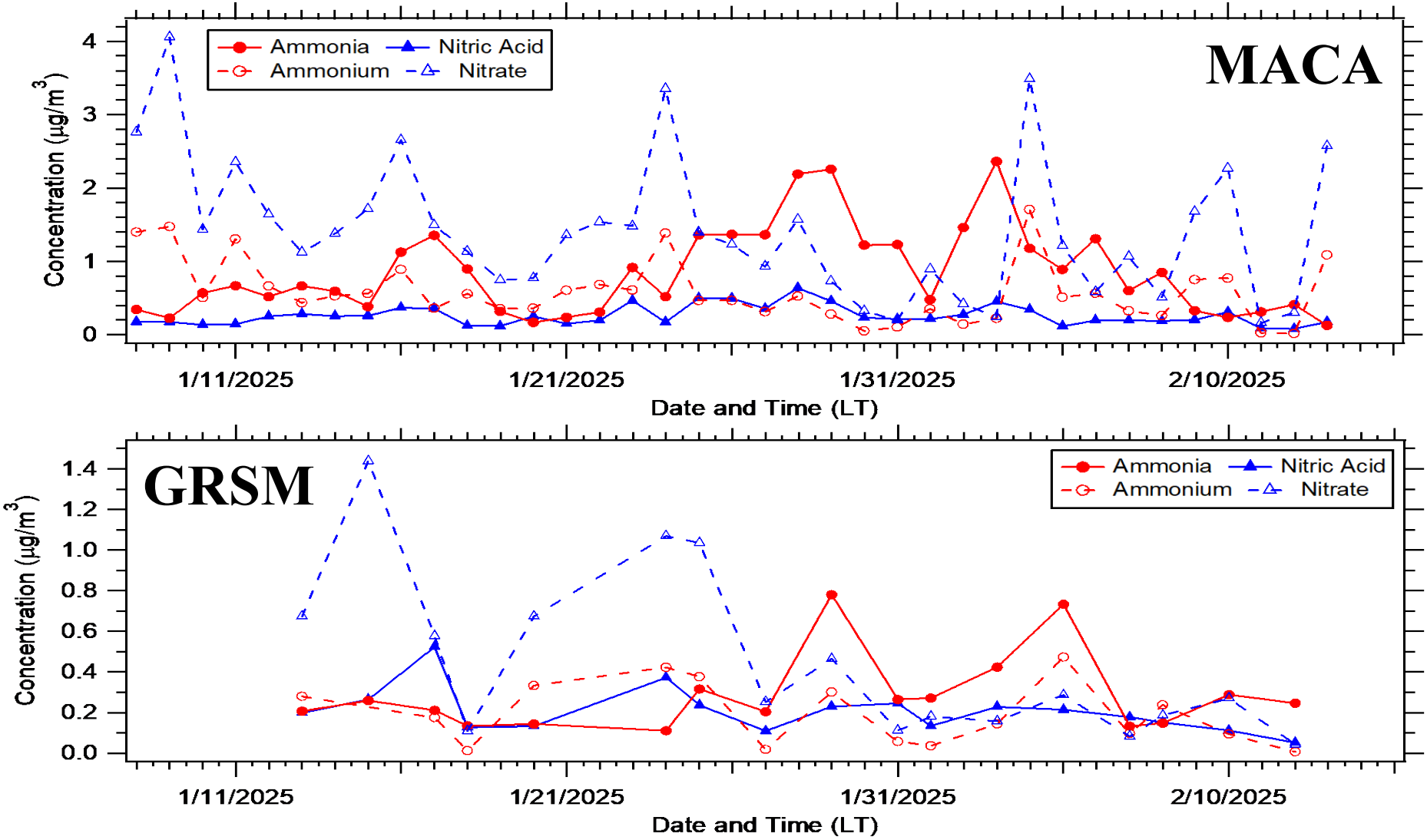
MACA Measurements

- URG Denuder/Filter Pack
  - 24 h integrated HNO_3 and NH_3 denuders, $PM_{2.5}$ and PM_{10} nylon filters
  - Daily from 00:00 LT to 00:00 LT
- PILS-IC
  - 15 min integrated $PM_{2.5}$ anions and cations
- Picarro G2508
  - 1 s NH_3, CH_4, CO_2
- Teledyne T640
  - 1 min $PM_{2.5}$ and PM_{10} mass
- Teledyne T500
  - 1 min NO_2

GRSM Measurements



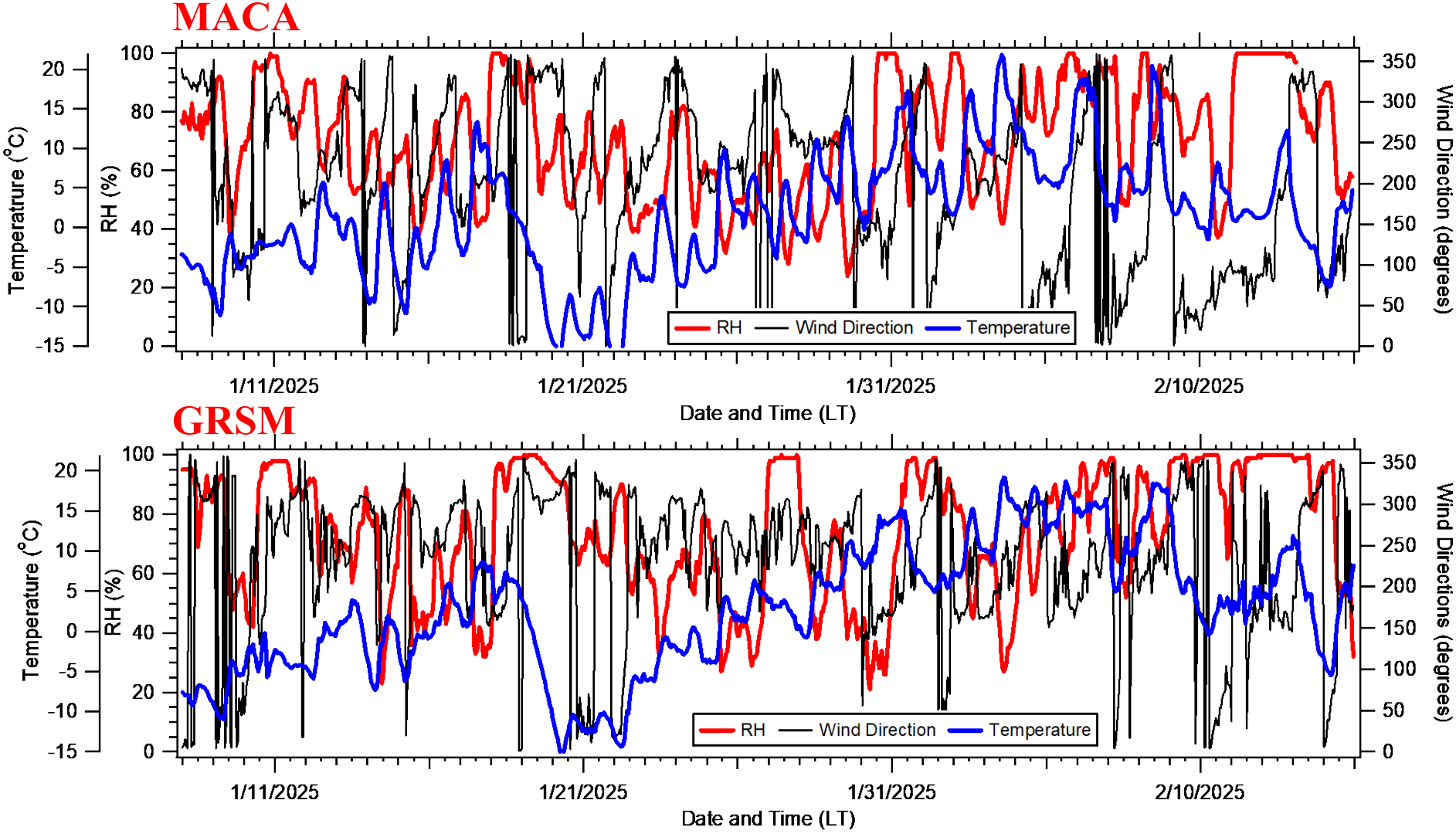
MACA and GRSM
Times Series of URG Denuders and Filters



