Gas-particle partitioning of atmospheric ammonia at the CalNex-LA ground site

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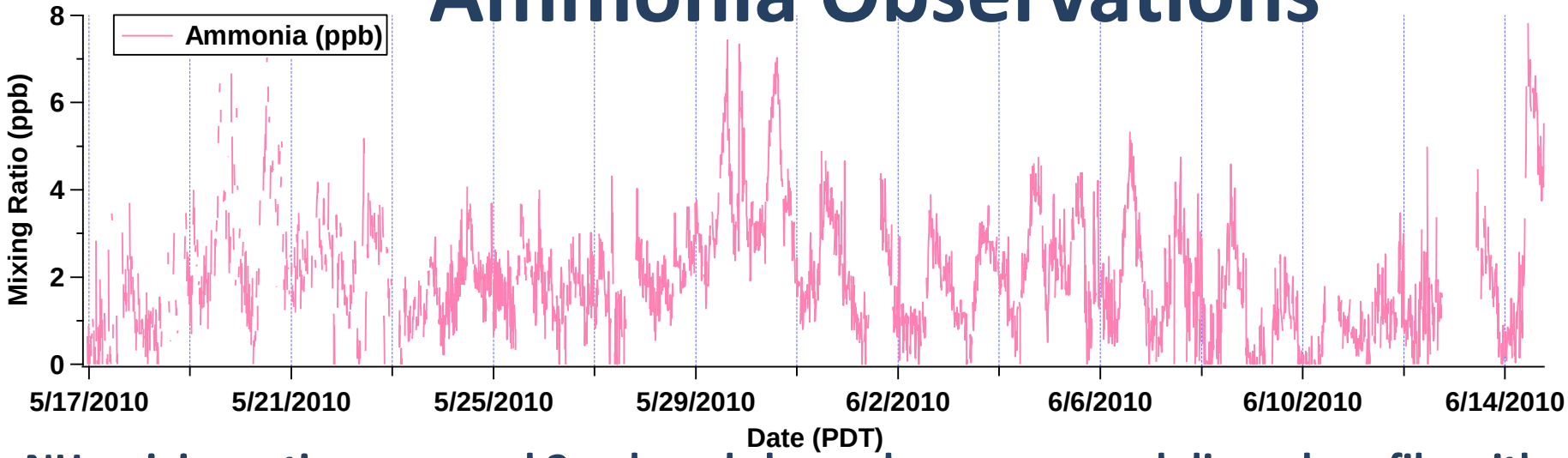
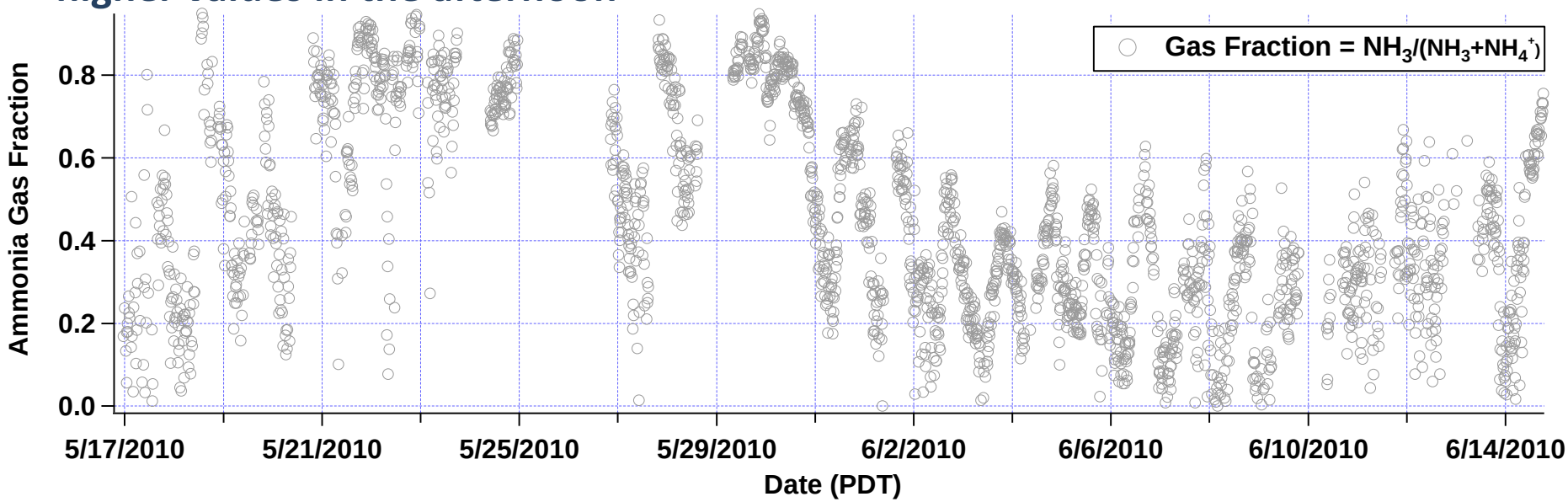
Ammonia Observations



