

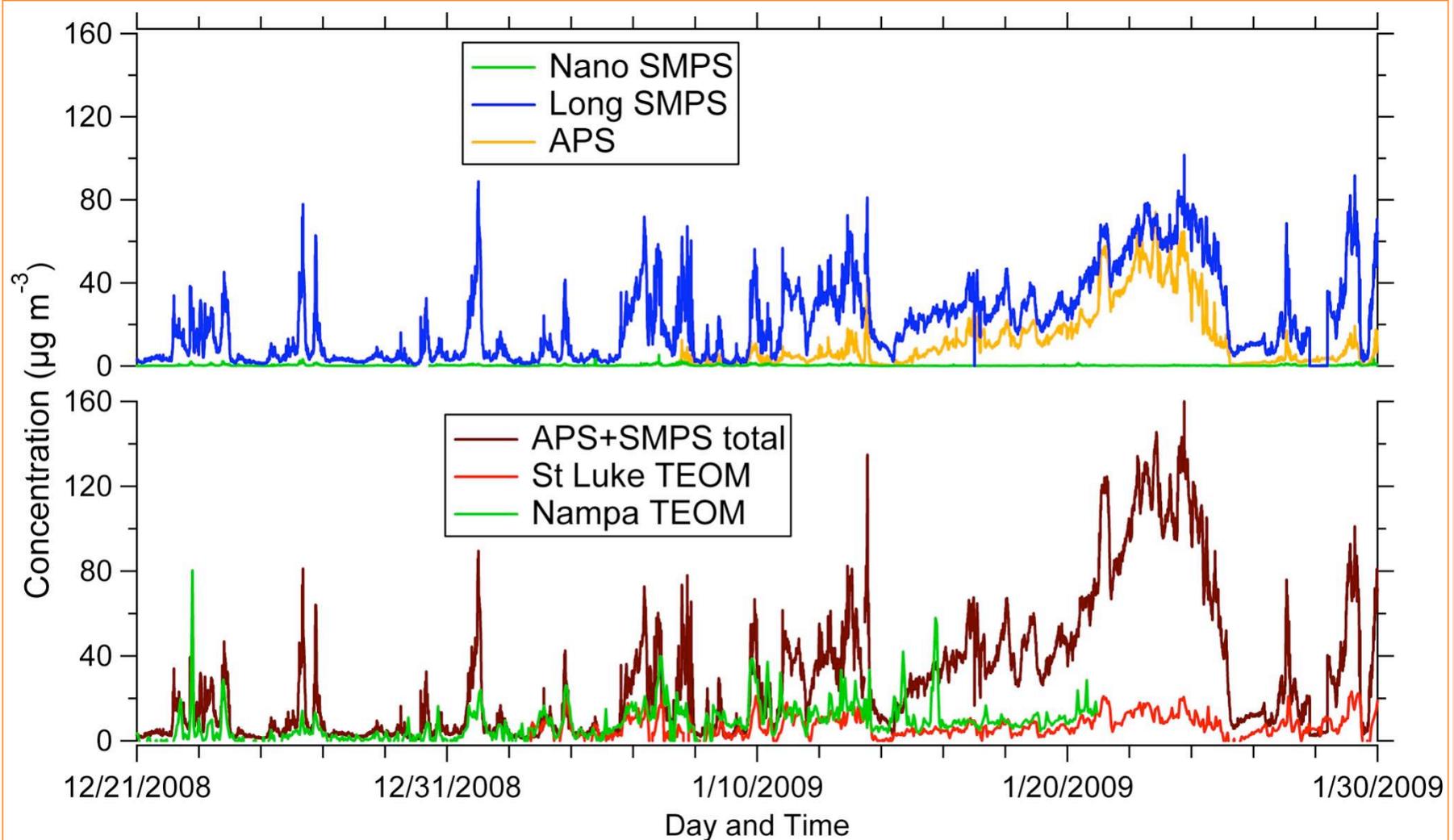
WINTERTIME FORMATION OF PARTICULATE NITRATE

