

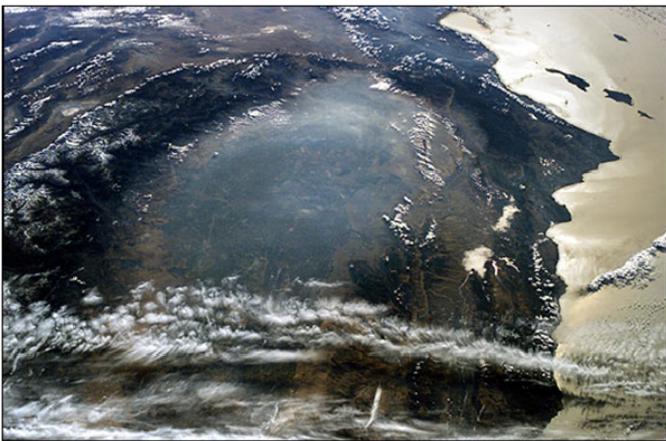
Measurements of soluble composition of fine atmospheric particulate matter (PM_{2.5}) and associated precursor gases in Bakersfield, CA during CalNex 2010



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- To make simultaneous measurements of $\text{PM}_{2.5}$, NH_4^+ , NO_3^- , and SO_4^{2-} and gas phase NH_3 and HNO_3 in Bakersfield, CA.
- To investigate if gas/particle partitioning is responsible for traditionally low summertime $\text{PM}_{2.5}$ levels at this location.
- Hypothesis: Very high $\text{NH}_{3(g)}$ and $\text{HNO}_{3(g)}$ concentrations are expected in the summertime due to particle-to-gas partitioning (dissociation) of semi-volatile ammonium nitrate in low RH and high T conditions.