-Observe similar pattern as IMPROVE data, concentrations higher at MACA

-This true in both gas and aerosol-phase

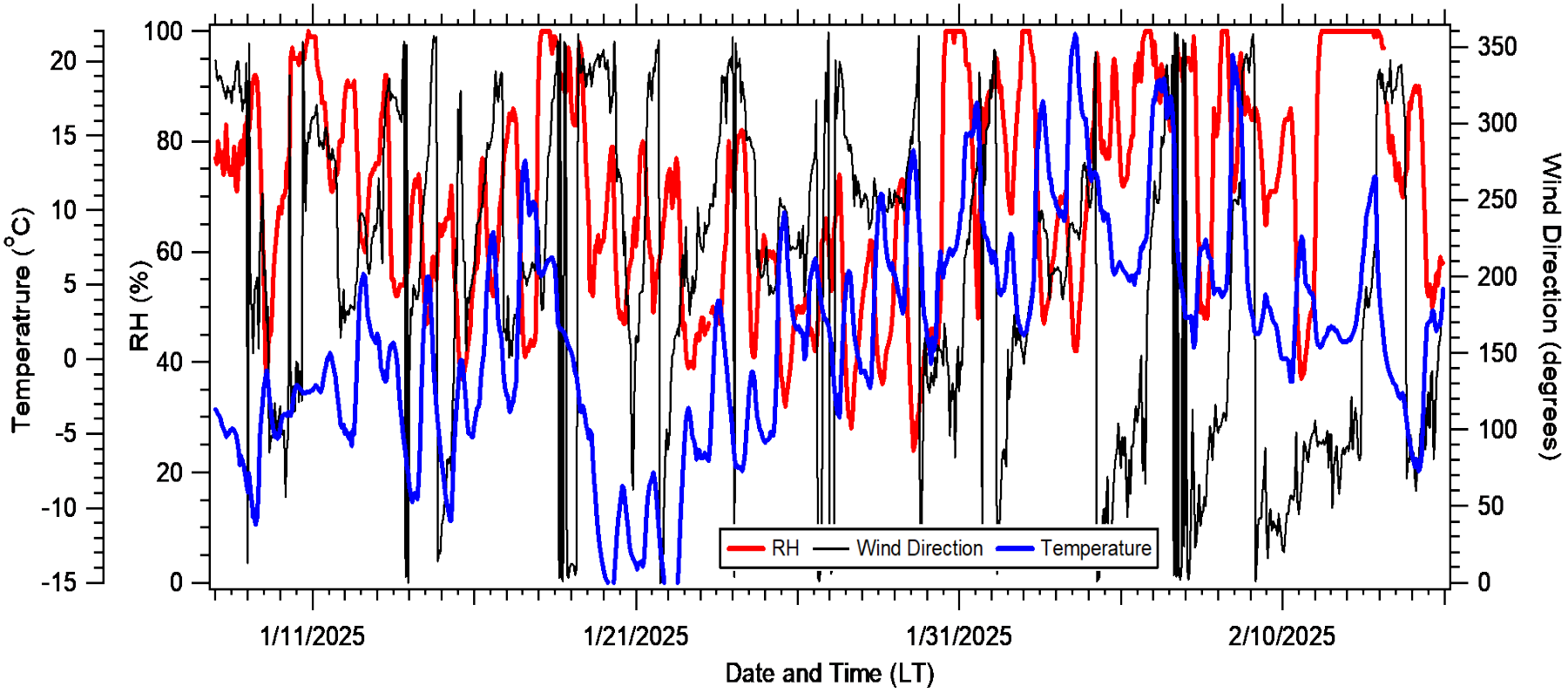
MACA and GRSM
Times Series of Temperature, RH, Wind Direction



-RH ranging from ~40 to 100%

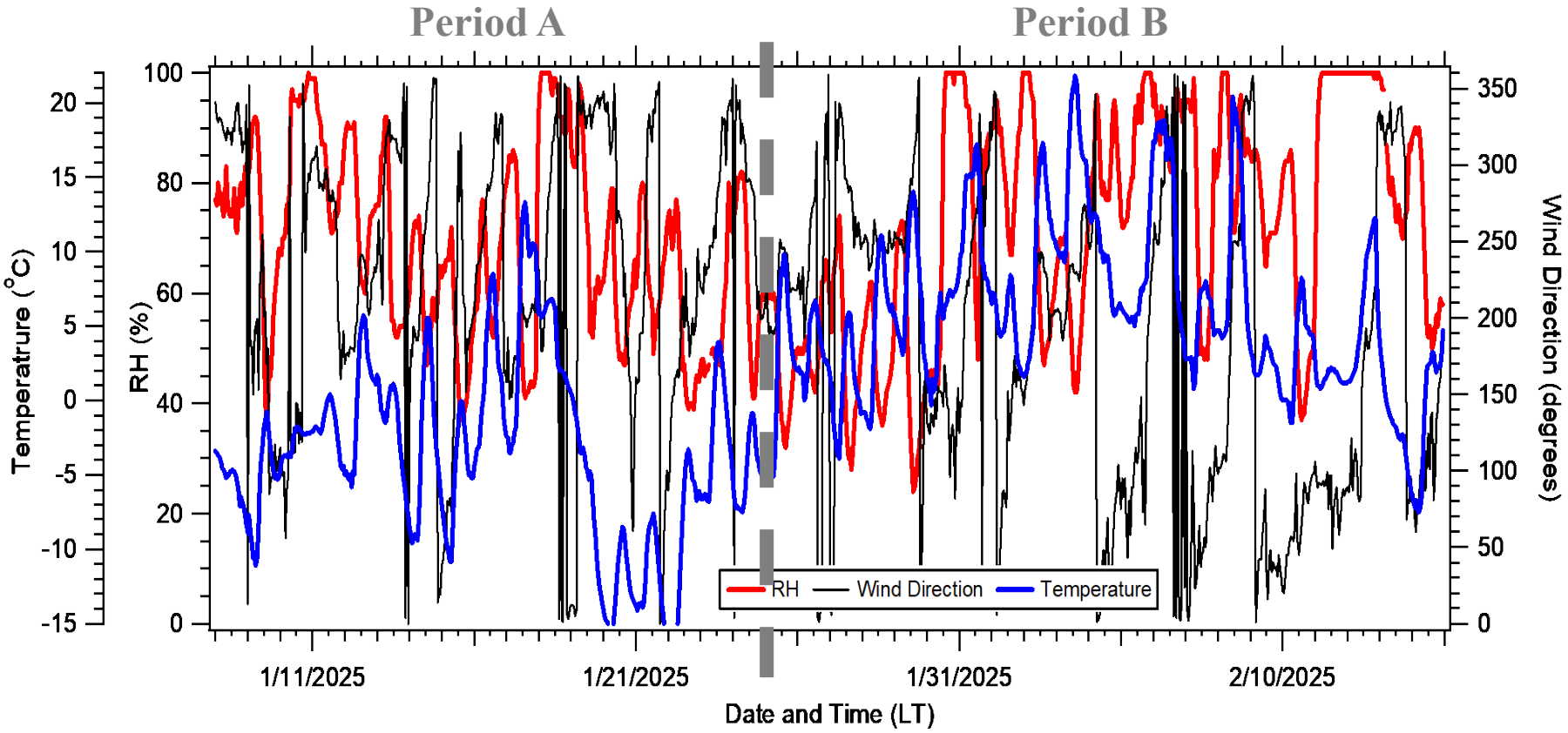
-Temperature pattern very similar at both sites