Results based on the
Treasure Valley PM_{2.5} Precursor Study
in December 2008 / January 2009

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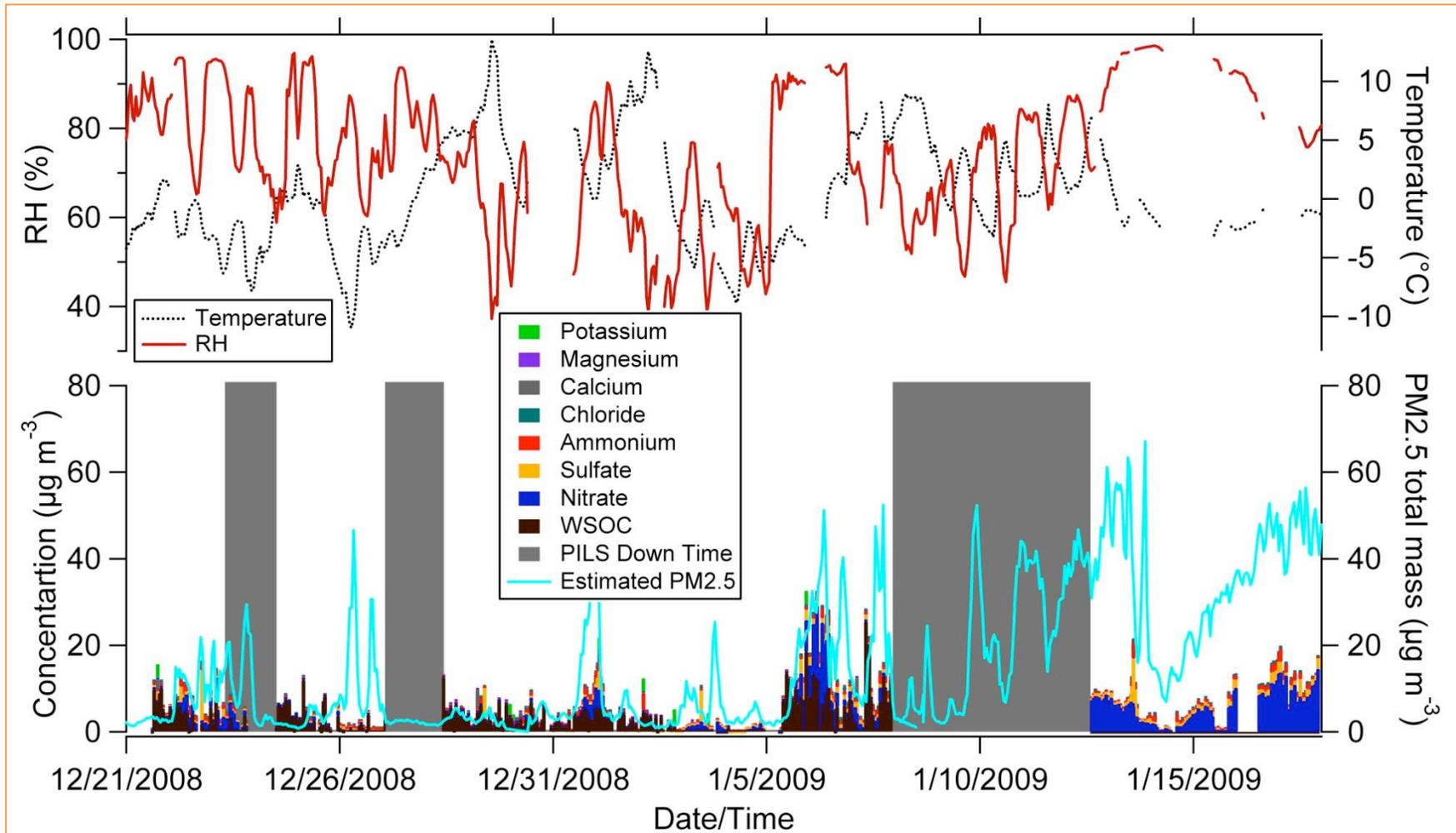


The high temperature difference between the ambient air and the TEOM heated inlet could have led to the evaporation of volatile aerosol mass.

