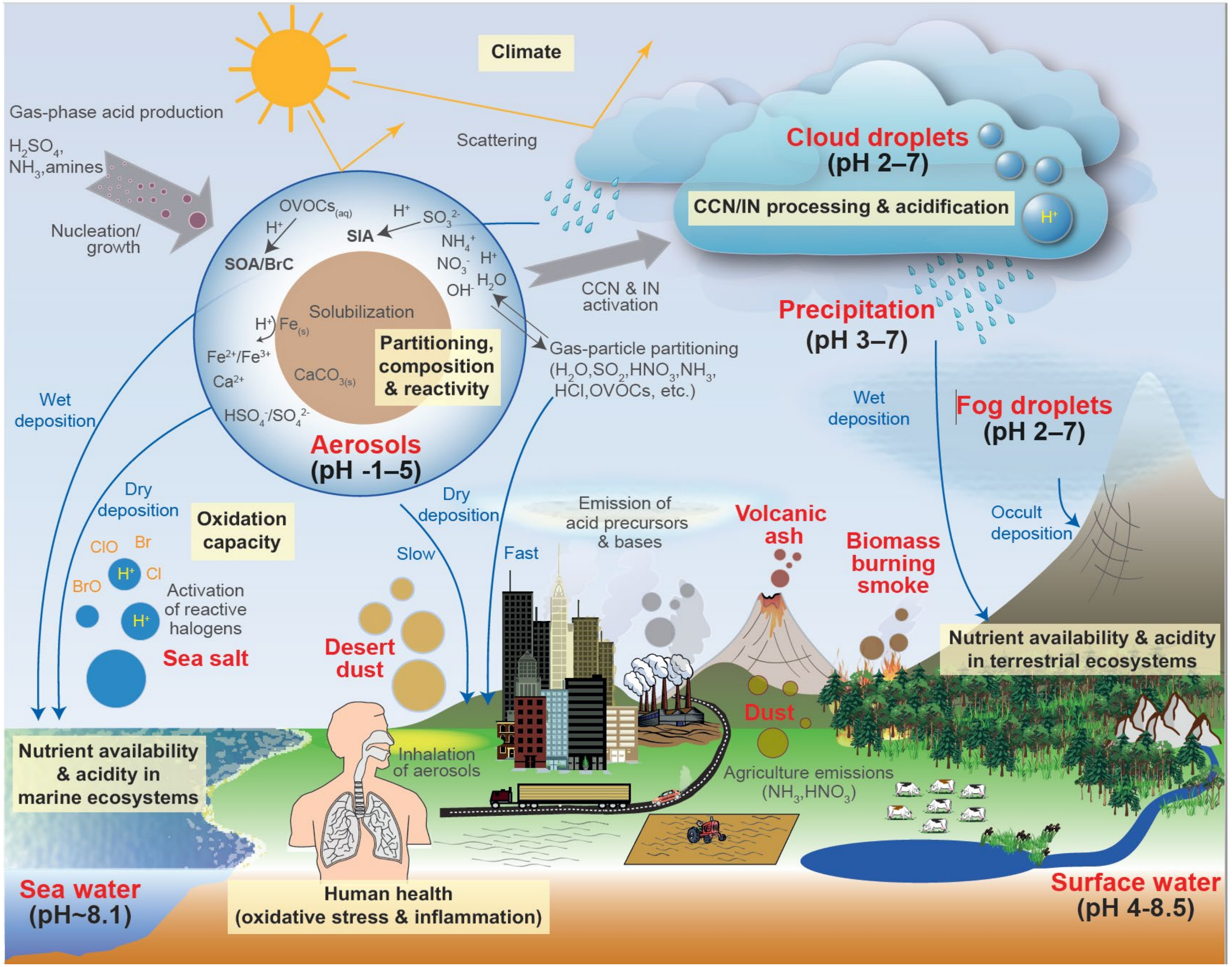
Fine Particle Acidity

Rodney Weber



The Acidity of Atmospheric Particles and Clouds

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Ammonium Nitrate Formation

(VOC)

$$NO_2 + OH$$

$$N_2O_5 + H_2O$$

$$\rightarrow HNO_{3(g)} \leftarrow \rightarrow NO_3^-{}_{(p)}$$

pH

gas

particle

Importance of Aerosol pH

Particle acidity is a critical air quality parameter that affects many aerosol environmental impacts:

- Mass (partitioning of semivolatile ions, NH_4NO_3, acid catalyzed SOA formation)
- Toxicity (concentration of trace species, eg, metal ions)
- Hygroscopicity (ionic composition), hence optical properties/climate

Particle acidity is better than proxies in analysis and conceptual thinking (molar ratios, ion balances)

Acidity currently most accurately determined by a thermodynamic model with full suite of observational inputs.