San Joaquin Valley(SJV), CA

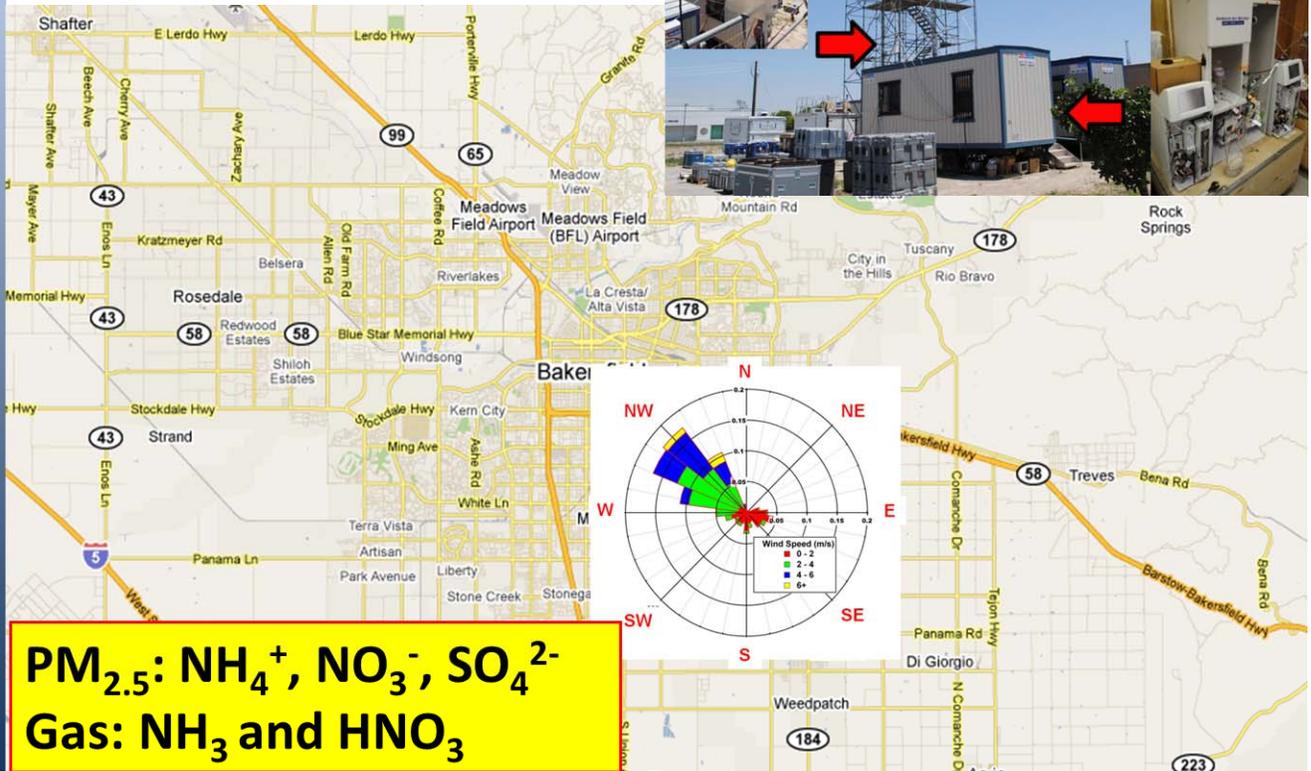


Bakersfield, CA

EXPERIMENTAL – CalNex 2010

Bakersfield, CA

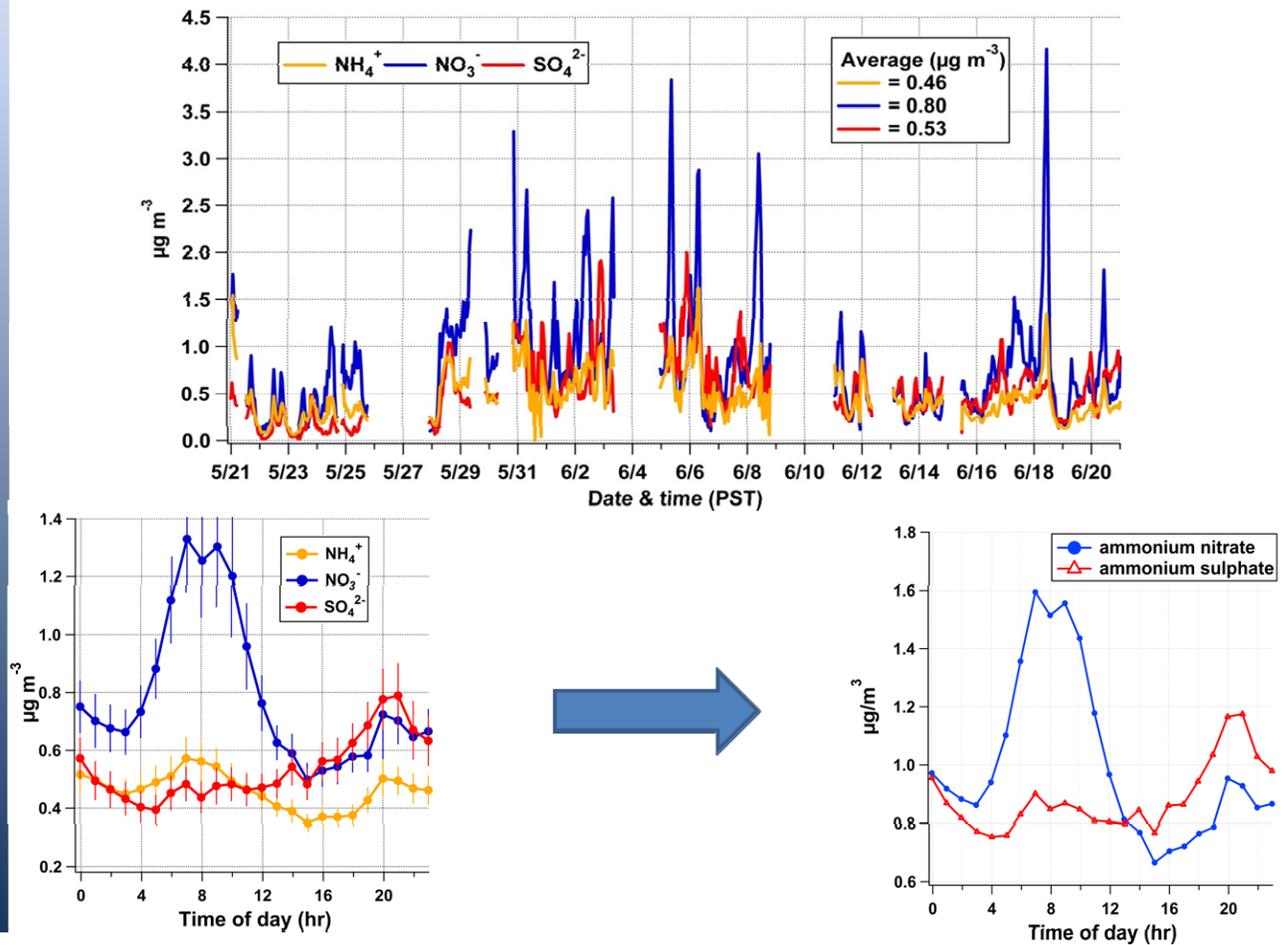
May – June 2010



- The sampling site was downwind of major highways and Bakersfield downtown core.
- A modified Ambient Ion Monitor- Ion Chromatograph (AIM-IC) from URG/Dionex was utilized to make hourly measurements of PM_{2.5} ammonium, nitrate, sulphate and gas phase ammonia and nitric acid among other chemical species.
- The main body of the instrument was housed inside of the trailer and the sampling inlet was on the tower (~ 4.5 m above ground).