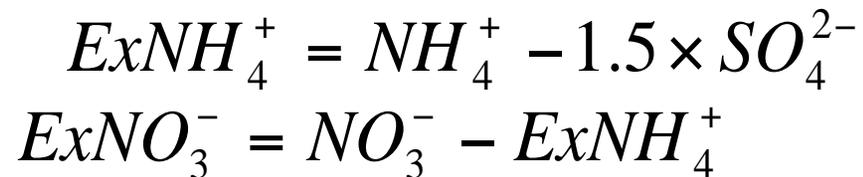
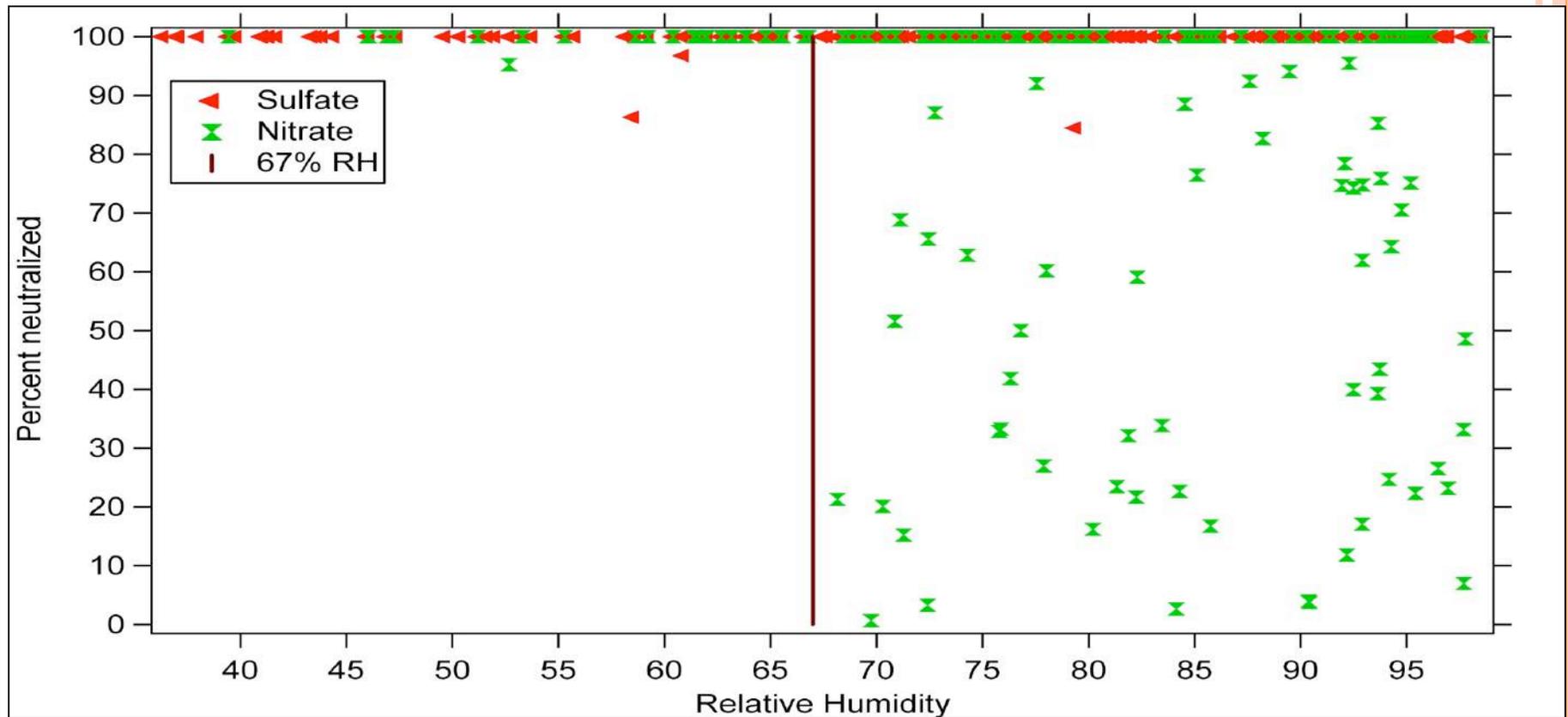