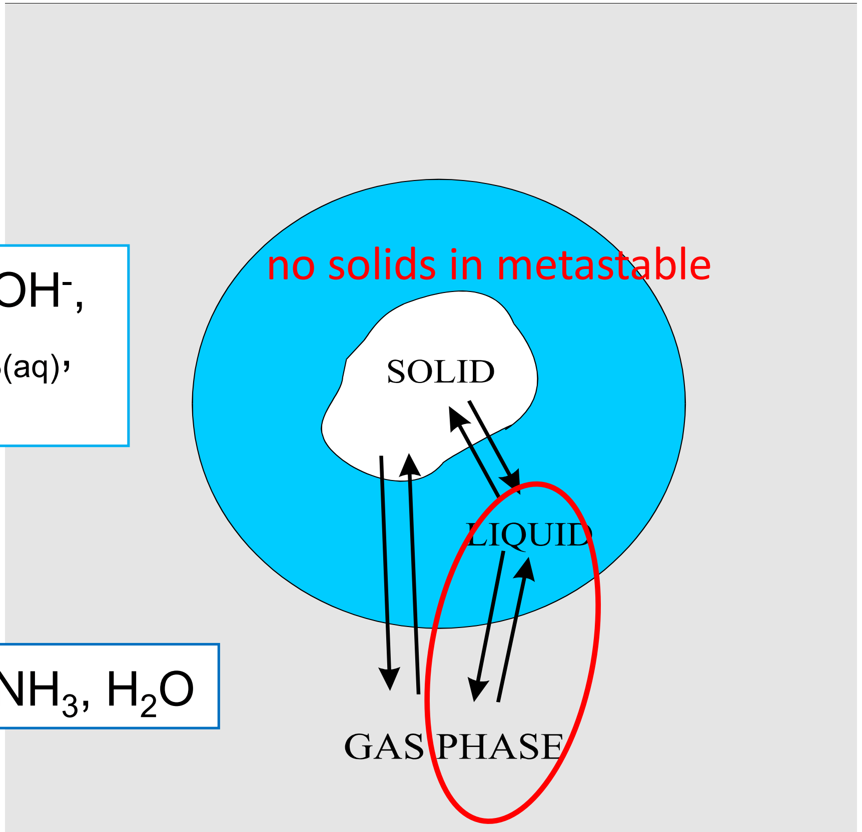
→Useful to report predicted pH (not just partitioning results)

→Accuracy of the thermodynamic model predictions should be assessed.

Determining aerosol pH with a thermodynamic model: e.g., ISORROPIA II

1. Solid phase: $NaHSO_4$, NH_4HSO_4, Na_2SO_4, NaCl, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaNO_3$, **K_2SO_4, $KHSO_4$, KNO_3, KCl, $CaSO_4$, $Ca(NO_3)_2$, $CaCl_2$, $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$**

2. Liquid phase: Na^+, NH_4^+, H^+, OH^-, HSO_4^-, SO_4^{2-}, NO_3^-, Cl^-, H_2O, $HNO_{3(aq)}$, $HCl_{(aq)}$, $NH_{3(aq)}$, Ca^{2+}, K^+, Mg^{2+}



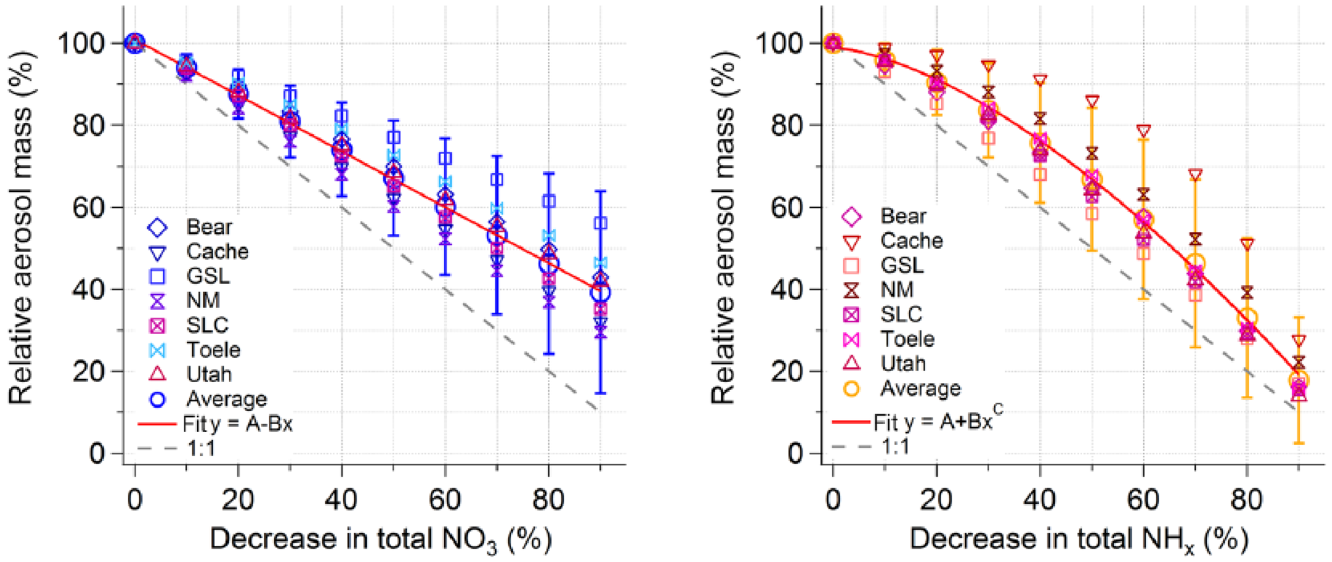
3. Gas phase: HNO_3, HCl, NH_3, H_2O

Modeling Options:

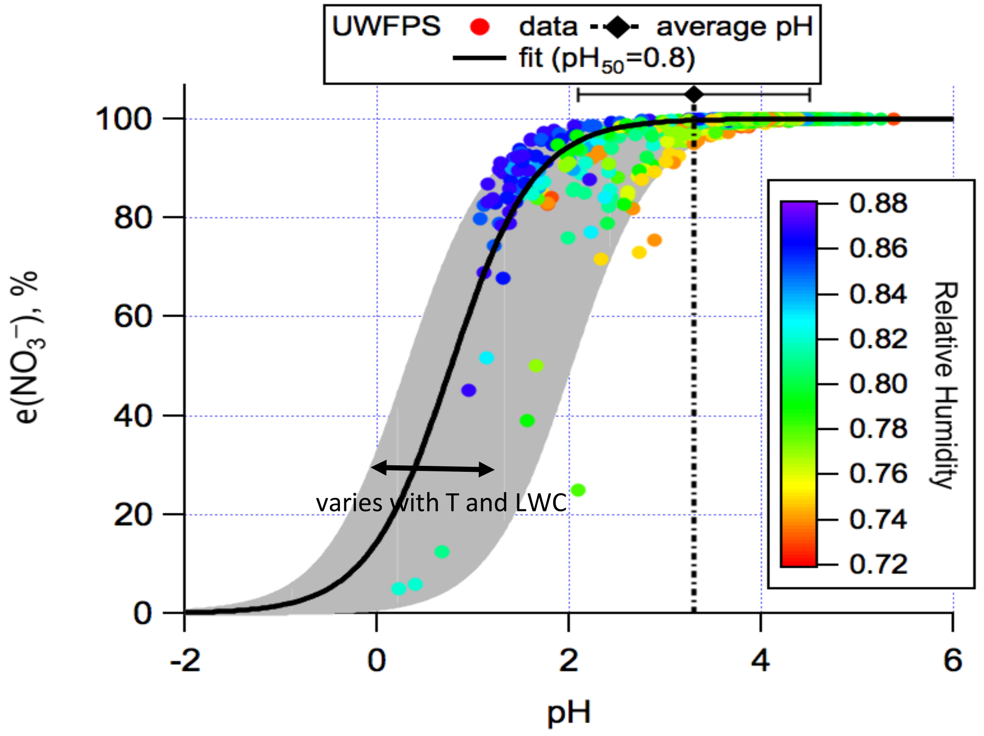
1. **Forward** vs reverse mode.
2. **Stable vs metastable (no precipitated salts)**

Example : UWFPS high pNO_3^- : HNO_3 vs NH_3 Control

Sensitivity analysis with ISORROPIA



Franchin et al, 2018



From Womack et al., GRL (supp. material)

$\varepsilon(NO_3^-) = NO_3^-/(NO_3^- + HNO_3)$; $NO_3^- = \varepsilon(NO_3^-) \times (NO_3^- + HNO_3)$

$\varepsilon(NO_3^-)$ depends on particle pH

ΔNH_3 x10 → ΔpH ~ 1 unit

(Guo et al, Sci Reports 2017)

S curve from:

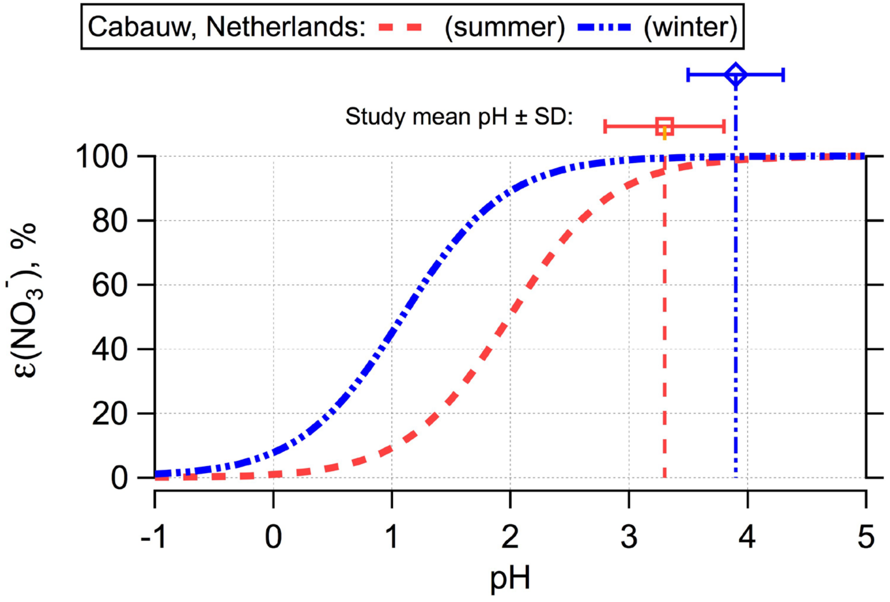
$$HNO_{3(g)} + H_2O \leftrightarrow HNO_3.H_2O \quad K_H$$