- Analyses was carried near real-time with a 2 hr delay.



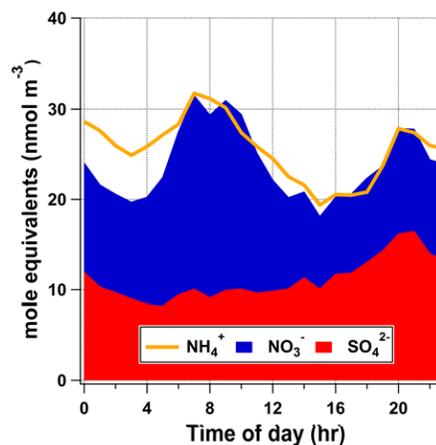
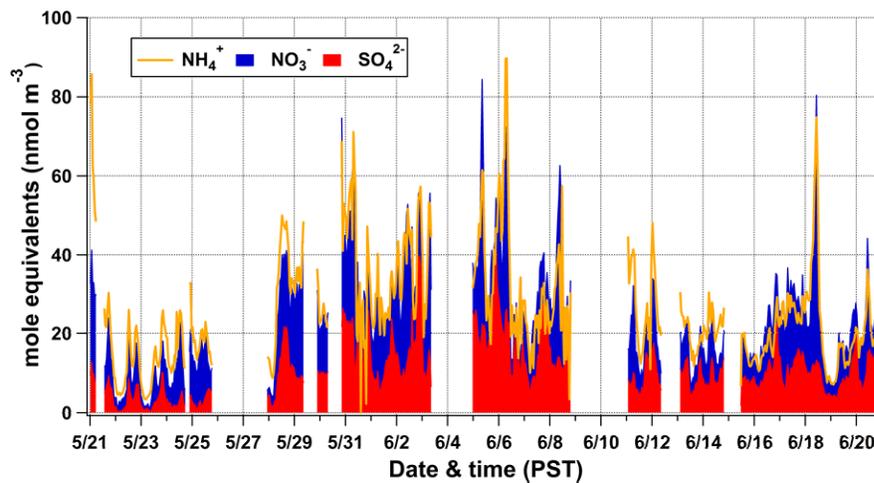
RESULTS – PM_{2.5}



- Overall, very low mass loadings of soluble PM_{2.5} were observed.
- PM_{2.5} nitrate was the most dominant component by mass.
- Sulphate was significantly lower compared to east coast which is consistent with the absence of major SO₂ sources in SJV.
- The time-of-day plots suggest that ammonium nitrate was the more dominant chemical species in the morning and ammonium sulphate in the evening.