MACA
Times Series of Temperature, RH, Wind Direction



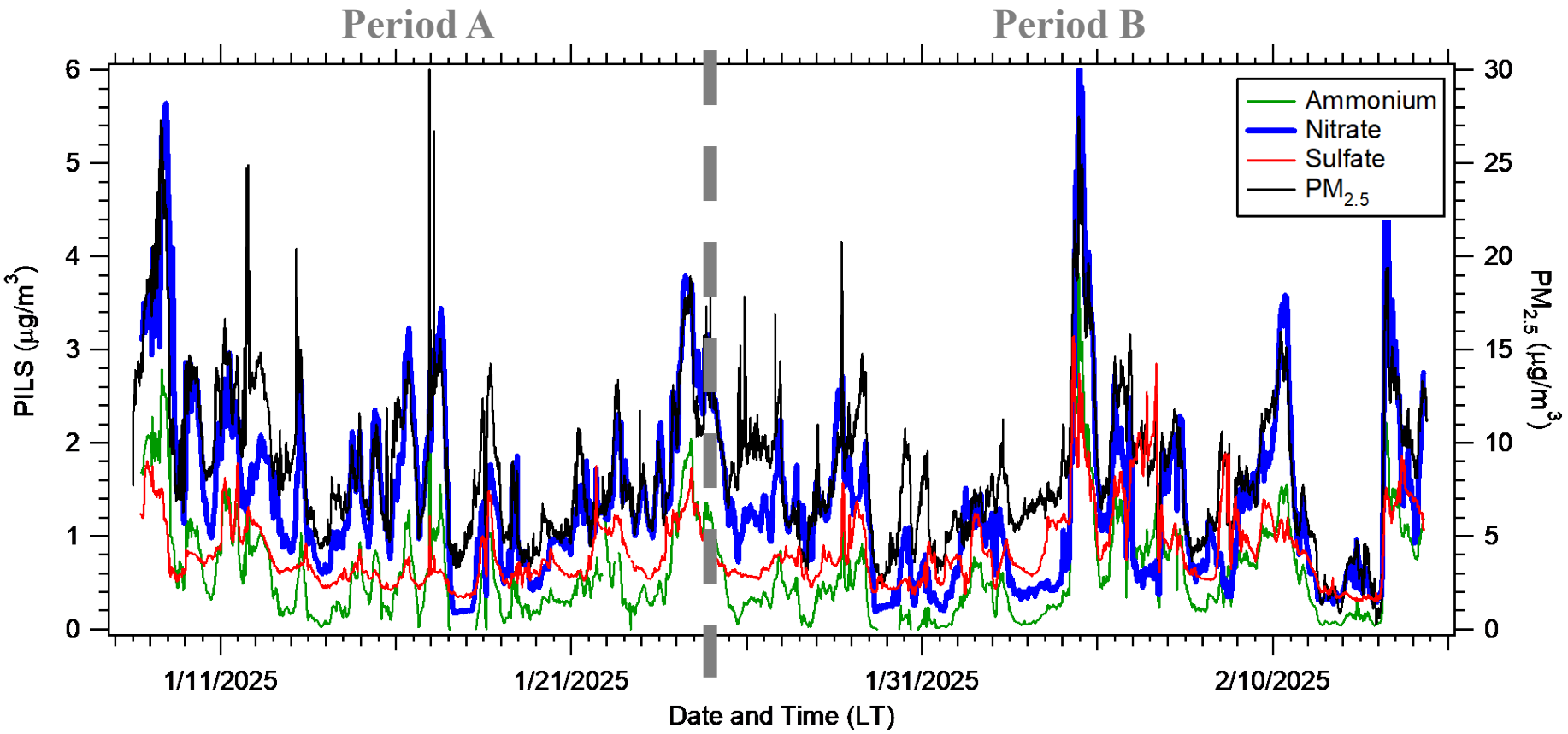
-Started cold with snow on ground, followed by increase in temperature
-Then had intense deep freeze and snow
-Following this temperature continued to increase, leading to hottest days observed
-Ended with week of on/off rain and different wind pattern

MACA
Times Series of Temperature, RH, Wind Direction



-Started cold with snow on ground, followed by increase in temperature
-Then had intense deep freeze and snow
-Following this temperature continued to increase, leading to hottest days observed
-Ended with week of on/off rain and different wind pattern

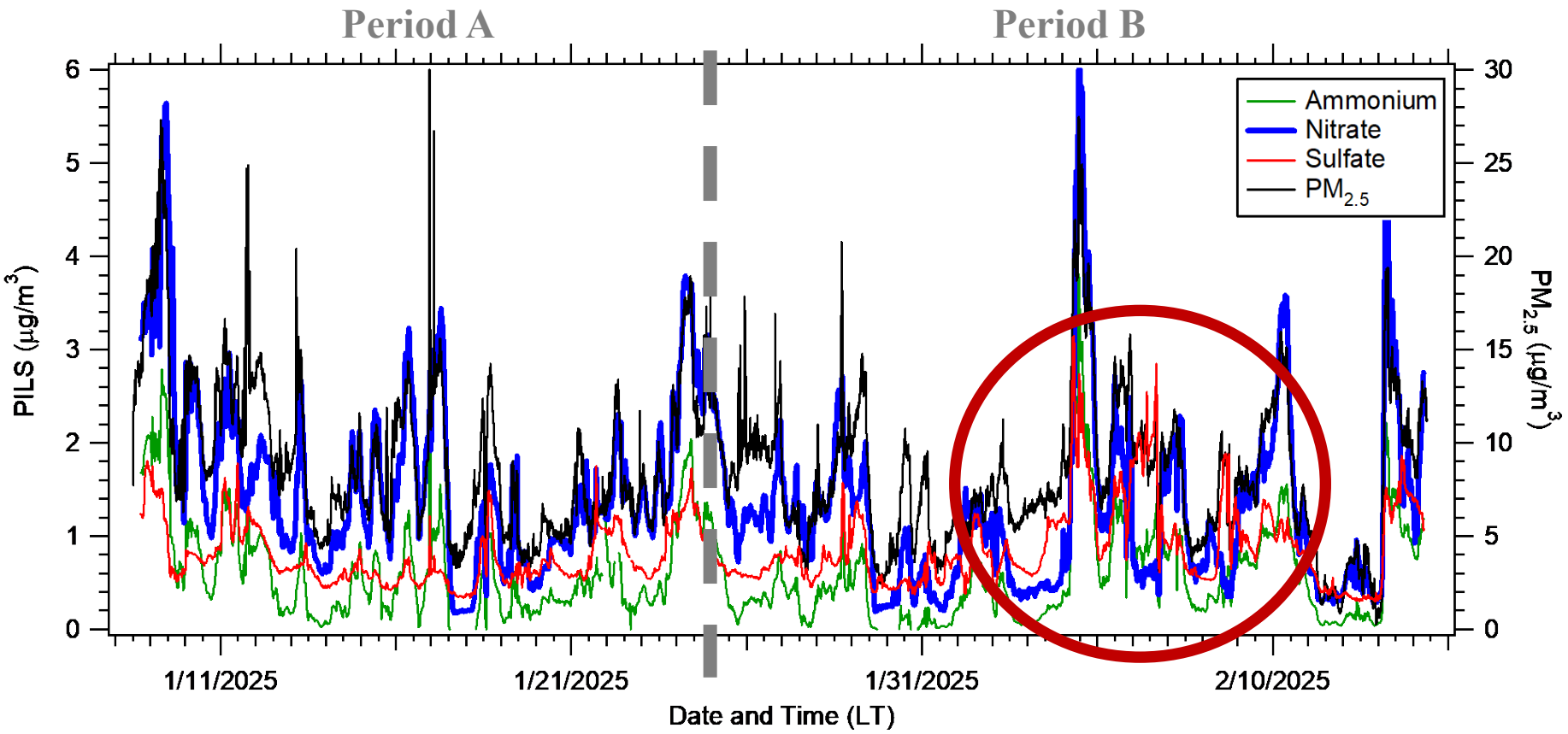
MACA
Times Series of PILS and $PM_{2.5}$ Mass