$$HNO_3.H_2O \leftrightarrow NO_3^- + H^+ \quad K_a$$

Control sources of HNO_3, sensitivity to NH_3 affected by pH

Alternate formulation that includes pH and LWC

Example, Cabauw Netherlands



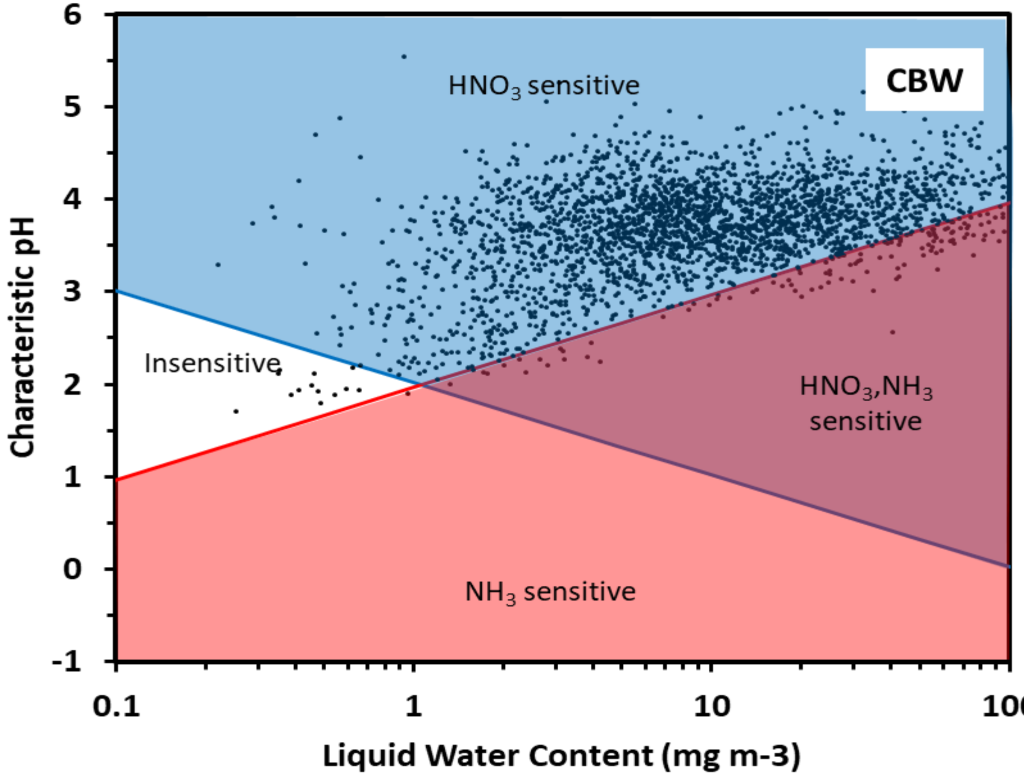
$$HNO_{3(g)} + H_2O \leftrightarrow HNO_3.H_2O \quad K_H$$

$$HNO_3.H_2O \leftrightarrow NO_3^- + H^+ \quad K_a$$

$$\varepsilon(NO_3^-) = \frac{H^*_{HNO_3} RTW_i \times 0.987 \times 10^{-14}}{\gamma_{H^+}\gamma_{NO_3^-} H^+_{aq} + H^*_{HNO_3} RTW_i \times 0.987 \times 10^{-14}}$$

Nenes, Pandis, Weber, Russell; ACPD Sept 26

all of 1 year (summer and winter)