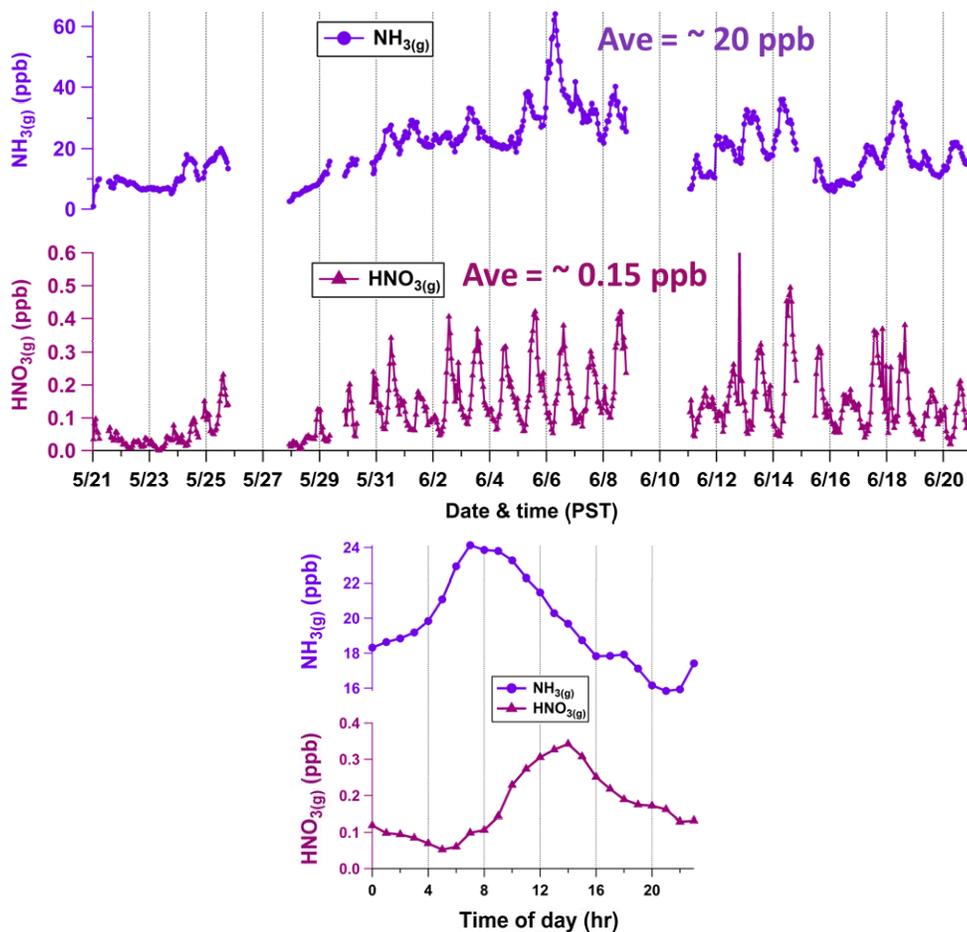
RESULTS – PM_{2.5} neutralization



- Nitrate mol eq. were “stacked” on top of sulphate mol eq. and ammonium mol eq. were plotted independently.
- For most part ammonium mol eq. were higher than or equal to the sum of nitrate and sulphate mol eq.