-Nitrate, sulfate, ammonium track with PM

-Nitrate generally dominates changes in PM, with some exceptions

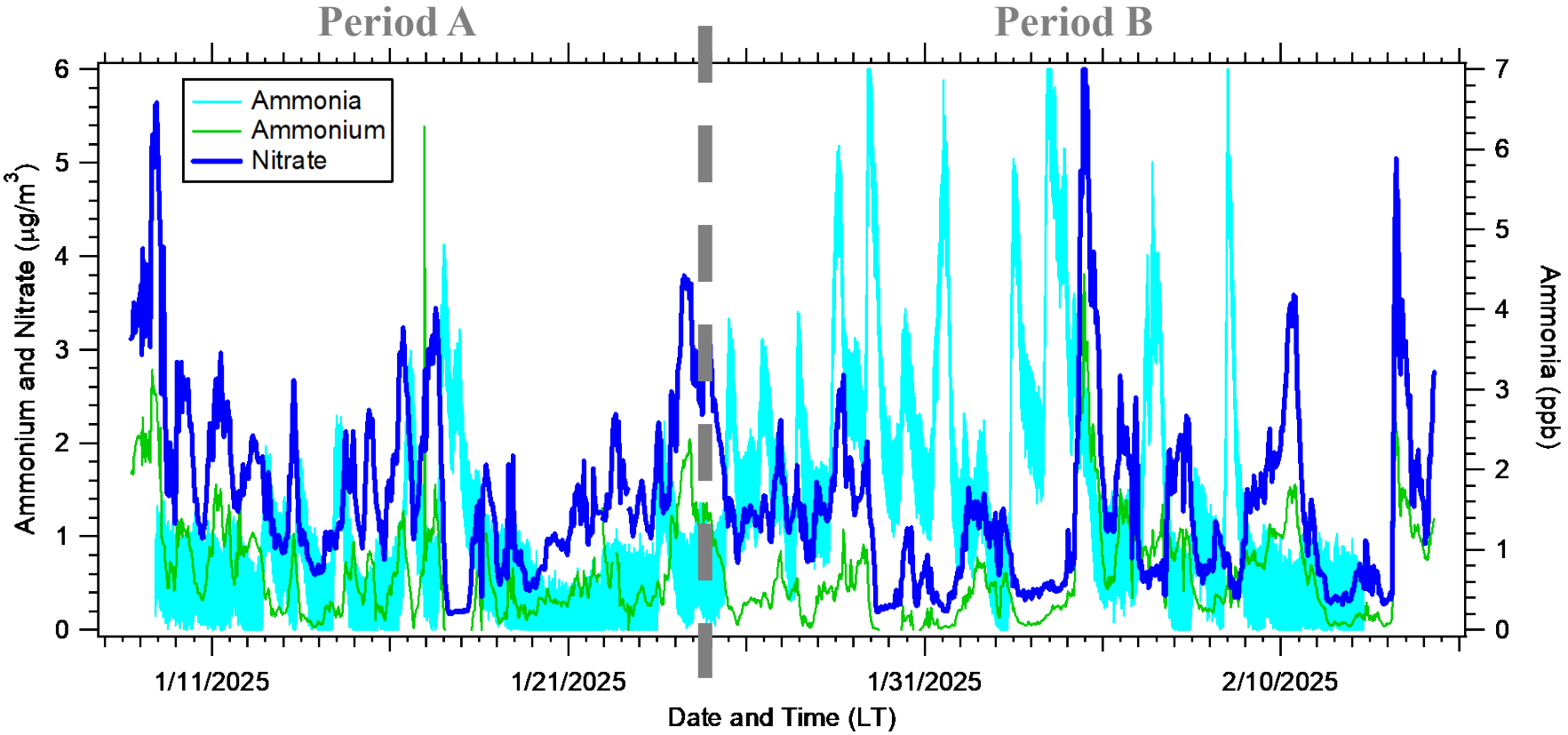
MACA
Times Series of $PM_{2.5}$ Mass



-Nitrate, sulfate, ammonium track with PM

-Nitrate generally dominates changes in PM, with some exceptions

MACA
Times Series PILS and Picarro Ammonia



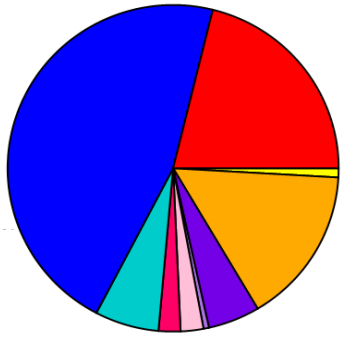
-Temperature appears to largely be driving pattern

-Ammonium and nitrate concentrations noticeably dropped when ammonia started increasing

MACA
Chemical Characteristics of Nitrate Episodes

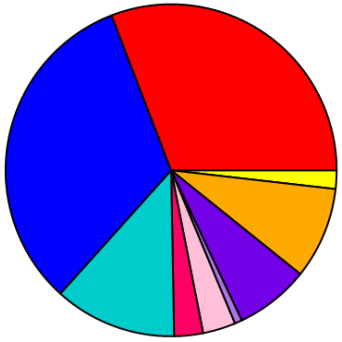
Sodium Ammonium Potassium
Magnesium Calcium Chloride
Nitrite Nitrate Sulfate

Higher than Nitrate 50th percentile

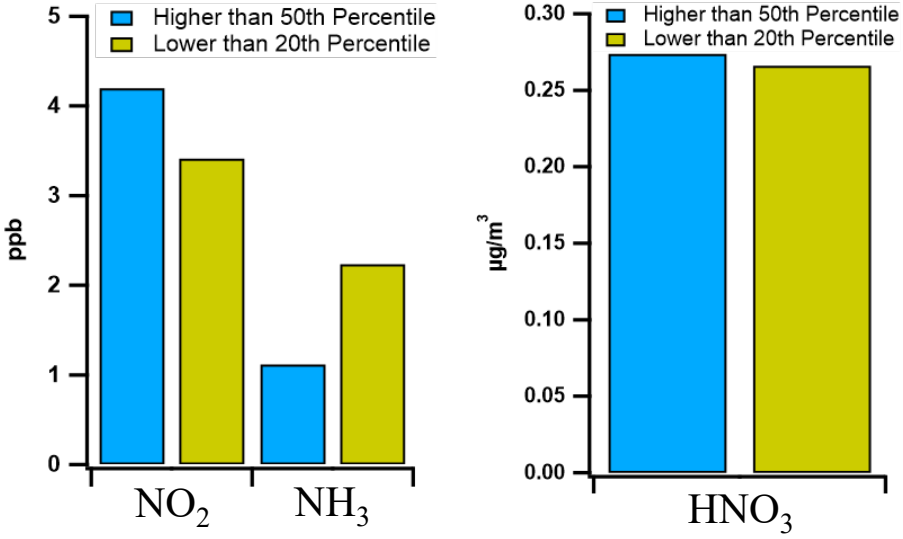


Average Inorganic $PM_{2.5}$ = 4.6 µg/m^3

Lower than Nitrate 50th percentile

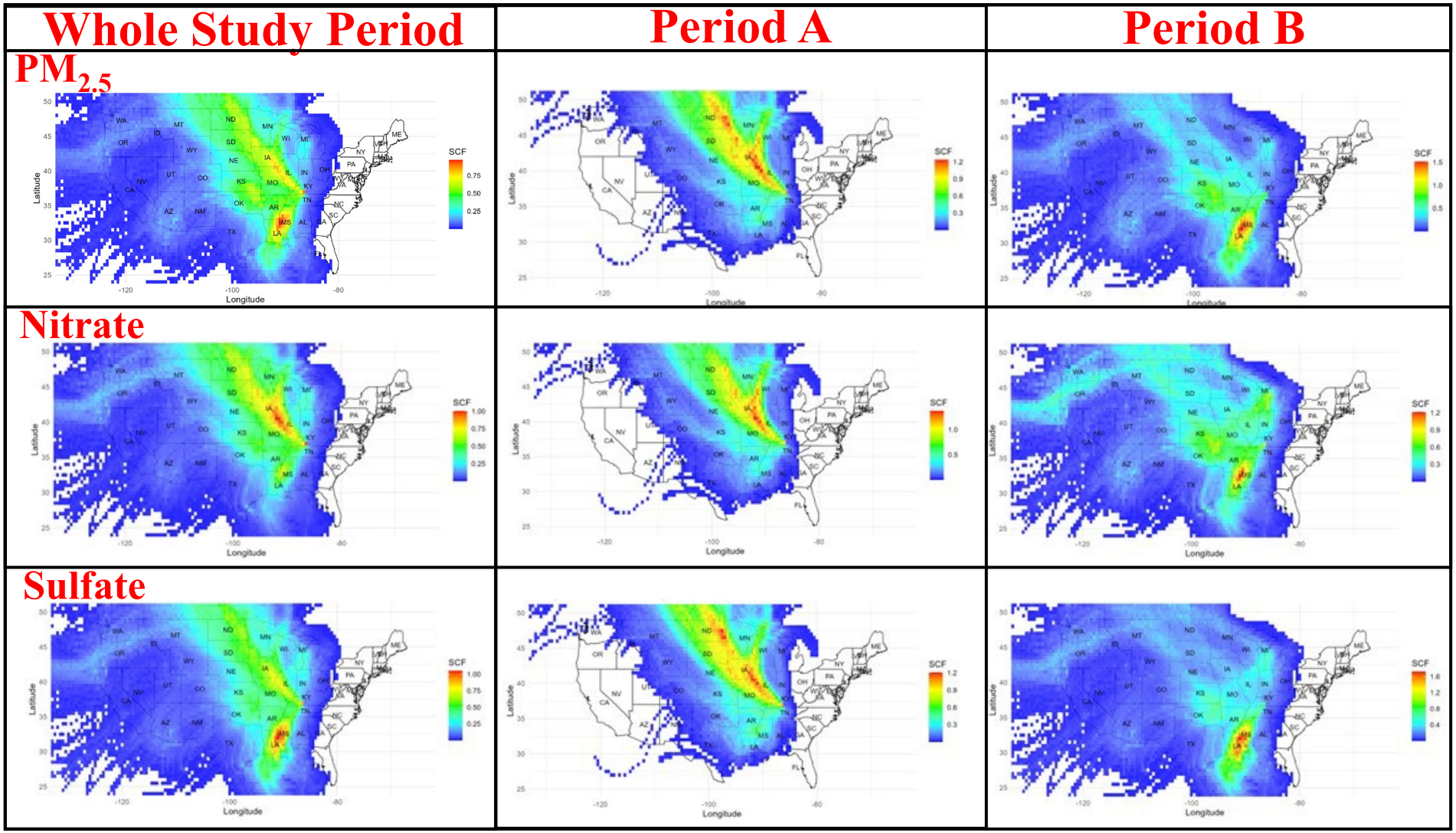


Average Inorganic $PM_{2.5}$ = 3.9 µg/m^3



- Nitrate episodes were identified using the 50th percentile threshold of nitrate concentrations
- During lower nitrate periods, elevated NH_3 levels were observed