- NH_3 mixing ratios averaged 2 ppb and showed a pronounced diurnal profile with higher values in the afternoon

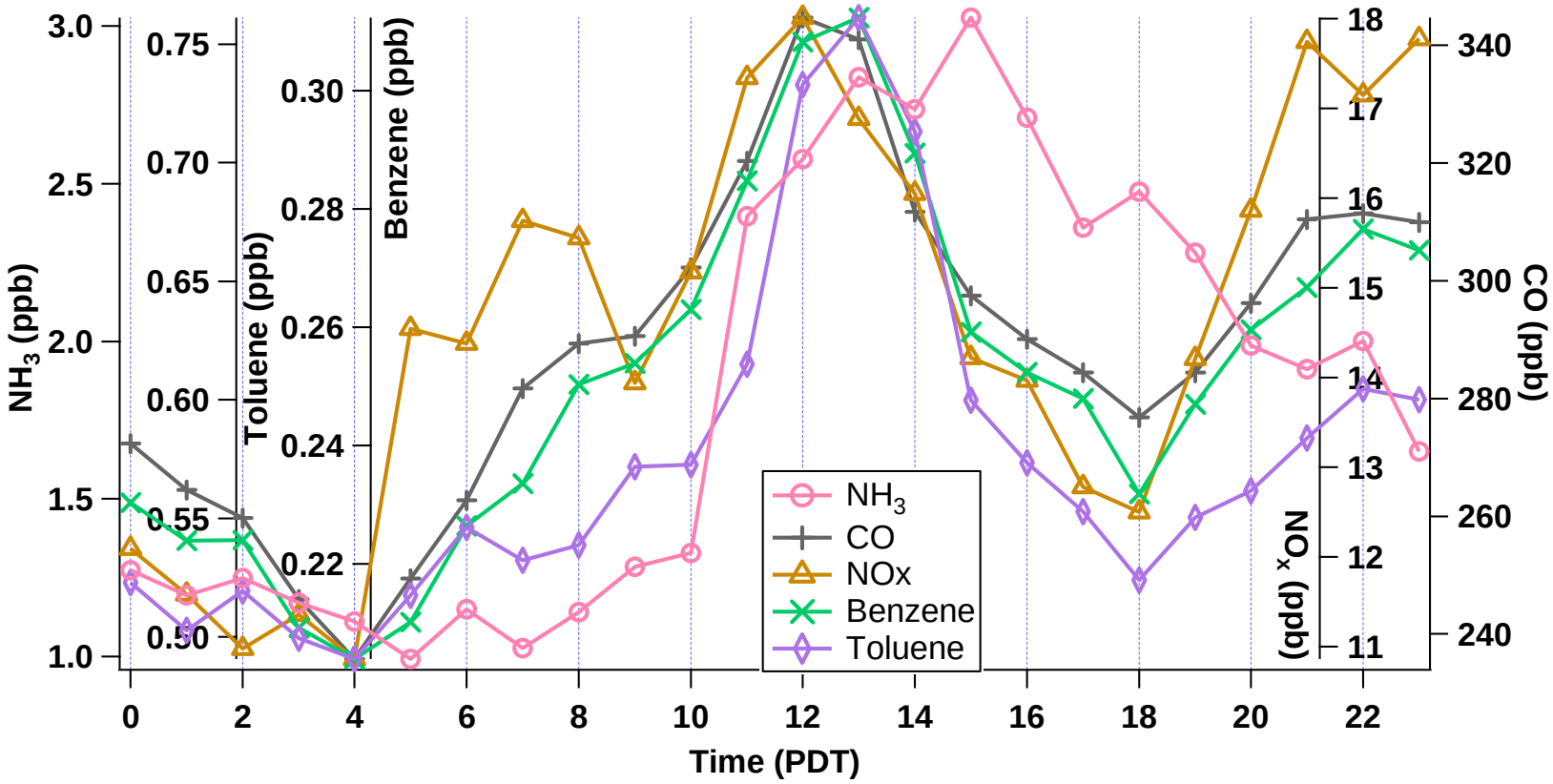


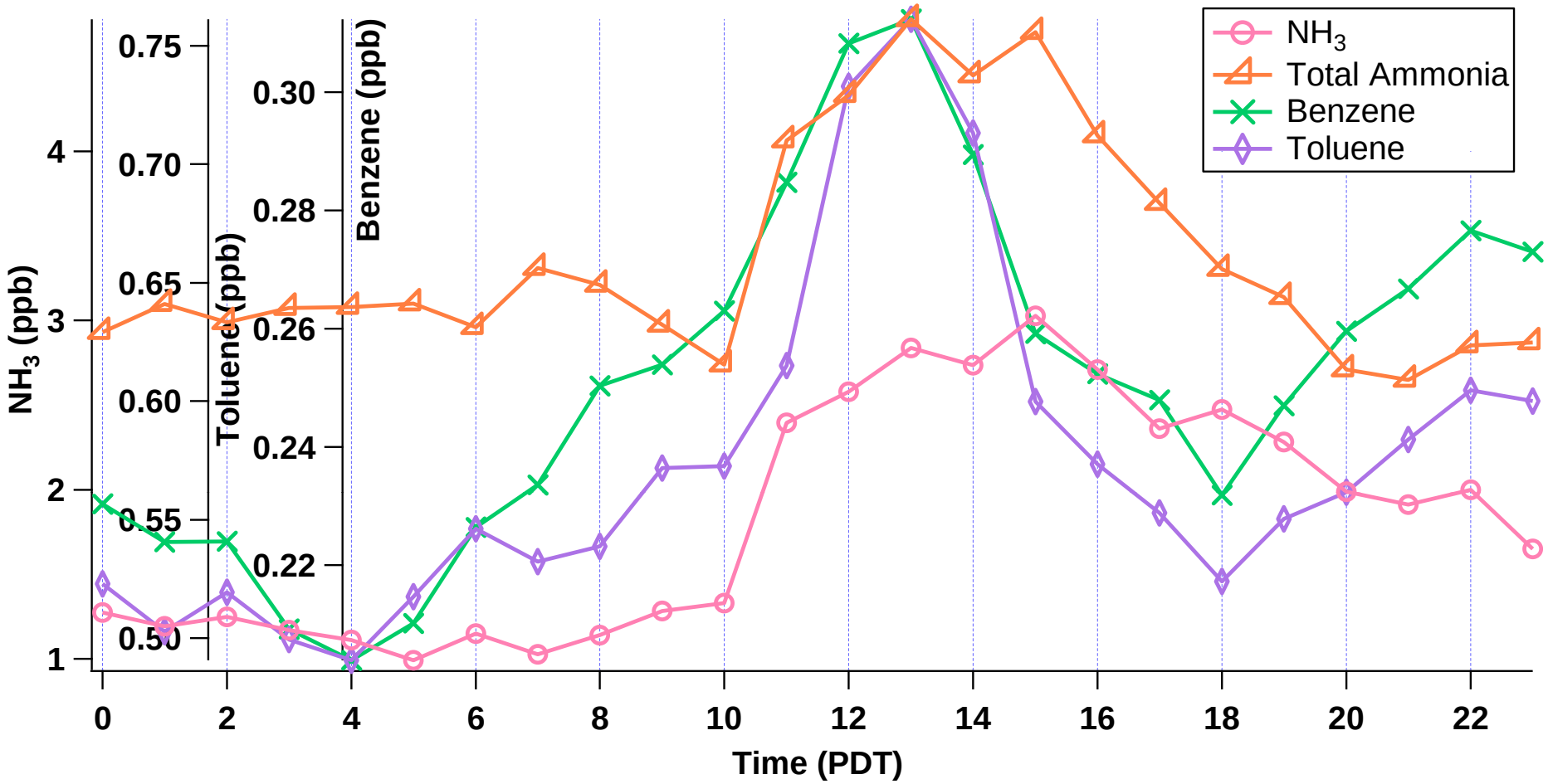
- NH_3 gas fraction shows two regimes with higher gas fractions in the beginning of the campaign and lower gas fraction towards the end of the campaign

Ammonia Traffic Analysis

Regression	Slope	Intercept	R
CO	0.0067	0.034	0.42
NO_x	0.027	1.67	0.16
Benzene	4.86	0.66	0.40
Toluene	1.73	0.93	0.36
CO_2	0.014	-4.03	0.13