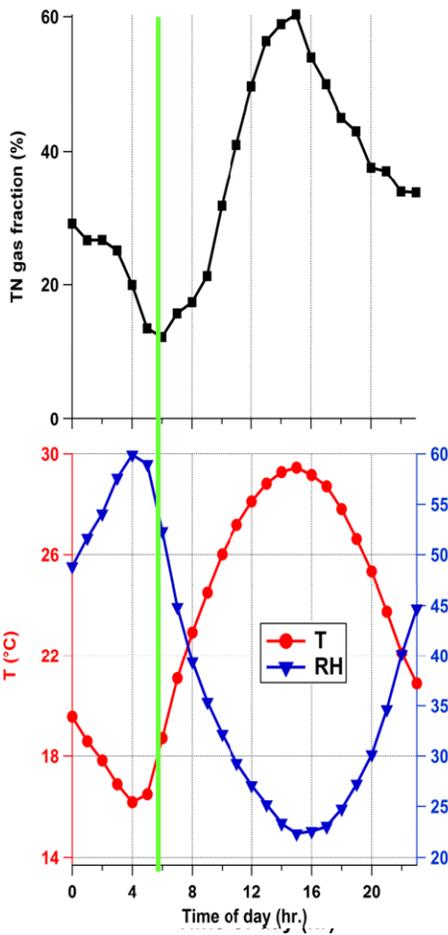
RESULTS – NH_{3(g)} and HNO_{3(g)}



- Very high NH_{3(g)} mixing ratios (max > 60 ppb)
- Very low mixing ratios of HNO_{3(g)} (max < 0.6 ppb)
- NH_{3(g)} maximized in the early morning most likely due to fresh emissions into a still shallow boundary layer.
- HNO_{3(g)} maximized in the early afternoon mostly due to particle-to-gas partitioning of nitrate.



RESULTS – The partitioning



$$\text{TN gas fraction} = \frac{\text{HNO}_{3(g)}}{\text{HNO}_{3(g)} + \text{NO}_3^-(\text{aq,s})} * 100 \%$$



FREE AMMONIA

$$\text{FA} = \text{TA} - 2 * \text{TS}$$

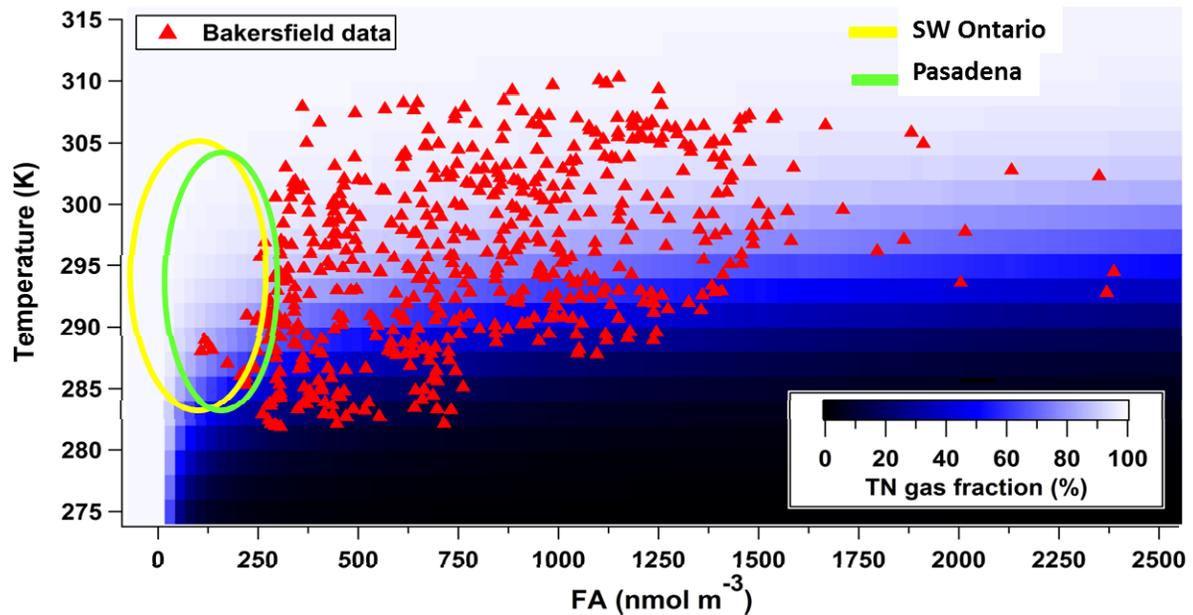
$$= [\text{NH}_4^+] + [\text{NH}_3(\text{g})] - 2 * [\text{SO}_4^{2-}]$$