- 1: Calculations assume a particle density of 1.5 g/cc.
- 2: Represents SMPS total only when APS was not operating.

PILS Data: The ionic mass of $PM_{2.5}$ showed a strong correlation with relative humidity, especially nitrate.



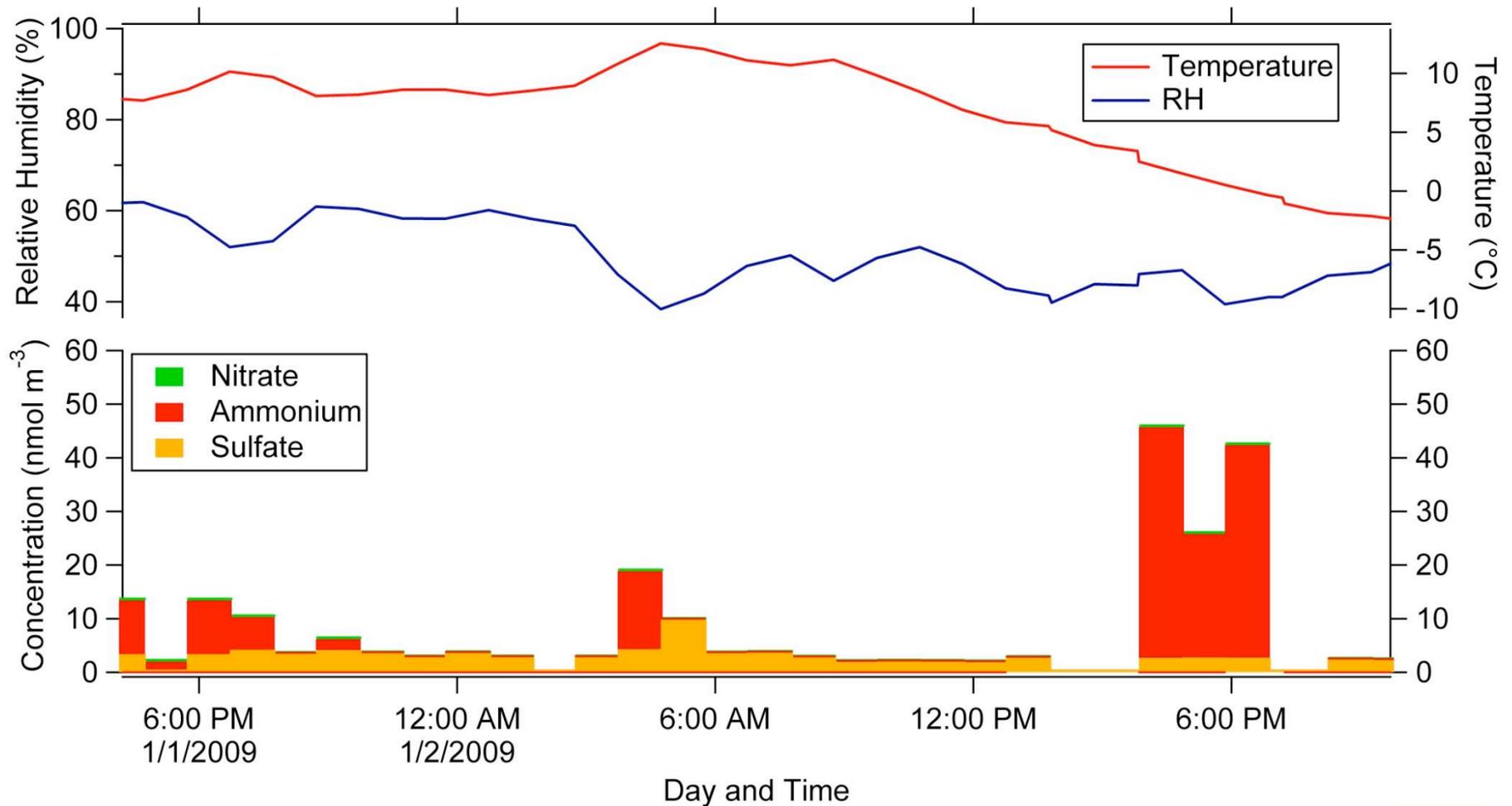
Above 67% RH, Excess Nitrate Concentrations Increased Considerably.