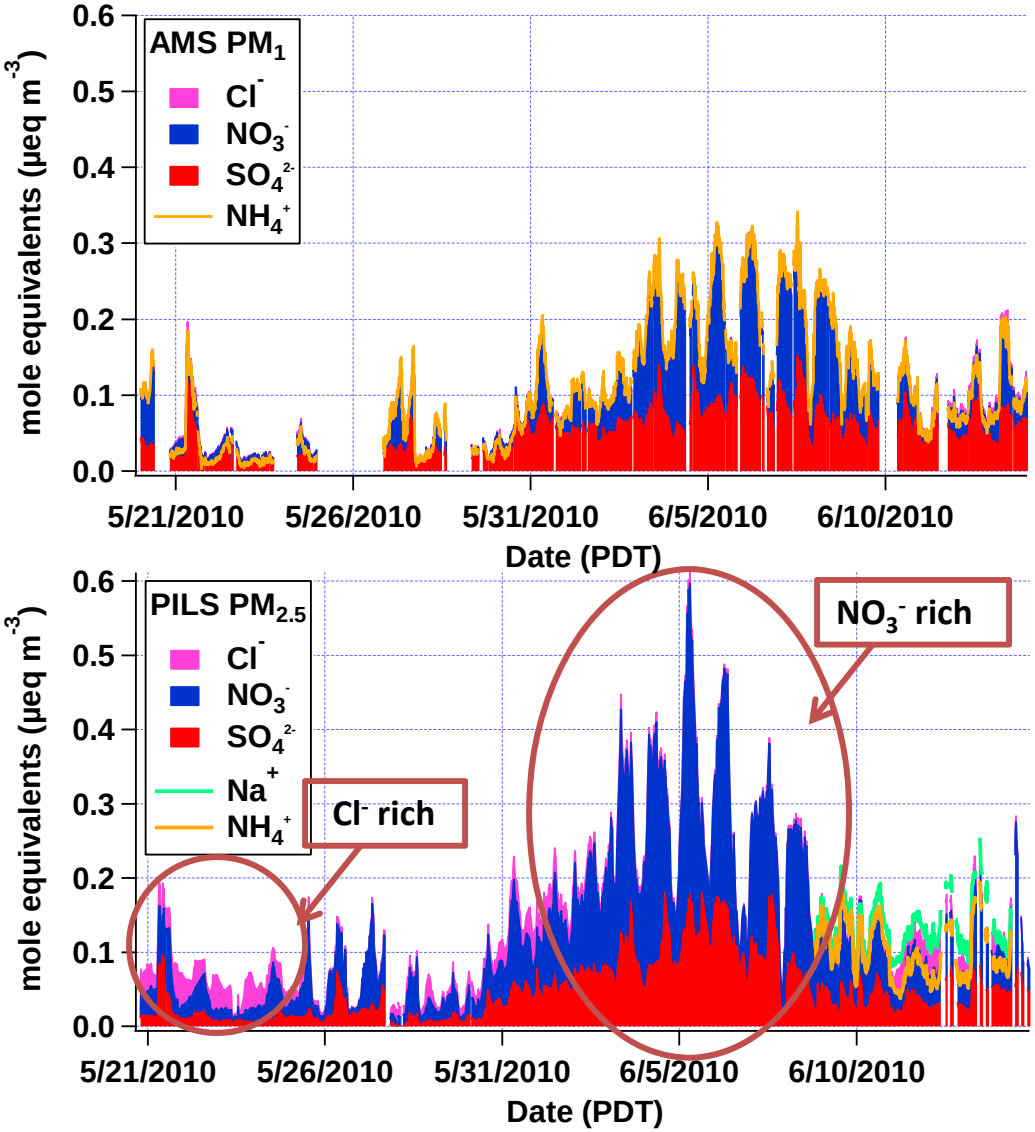
- **Little/no correlation was found between NH_3 and other traffic pollutants**
- **NH_3 peaks in the afternoon around 15:00, whereas traffic pollutants peak earlier between 12:00-13:00**





- NO_x is mainly attributed to diesel traffic, while NH_3 emissions arise from light duty vehicles equipped with three-way catalytic converters, and is best compared to Benzene and Toluene
- Since the majority of the traffic signal arises from LA traffic, which is transported to our site around noon, some NH_3 may be processed to NH_4^+ en route, thus total ammonia (NH_3+NH_4^+) may match traffic pollutants better

Aerosol balance



- AMS ~PM_1

→NH_4^+ sufficient to account for equivalents of SO_4^{2-} and NO_3^- for the most part

→formation of NH_4NO_3 from June 3 to June 9

- PILS $PM_{2.5}$

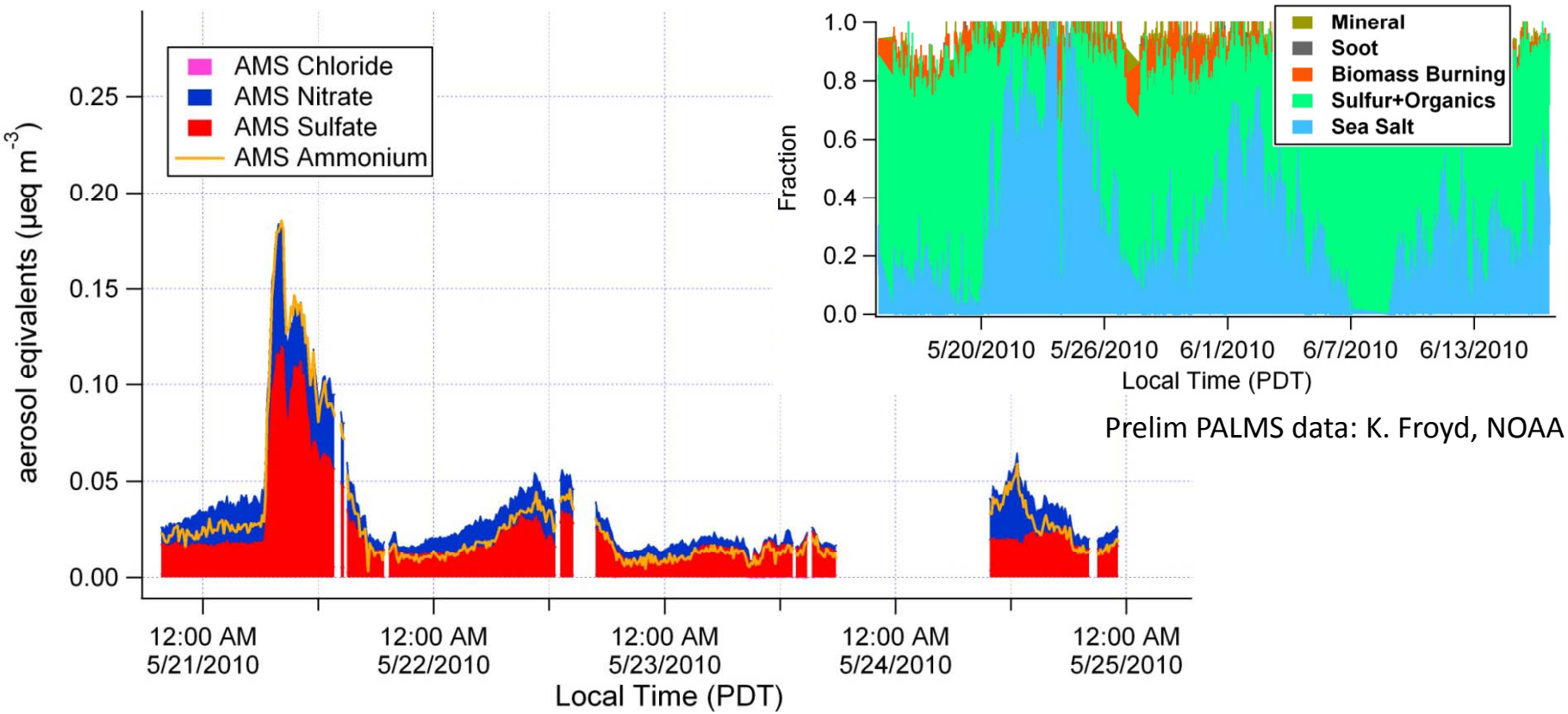
→more NO_3^- than in the smaller size fraction