FA > 0, NO₃⁻(aq,s) formation favorable

FA < 0, NO₃⁻(aq,s) formation not favorable

- TN gas fraction increased with increase in T and decrease in RH and vice versa.
- Partitioning of nitrate between particle and gas phase definitely occurred and could explain increases in HNO_{3(g)} mixing ratios in the early afternoon.

RESULTS – FA CHEMICAL MAP



Conditions:

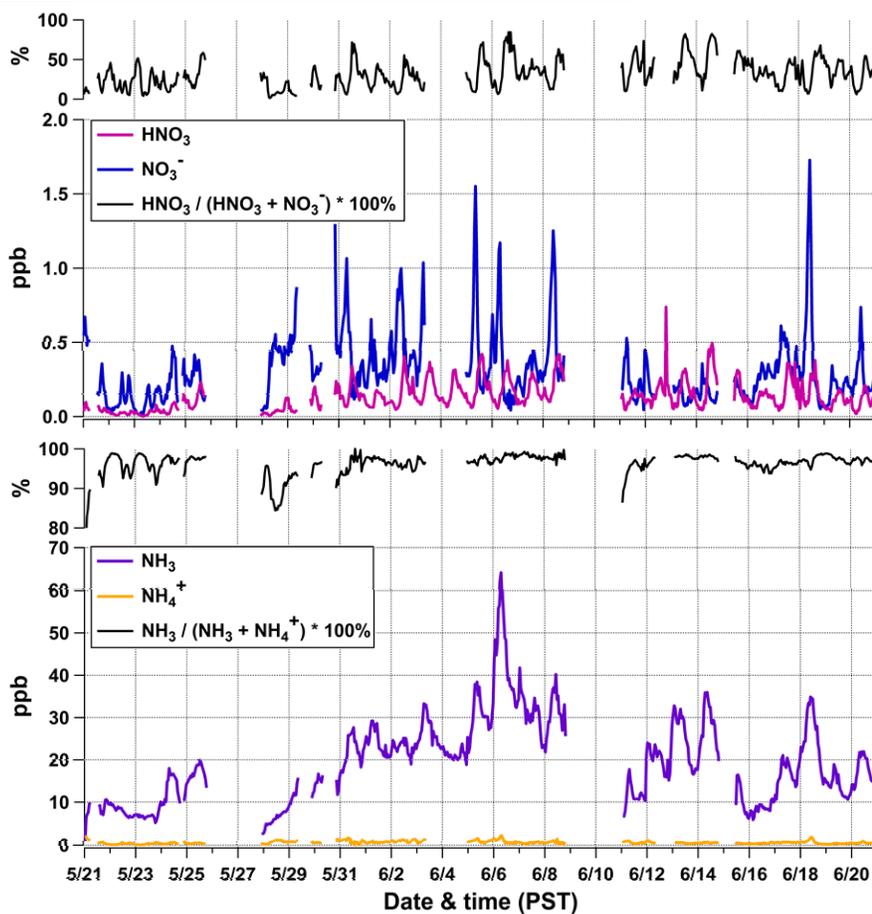
$T = 275 - 315$, $RH = 40\%$, $TN = 20 \text{ nmol m}^{-3}$, $TS = 21 \text{ nmol m}^{-3}$, $TA = 0 - 2750 \text{ nmol m}^{-3}$
 $FA \text{ values during the campaign} = (-42 \text{ nmol m}^{-3} \text{ to } 2750 \text{ nmol m}^{-3})$