Pathak et al, 2009

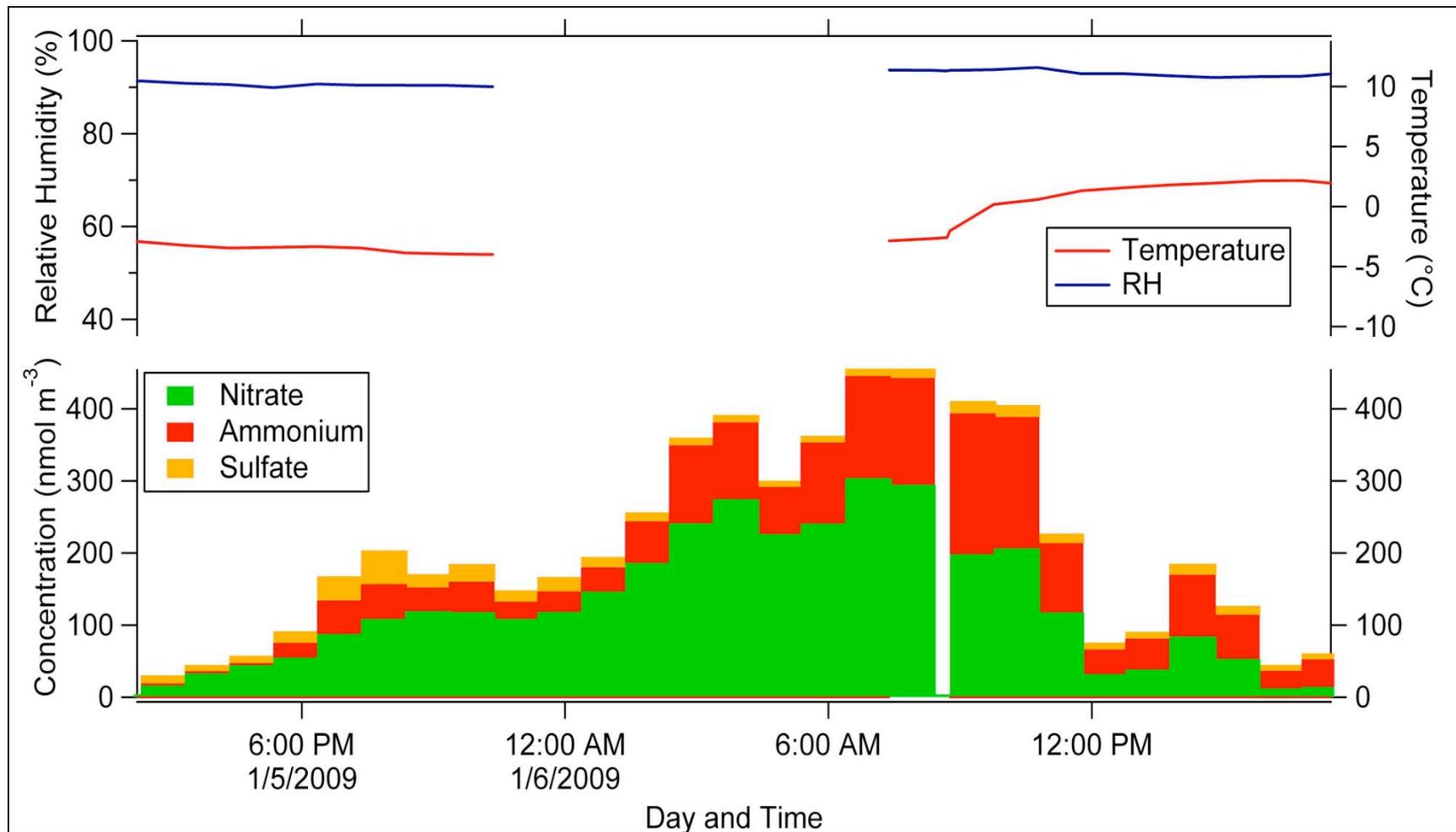
Pathak, R.K., Wu W.S., and Wang T. 2009. Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmos. Chem. Phys.* 9,1711-1722