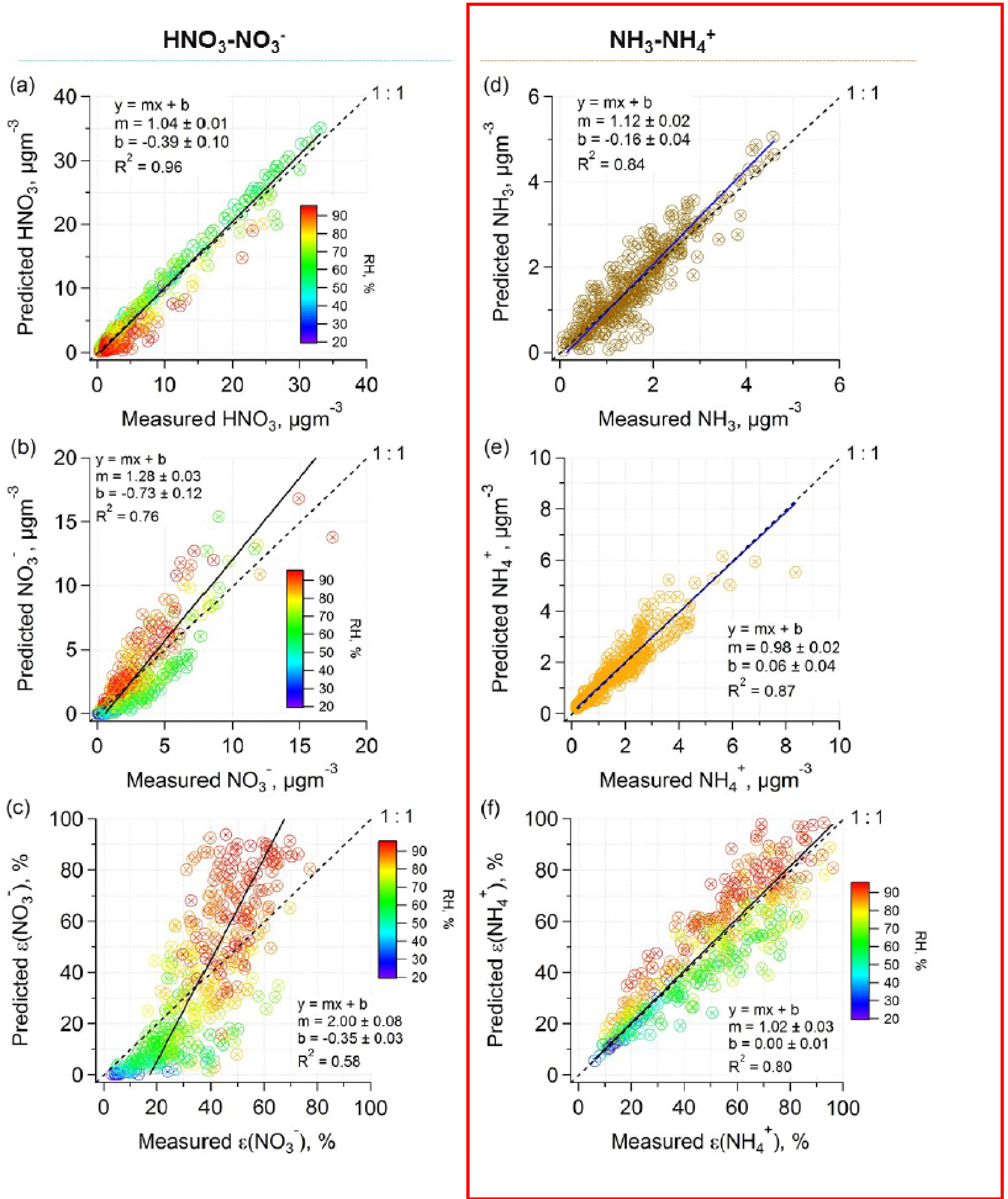


Assessing the accuracy of predicted pH and effects

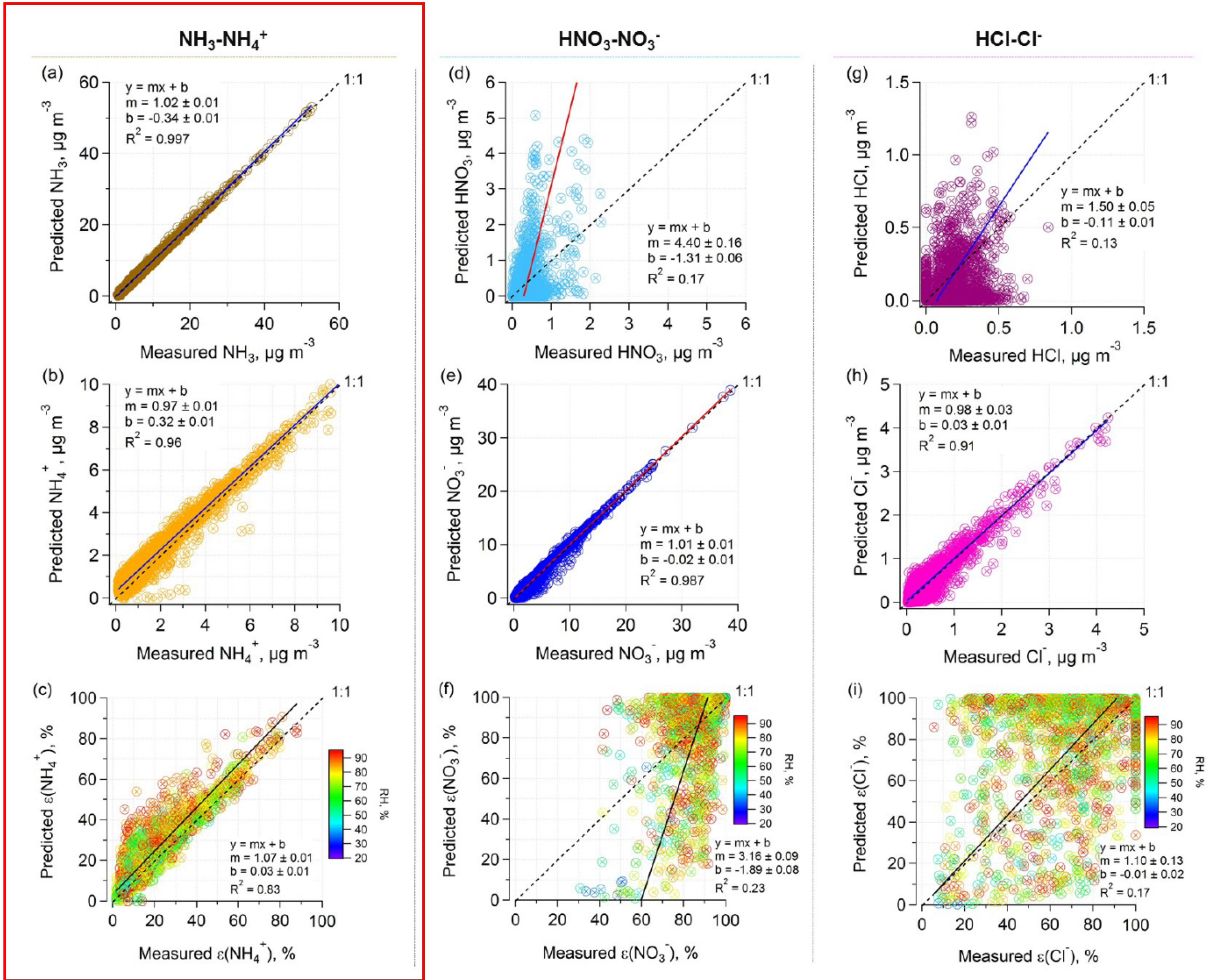
- Currently best way to assess model prediction is to compare measured vs predicted gas/particle partitioning <u>of a suite</u> of semivolatile species