Residence Time Analysis



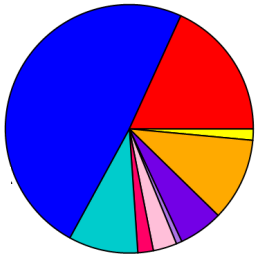
- Clear shift in major transport pathway from Period A to Period B
  - Period A : northwesterly flow
  - Period B : south/southwesterly flow

Period A Nitrate Dominated Episode - Jan. 15-17

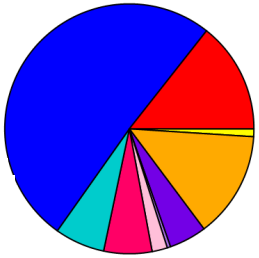
Sodium Ammonium Potassium
Magnesium Calcium Chloride
Nitrite Nitrate Sulfate

Inorganic $PM_{2.5}$

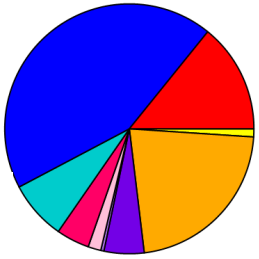
Jan. 15



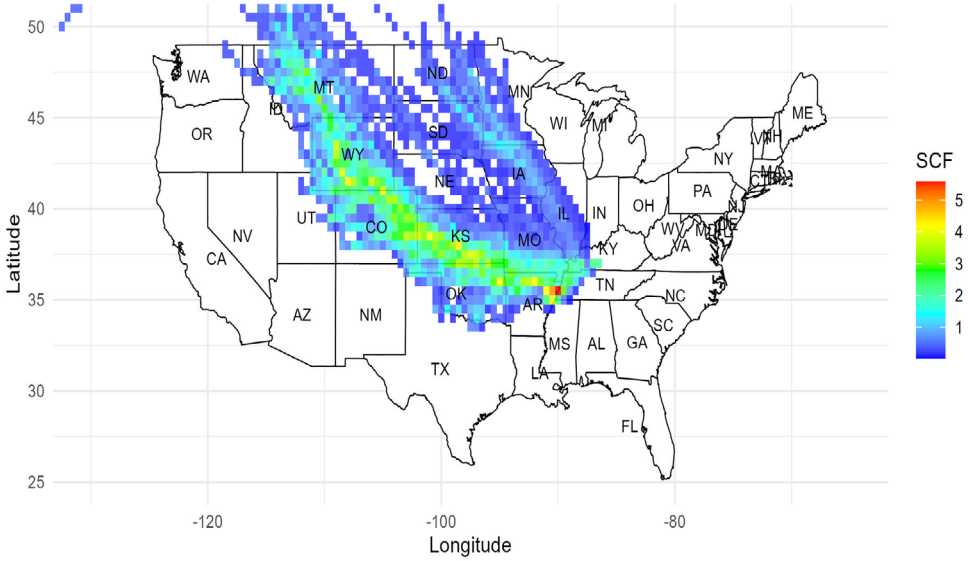
Jan. 16



Jan. 17



Nitrate – 90th threshold



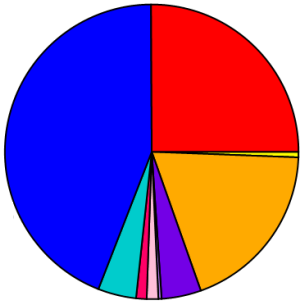
- Inorganic $PM_{2.5}$ dominated by nitrate
- Consistent northwesterly/central US air mass inflow
- Suggests transport of regional emissions (e.g., agricultural NH_3, combustion NO_x)

Period B Transition from Nitrate to Sulfate Dominated Episode – Feb. 4-6

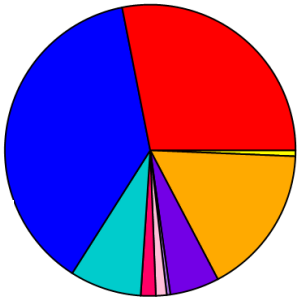
Sodium Ammonium Potassium
Magnesium Calcium Chloride
Nitrite Nitrate Sulfate