LOW RH PERIOD



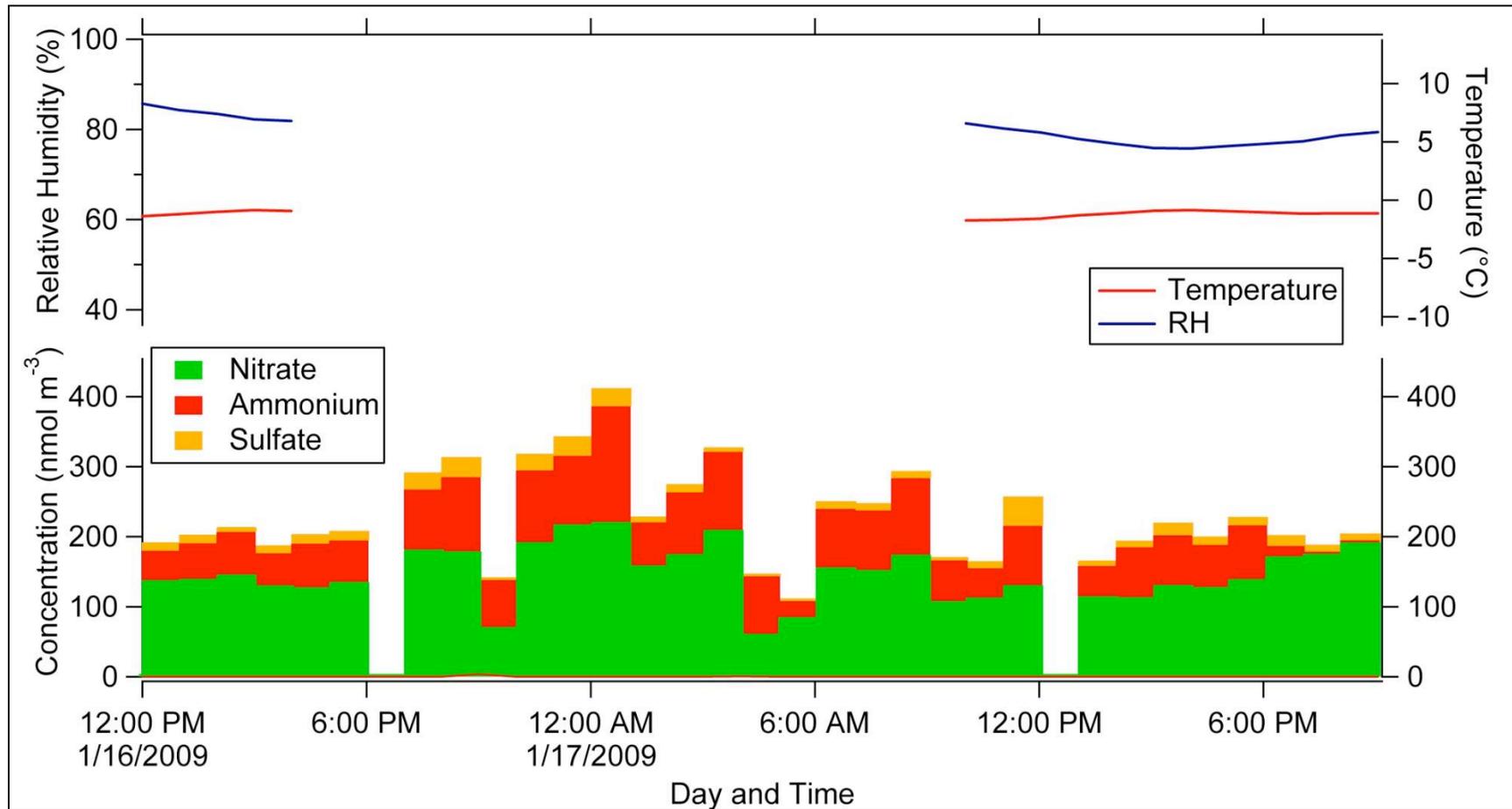
Sulfate was the dominant species in the Aerosol mass with a few spikes of ammonium.