CalNex: Pasadena, CA

- ➢ **Generally good, but NH_3/NH_4^+ seems better than HNO_3/NO_3^-**



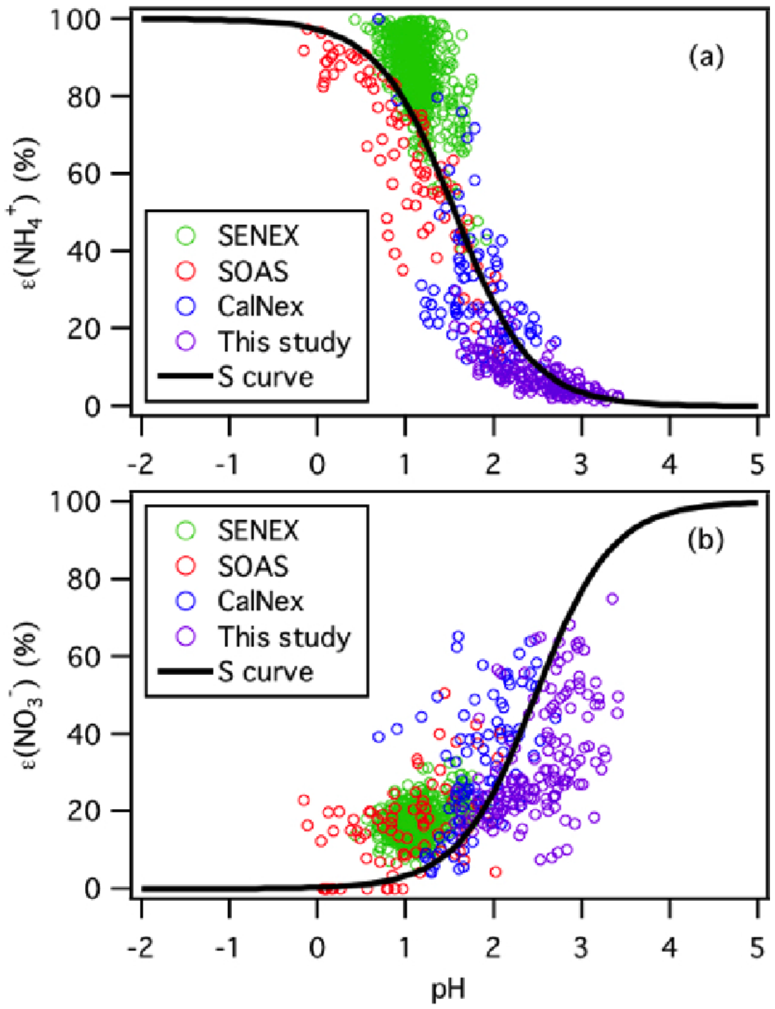
Cabauw, Netherlands



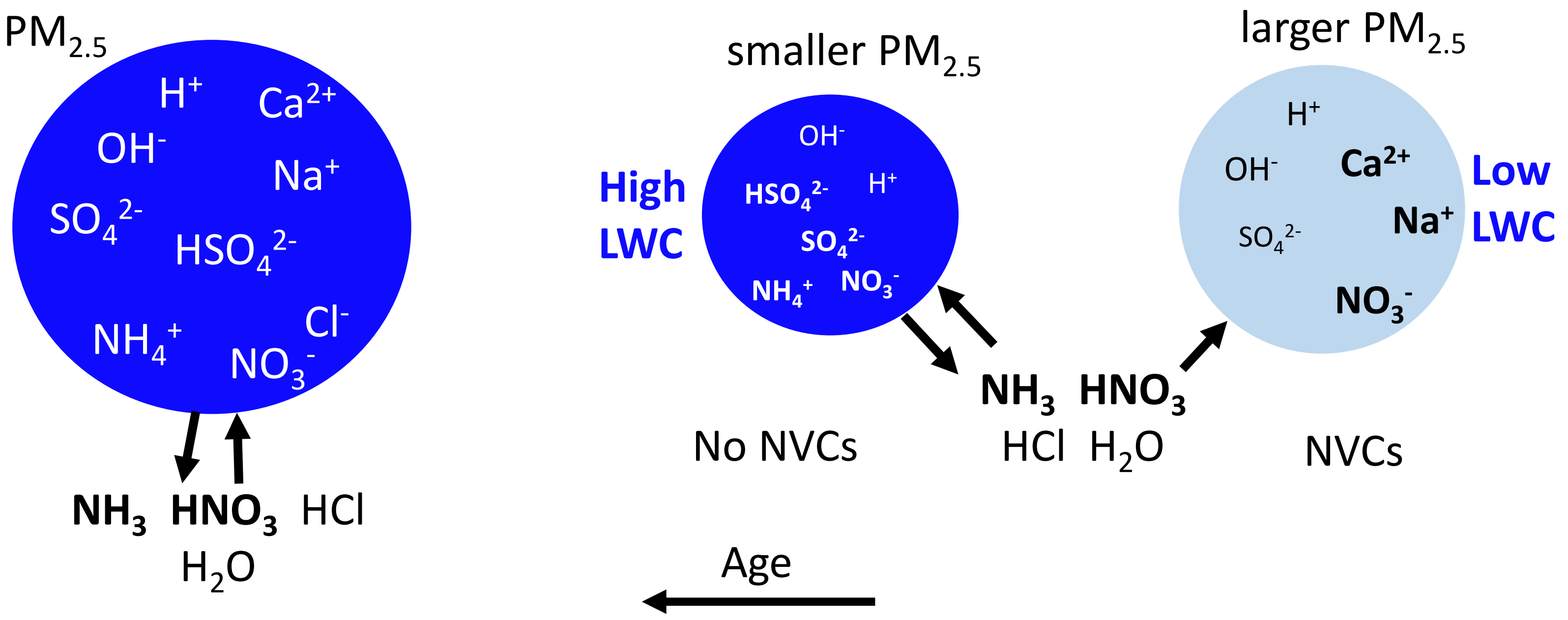
- **Best is NH_3/NH_4^+**

Assessing the Accuracy of predicted pH, role of mixing state

NH_3/NH_4^+ partitioning in almost all cases is the best, why ?