Inorganic $PM_{2.5}$

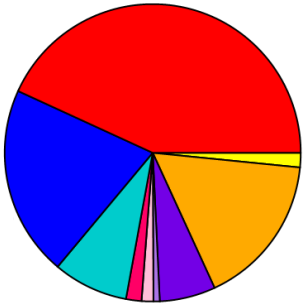
Feb. 4



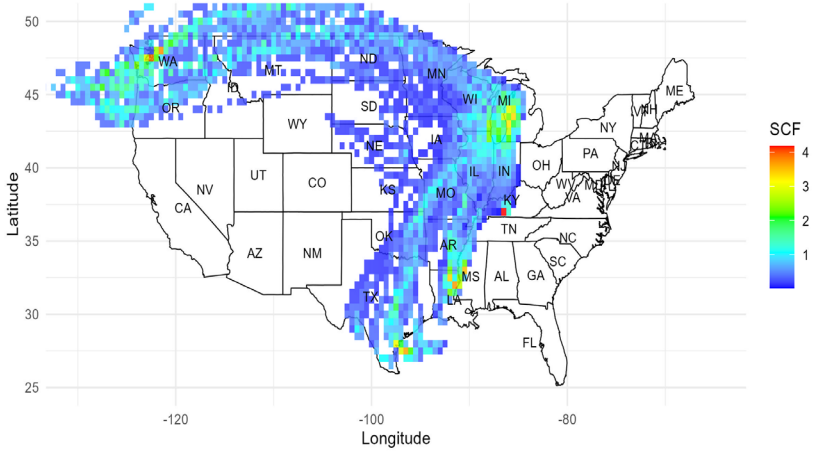
Feb. 5



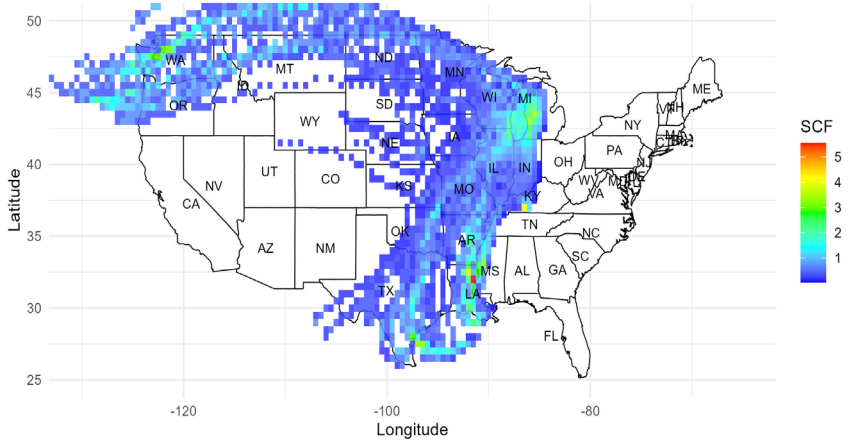
Feb. 6



Nitrate – 90th threshold

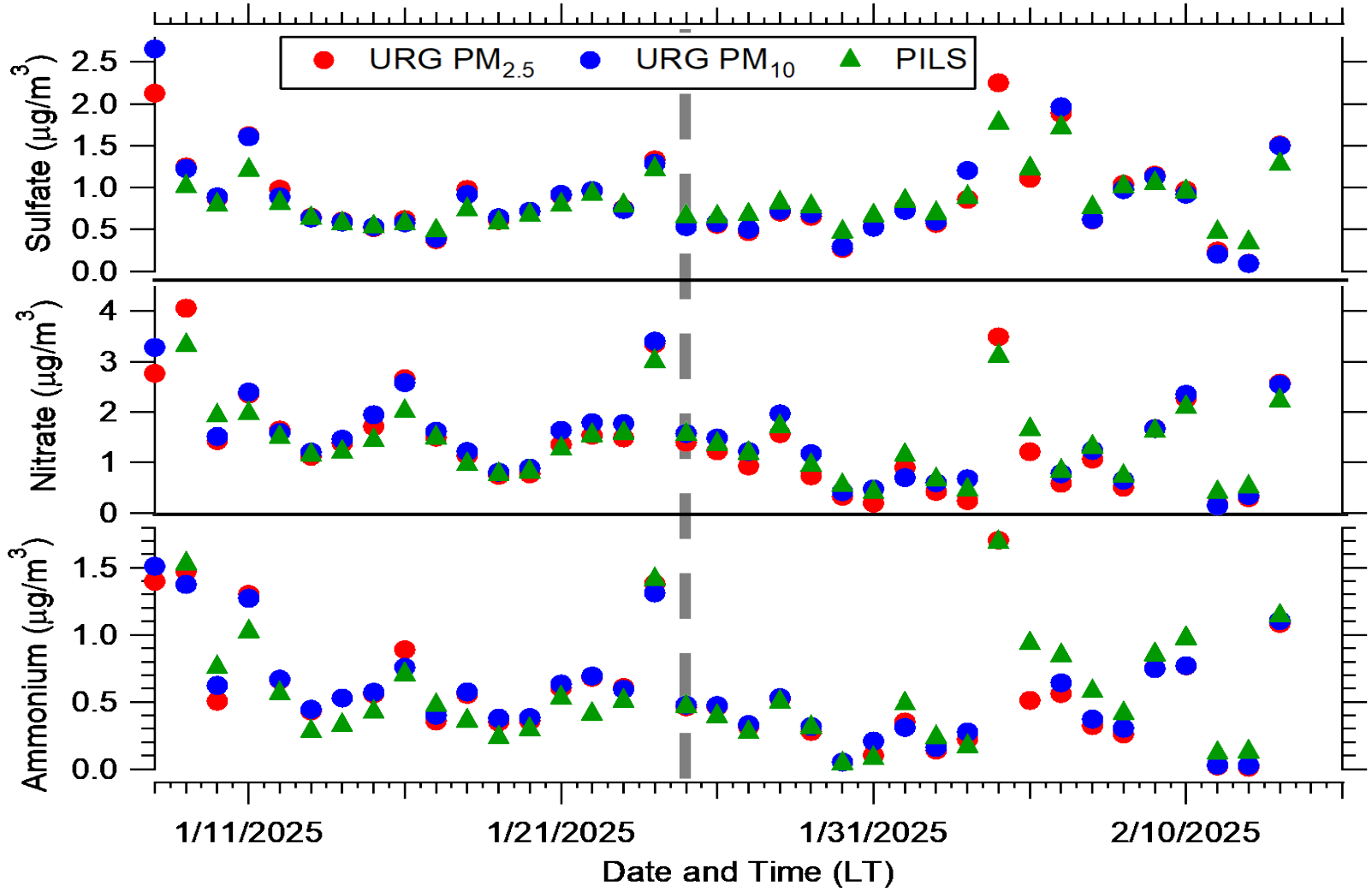


Sulfate – 90th threshold



- Larger fraction of Inorganic $PM_{2.5}$ contributed to sulfate across episode
- Observe switch in flow to include a southeasterly component

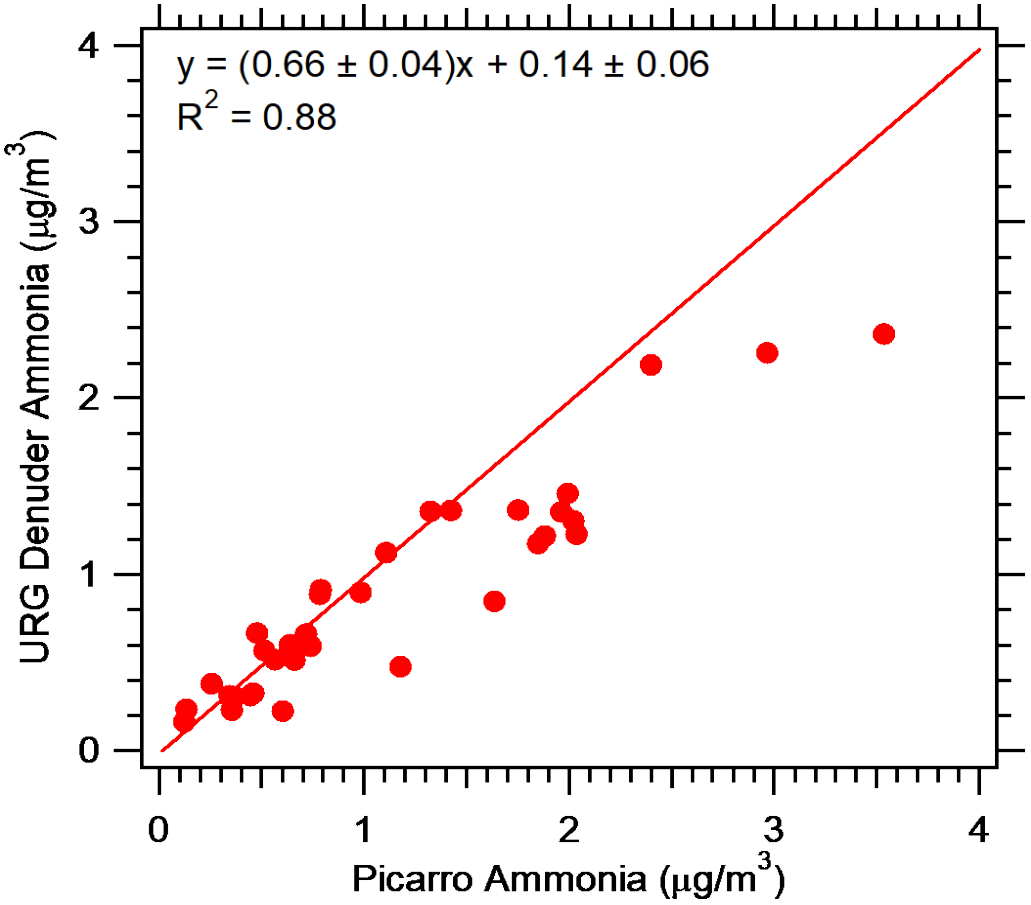
MACA
Times Series of PILS and URG Filters



-Good agreement between PILS and URG filters

-URG filters suggest little PM_{10} nitrate

MACA
URG Denuder vs. Picarro Ammonia

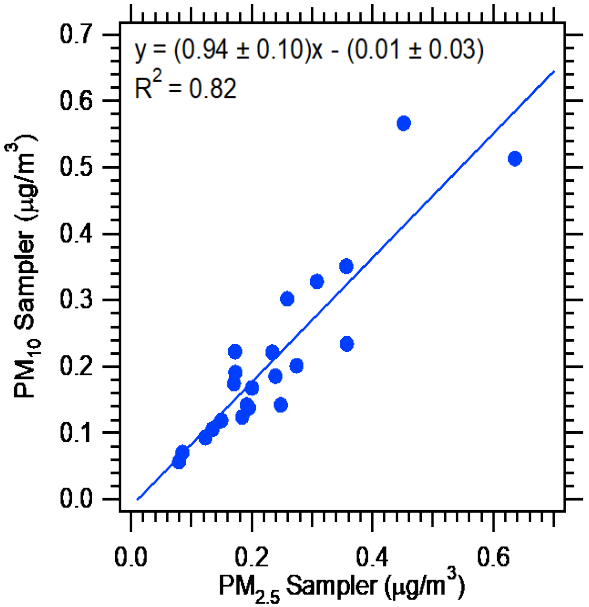


-Well correlated, but slope < 1

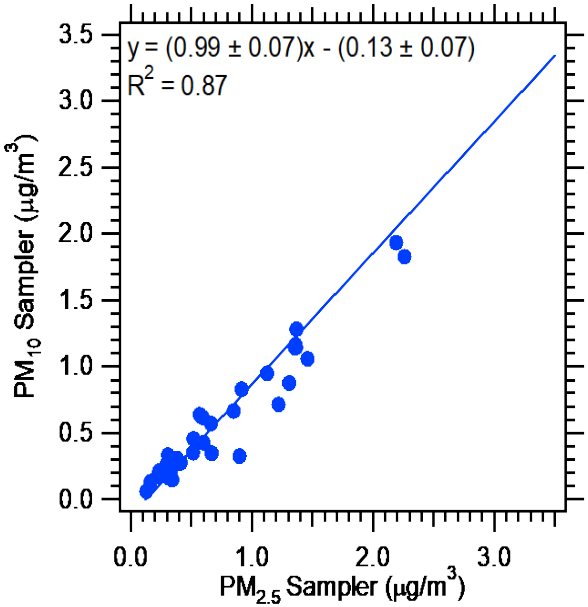
-Periodic sampling evaporated particle from inlet filter?