HIGH RH PERIOD BEFORE THE STAGNATION



Excess nitrate was evident during this period especially at night.

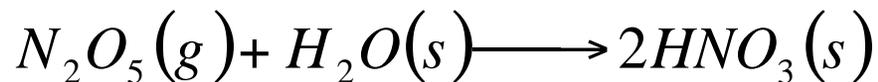
HIGH RH DURING THE STAGNATION EVENT



Ammonium and nitrate concentrations increased but sulfate remained unchanged.

GOVERNING REACTIONS

- Nighttime chemistry.



- NO₃ is a major atmospheric oxidant during the night.
- At low temperatures the reversible reaction equilibrium favors the production of N₂O₅.
- The heterogeneous hydrolysis of N₂O₅ can account for up to 50 % of annual removal of NO_x. (Dentener and Crutzen, 1993)

DURING THE STAGNATION

- $PM_{2.5}$ mass was dominated by WSOC as opposed to the high RH days before the inversion where nitrate dominated the $PM_{2.5}$ mass.
- Possibly VOCs were trapped in the boundary layer due to the limited vertical mixing leading to the formation of SOA.
- As the SOA aged they become more oxidized and hence more water soluble leading to an increase in the mass of WSOC in the $PM_{2.5}$ mass.
- The relative increase in excess nitrate during this period was lower compared to the high RH periods before the inversion.