→no cation data to indicate if it was neutralized by NH_4^+

→high Cl^- in larger size fraction pointing to presence of NaCl

Prelim AMS data: J. Jimenez, CU Boulder
Prelim PILS data: R. Weber, Georgia Tech

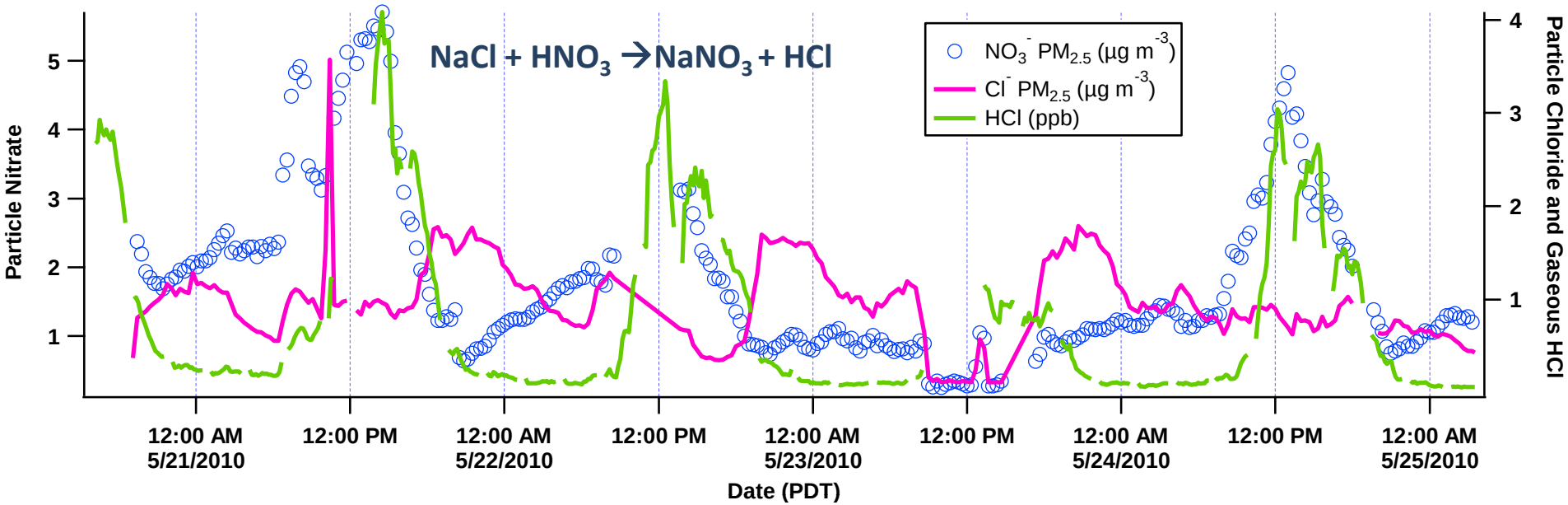
Chloride-rich period



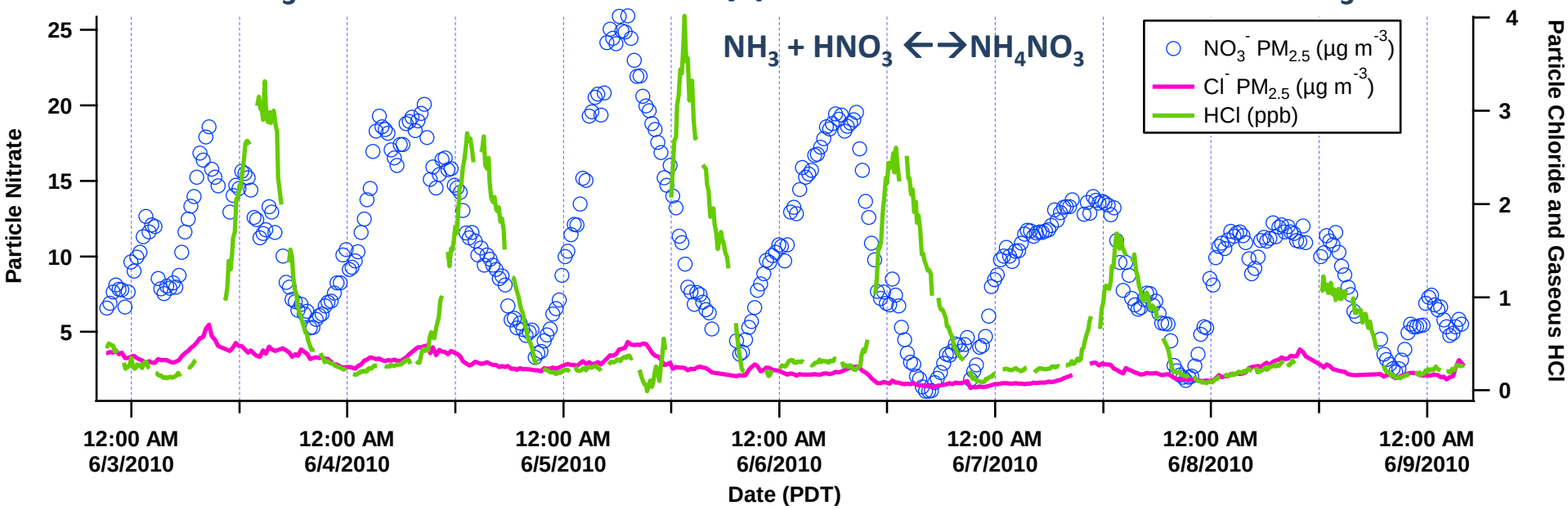
Prelim PALMS data: K. Froyd, NOAA