MACA
URG Denuder PM_{10} vs. $PM_{2.5}$

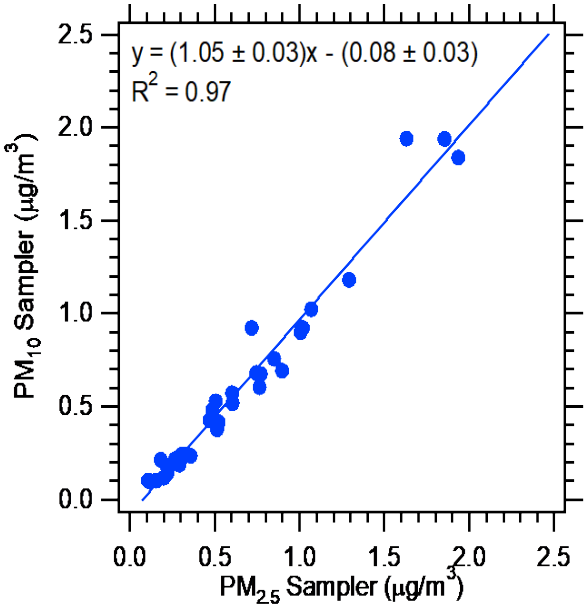
Nitric Acid



Ammonia

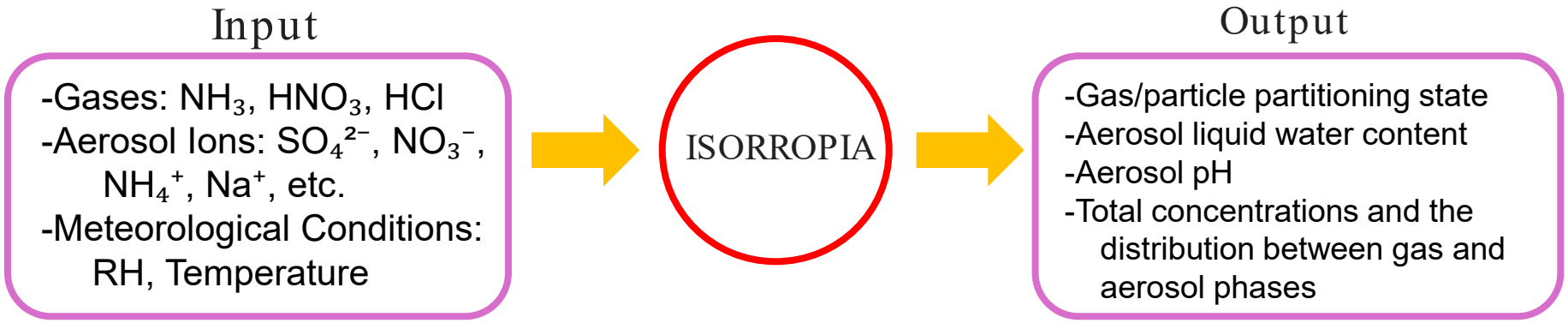


Sulfur Dioxide



-PM_{10} and $PM_{2.5}$ URG Samplers well correlated for gas-phase measurements

Thermodynamic Model – ISORROPIA-II

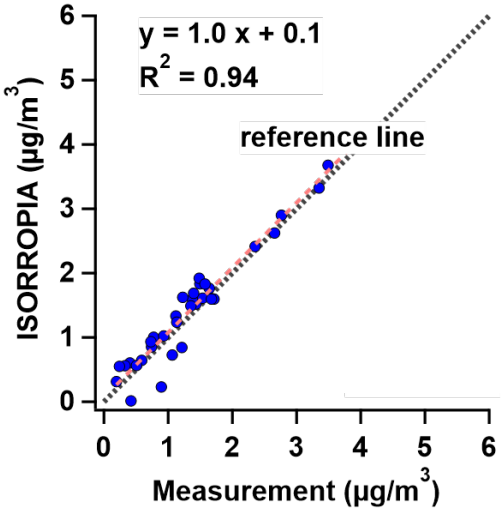


- ISORROPIA-II is a thermodynamic equilibrium model designed to simulate the partitioning of atmospheric inorganic aerosols and their precursor gases

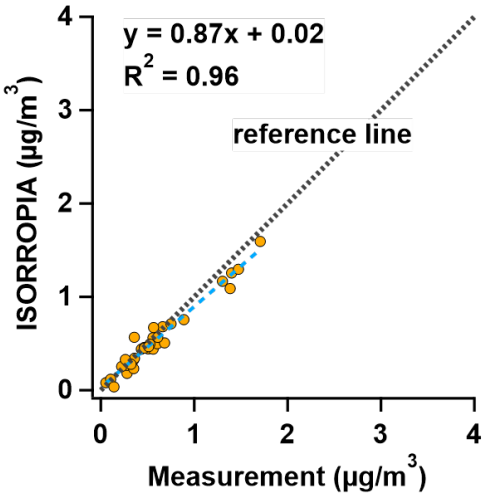
- Model additionally provides valuable insights into drivers of aerosol formation and can support air quality management strategies
  - Adjust precursor concentrations to estimate how $PM_{2.5}$ mass and composition change
  - Test different scenarios (e.g., reducing SO_2, NO_X, or NH_3 emissions) and evaluate their effectiveness in reducing $PM_{2.5}$

MACA
ISORROPIA-II Modeled vs. Measurements
URG Filters and Denuders

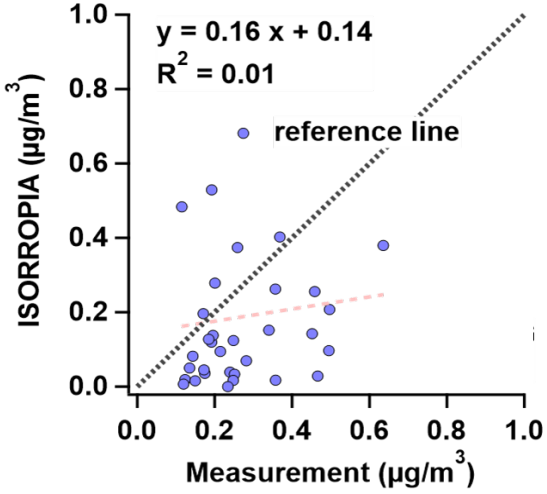
Nitrate



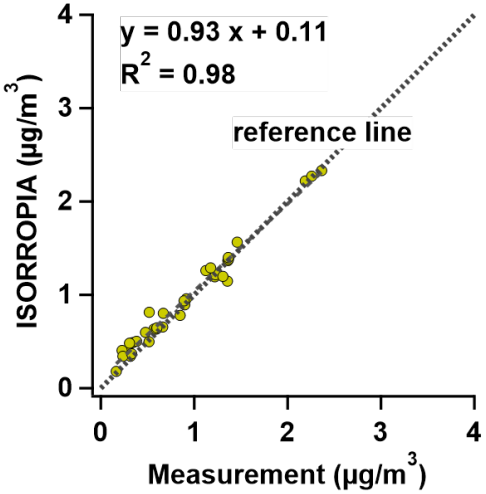
Ammonium



Nitric Acid



Ammonia

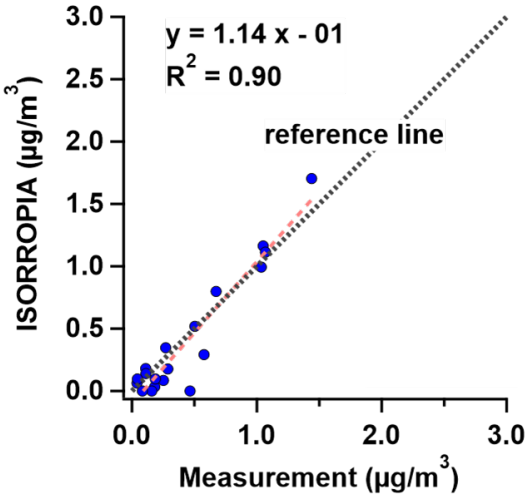


-Good agreement for nitrate, ammonium, and ammonia

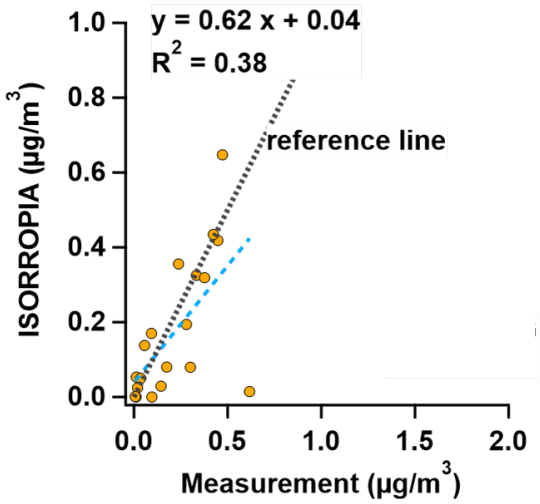
-Agreement not as good for nitric acid, possibly due to challenges with modeling low concentrations