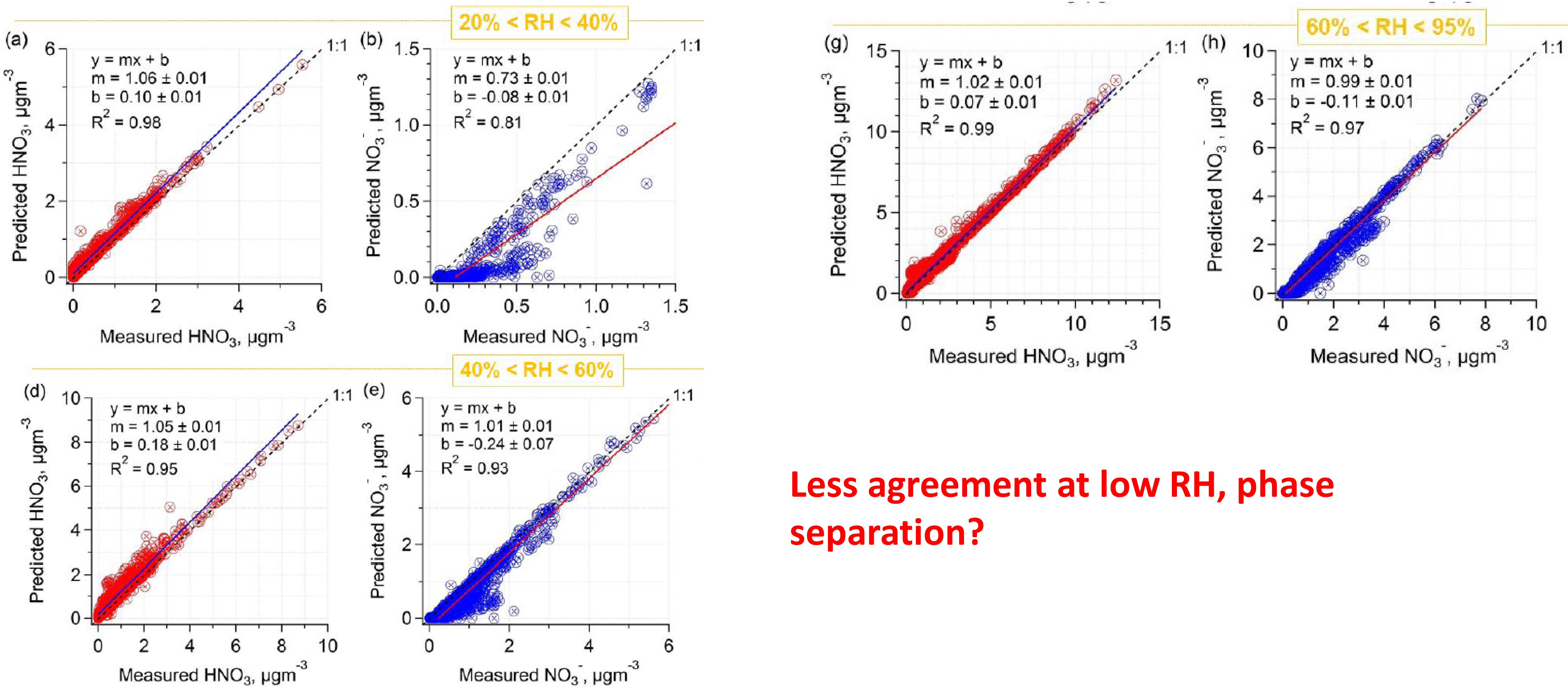
Effect of external mixing (NVCs)?



1. HNO_3 interacts with both species in smaller (semivolatile NH_4NO_3) and larger sizes pf $PM_{2.5}$ (nonvolatile, $NaNO_3$, $Ca(NO_3)_2$), same for HCl.
2. NH_3, no comparable anion in larger sizes.

WINTER: Northeastern US in winter (aircraft, no NH_3 data)

HNO_3/NO_3^- partitioning vs RH



Less agreement at low RH, phase separation?

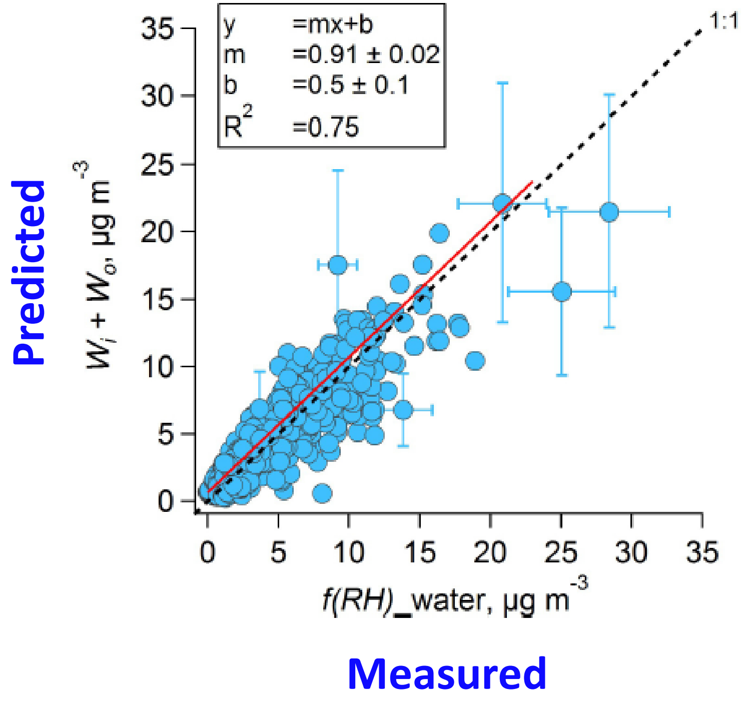
Assessing the accuracy of predicted pH and effects