- **No cation data for PILS $PM_{2.5}$ but AMS suggests observed NO_3^- exceeds observed equivalents of NH_4^+ between May 21-25**
- **Also measured the highest fraction of sea salt in aerosol from PALMS**
- **NO_3^- may be associated with Na^+ from the acid displacement reaction:**

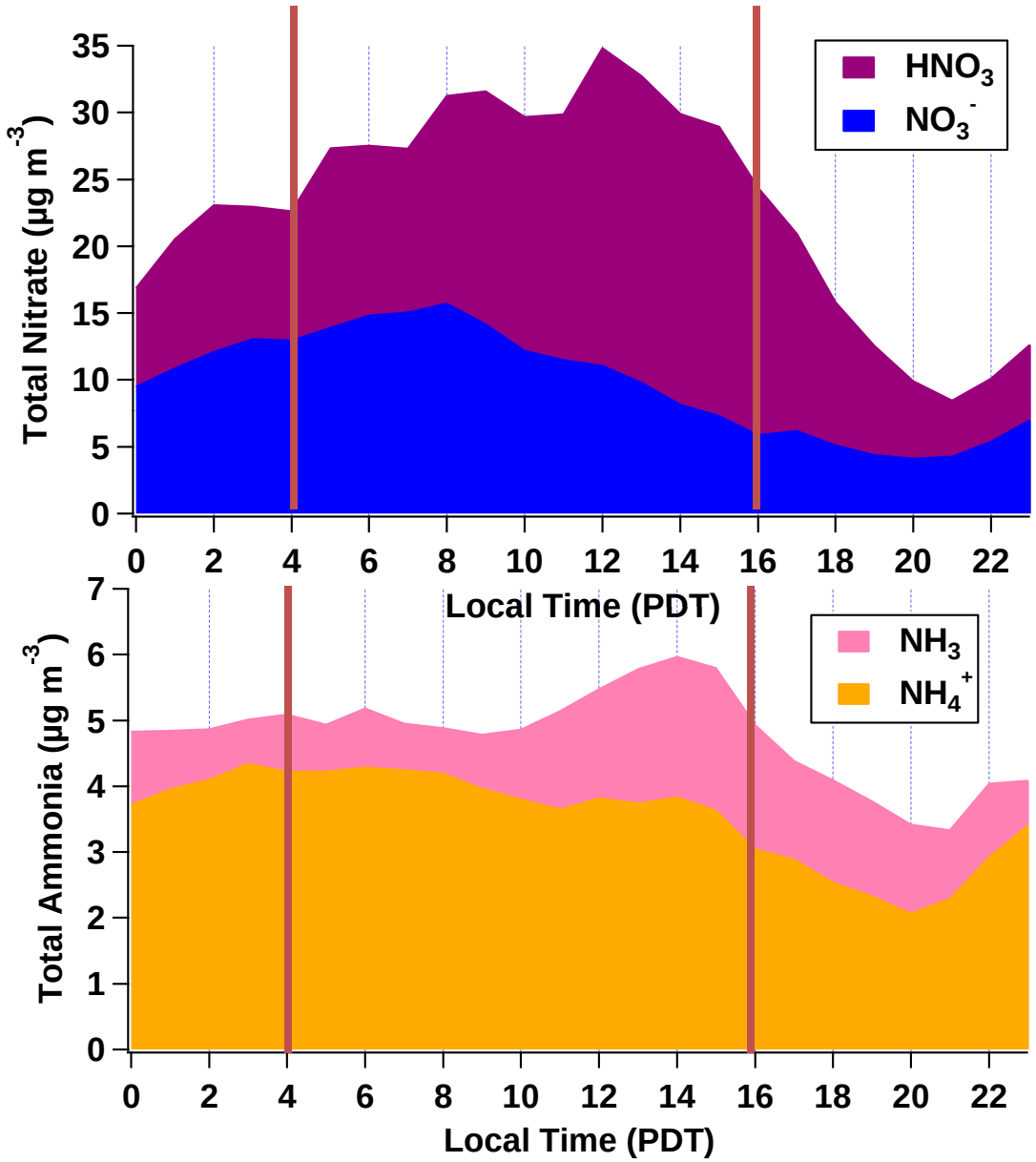
$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$$