GRSM
ISORROPIA-II Modeled vs. Measurements
URG Filters and Denuders

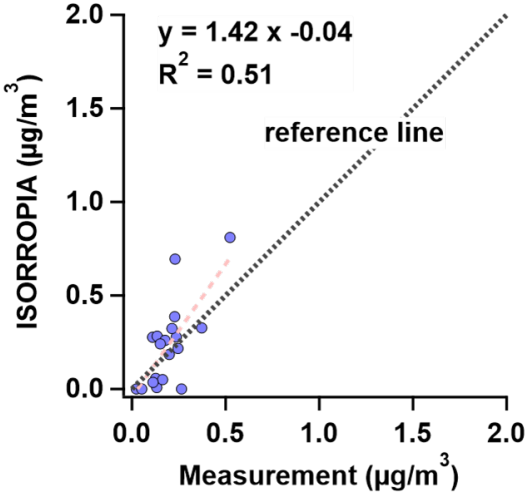
Nitrate



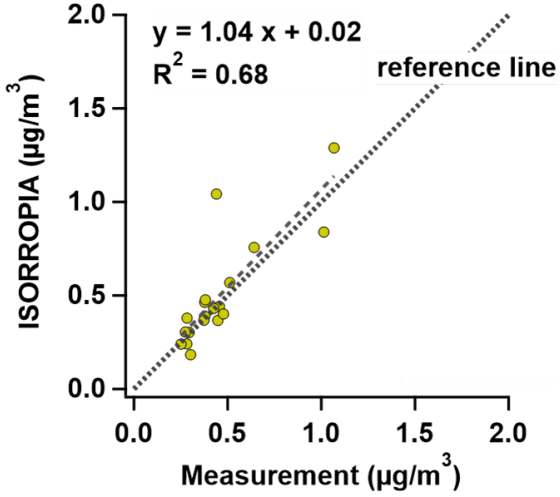
Ammonium



Nitric Acid



Ammonia

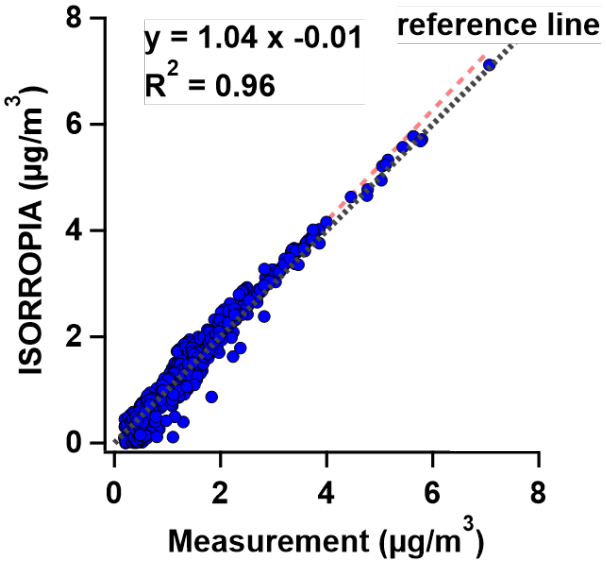


-Good agreement for nitrate and ammonia

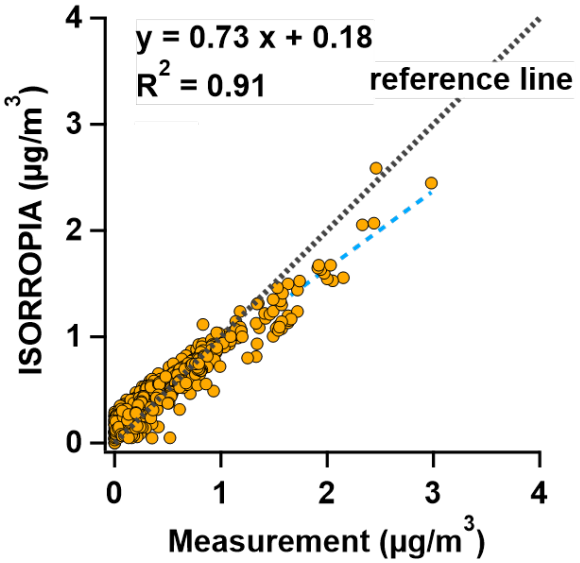
-Agreement not as good for lower concentration ammonium and nitric acid

MACA
ISORROPIA-II Modeled vs. Measurements
PILS and Picarro Ammonia

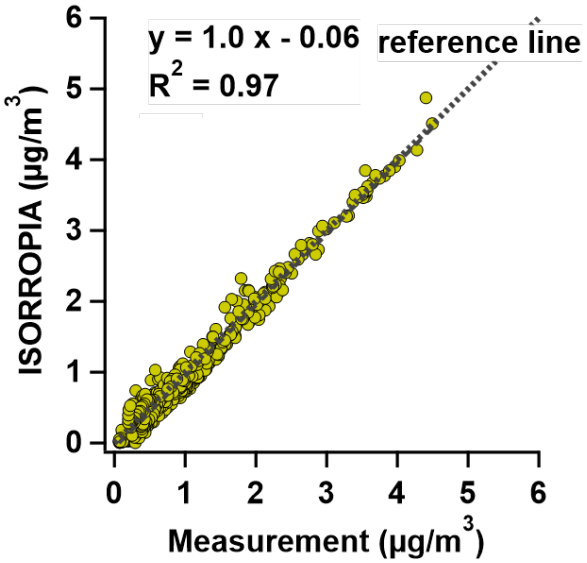
Nitrate



Ammonium



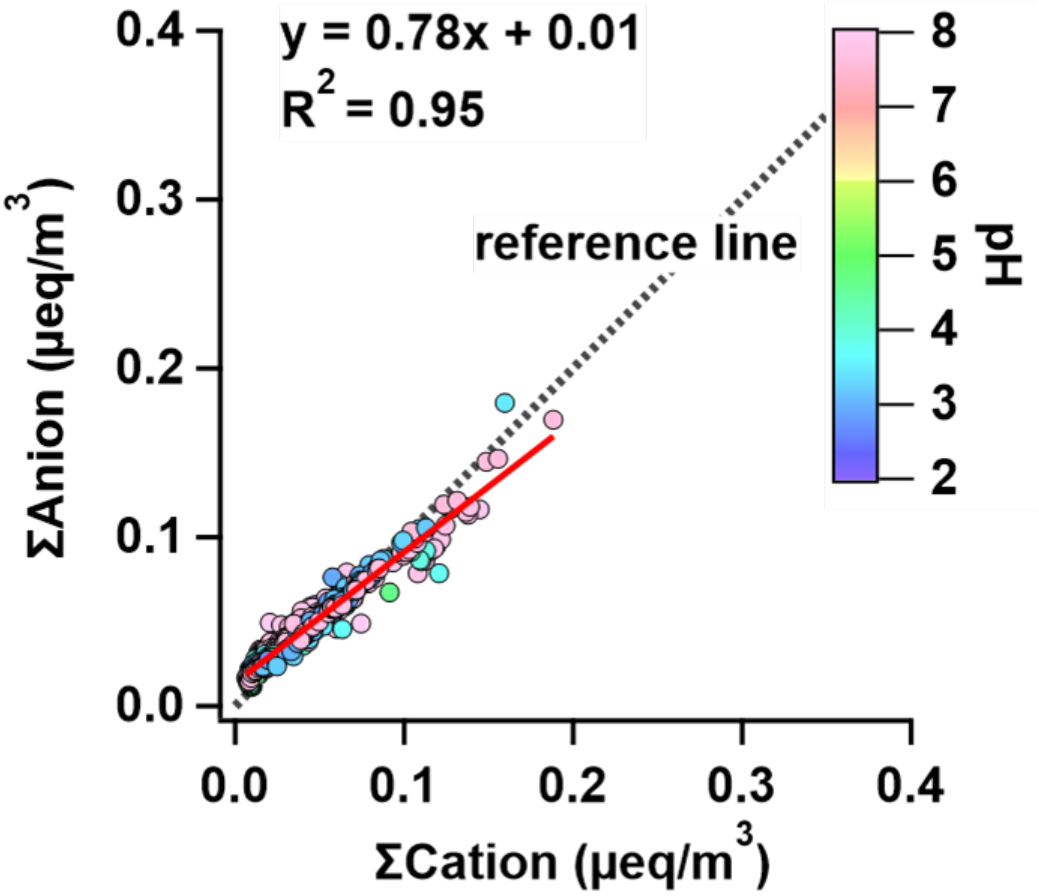
Ammonia



-Good agreement between model and measurement

-But model systematically underestimates the measured ammonium

MACA
ISORROPIA-II Modeled Sum of Anions vs. Cations



-Ion balance analysis reveals a persistent cation deficit, suggesting presence of missing cations or acids in model

Summary

- Wintertime nitrate consistently emerged as the dominant component of $PM_{2.5}$ at MACA and GRSM

- Nitrate-dominated episodes (Jan. 15–17) were linked to northwesterly air masses, while a transition to sulfate dominance (Feb. 4–6) reflected southeastern inflow

- ISORROPIA-II showed strong agreement with both URG and PILS measurements, confirming reliable model–measurement performance
  - ➢ This validation enables scenario-based simulations to assess precursor emission controls and their impacts on $PM_{2.5}$ composition

- Initial findings suggest that local thermodynamics, precursor availability, and regional transport jointly drive wintertime nitrate variability