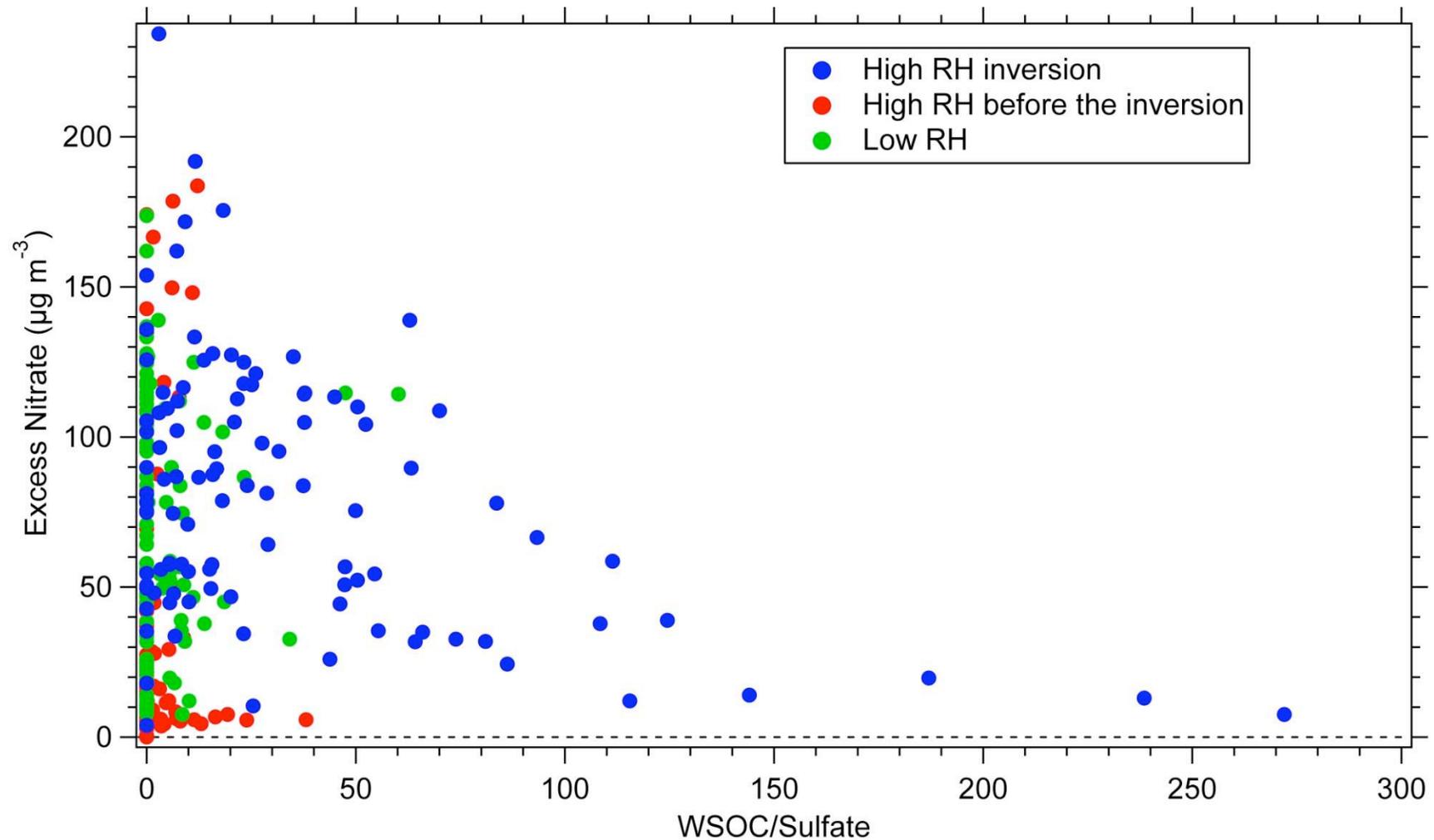


DURING THE STAGNATION

- High WSOC during this period inhibited the reactivity of N_2O_5 onto the hydrated aerosol surface, leading to a reduced concentration in the excess nitrate.
- This inhibition in the N_2O_5 reactivity is thought to be as a result of suppressed N_2O_5 accommodation reaction and reduced water availability at the surface of the hydrated aerosol. (Folkers et al., 2003)
- Bertram et al. (2009) found that N_2O_5 reactivity decreased exponentially with the increase in POM to sulfate ratio.



Effect of WSOC on N_2O_5 Heterogeneous Hydrolysis on Hydrated Aerosol.



CONCLUSIONS

- The particulate nitrate was found to be a function of RH and WSOC.
- Due to the diurnal patterns exhibited by the excess nitrate, the most likely source is likely to be the heterogeneous hydrolysis of N_2O_5 .
- During the inversion period, WSOC concentration increased considerably, due to the aging of the SOA.
- The increase in WSOC corresponded with a decrease in the excess particulate nitrate, suggesting that WSOC was inhibiting the reactivity of the N_2O_5 on the hydrated aerosol surface.