- We observe a decrease in Cl^- and increase in NO_3^- and HCl
- In contrast with the nitrate-rich period below, here NO_3^- and HCl do not correlate, and the NO_3^- measured is more likely produced from reaction with NH_3



Nitrate- rich period



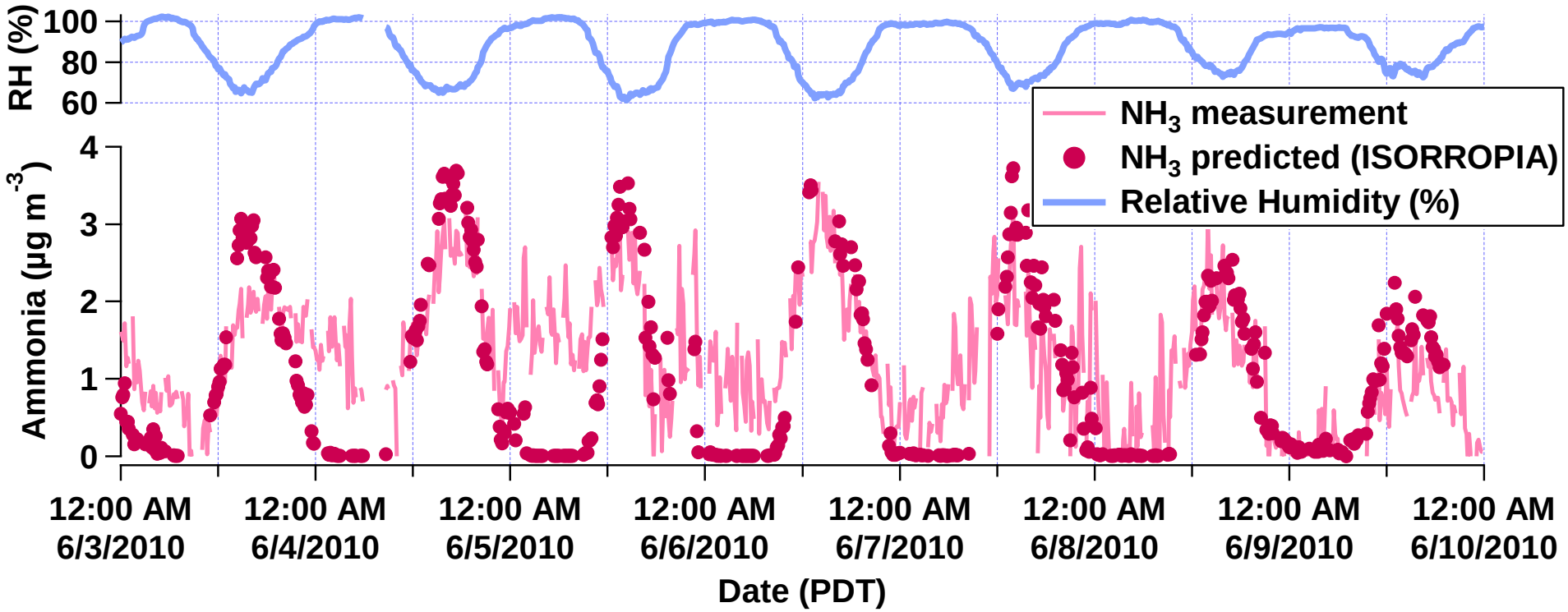
- Total Nitrate (TN)
  $= HNO_3\ (g) + p\ NO_3^-$
- Total Ammonia (TA)
  $= NH_3\ (g) + p\ NH_4^+$
- TA < TN, NH_3 limiting factor in formation of NH_4NO_3
- TA and TN same at 04:00 and 16:00, but shifts from particle phase to gas phase