- 1) Markovic *et al* 2011, *Atmos. Chem. Phys.*
- 2) Nenes *et al.*, 1998, *Aq Geochem*

- FA chemical map¹ was generated by utilizing ISORROPIA² to re-partition semi-volatile ammonium nitrate between the gas and the particle phase according to thermodynamic equilibria under campaign-relevant (see above) chemical and meteorological conditions. Temperature and FA values were varied so that we can simulate the partitioning of nitrate over the range of T and FA values.
- In Bakersfield, partitioning of nitrate was mainly controlled by T because FA values were very high.
- In Pasadena and SW Ontario, both FA and T controlled the partitioning of nitrate (much lower TA and hence FA at these locations).



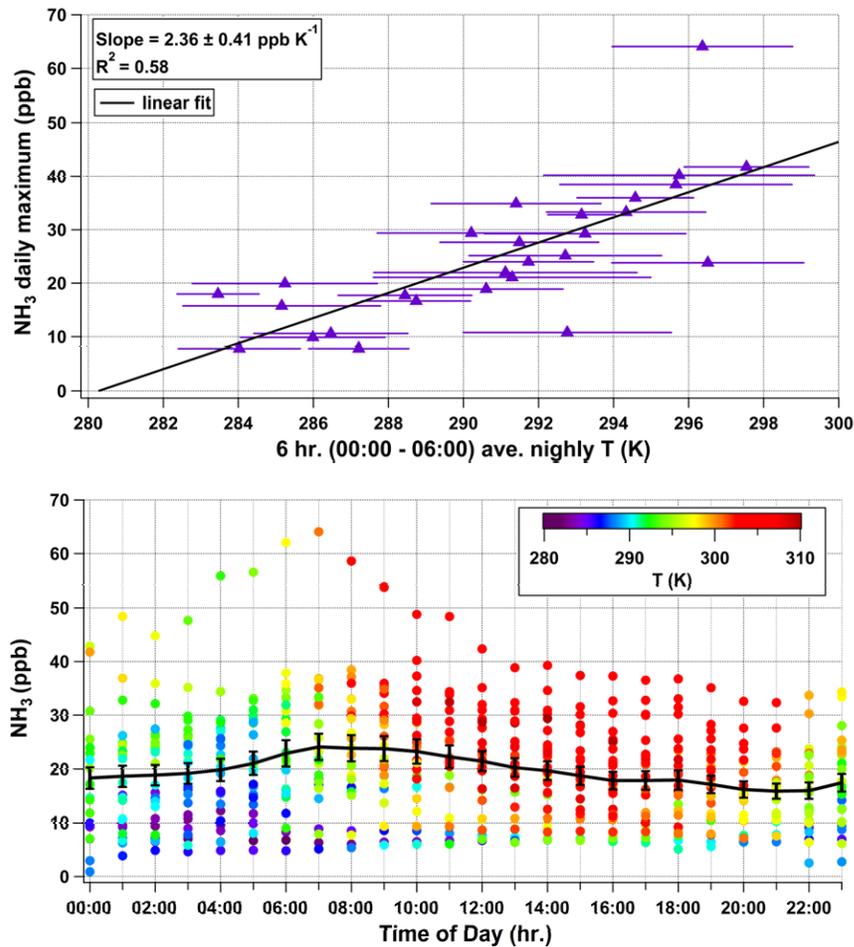
RESULTS – TN and TA



- Significant levels of TN were present in both gas and particle phase. On average, TN was $\sim 35\%$ $\text{HNO}_{3(g)}$ and $\sim 65\%$ NO_3^- .
- TA was almost exclusively in the gas phase ($\text{NH}_{3(g)} > 90\%$ of TA).



RESULTS – NH_{3(g)}



- Daily maxima of NH_{3(g)} were well correlated ($R^2 = 0.58$) with the 6 hour averages of previous night's temperatures.
- Day-to-day variability in NH₃ mixing ratios was correlated to day-to-day variability in temperature for the same time of day.



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