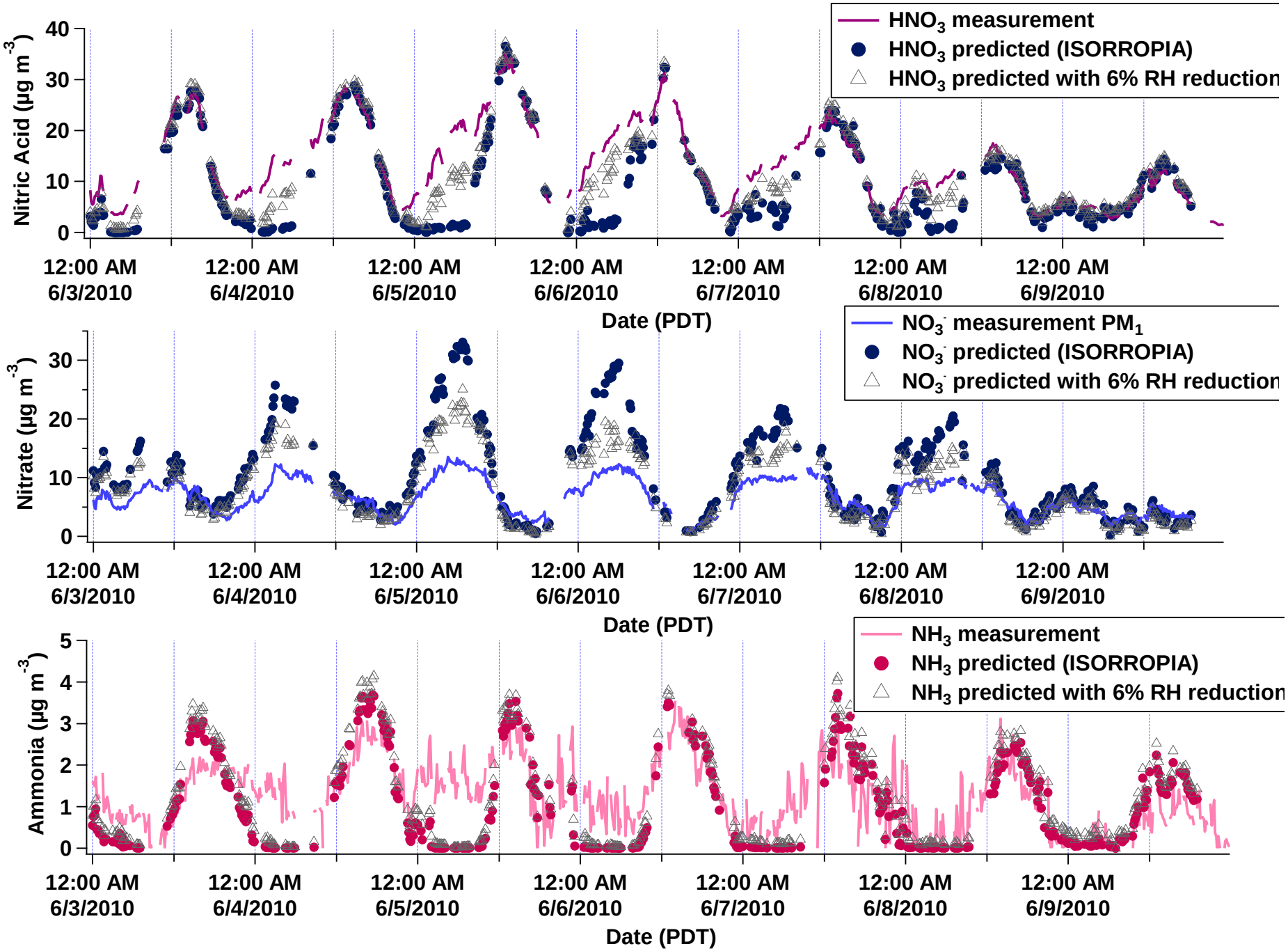
$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$$

- Partitioning due to higher temperatures in the afternoon

ISORROPIA predictions

- Repartitioning measurements of TA, TN and SO_4^{2-} yield good results, except when there are appreciable amounts of NO_3^- at night
- ISORROPIA predicts zero gas phase NH_3, HNO_3 and overestimates NO_3^- at night
- Relative humidity at night was extremely high (~100 %), and RH probe may be inaccurate at such high RH
- Re-ran ISORROPIA, each time decreasing the measured RH by 2 %, up to 10 %





Approach successful with HNO_3 and NO_3^-, but made little difference to NH_3