1. Partitioning comparison is useful to assess thermodynamic model, LWC is an additional constraint.

2. Aerosol phase? Solids phases, liquid organic phases with dissolved ions … ?
   - Predicted liquid water (LWC) is sensitive to phases state

The thermodynamic model also predicts W_i, which can be used as a further test:

Example: SOAS predicted and measured particle water

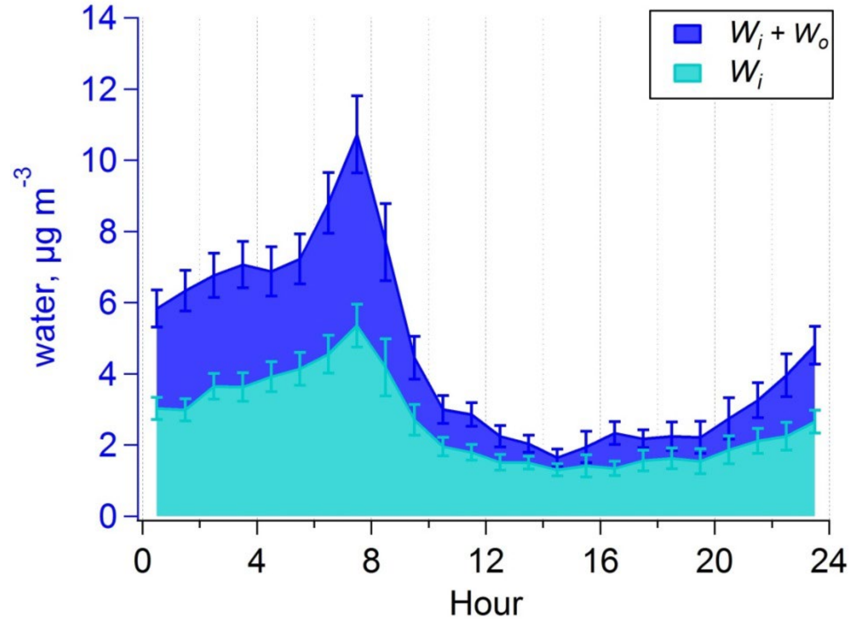


Particle Water and the role of organic species on pH:

W_i is just water from inorganic species, can test role of organic species on water, which could affect actual pH

$$pH = -\log_{10}\gamma_{H^+}H^+_{aq} = -\log_{10}\frac{1000\gamma_{H^+}H^+_{air}}{W_i + \boldsymbol{W_o}} \cong -\log_{10}\frac{1000\gamma_{H^+}H^+_{air}}{W_i}$$

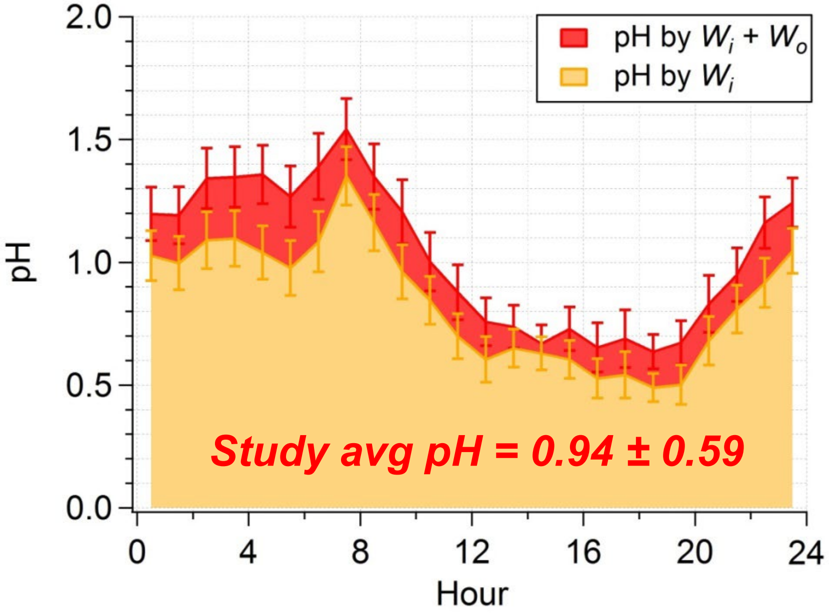
SOAS diurnal variation in particle water and pH



W_o ~35% of total LWC

W_o = water from organic species

W_i = water from inorganic species



W_o minor effect on pH (0.2 units)

pH varies diurnally (1.5 night & 0.5 day); mainly caused by LWC (RH).

(Guo et al. ACP, 2015)

Specific Questions

Some Possible Key Scientific Questions

1. What is the pH of fine particles (1-5, avg ~3.5, Womack) how does it vary and why (T, RH, NHx, $SO_4^{=}$)?
2. How accurate is the thermodynamic model, pH, HNO_3/NO_3^-, HCl/Cl^-…?
3. What is the particle LWC, how accurately is it determined ?
4. Effect of NVCs and mixing state on pH, HNO_3/NO_3^-, do NVCs need to be considered (is AMS data ok) ?
5. Toxicity of the aerosol (oxidative potential, concentration of metal ions, etc)?

Recommendations

1. Measure full suite of fine particle anions and cations (including NVCs, possibly organic acids), LWC, possibly size distributions and size resolved composition MOUDI) **AND** gases HNO_3, NH_3, HCl
2. Measure toxicity, contrasts to other locations: Oxidative potential, PAHs/Quinones, metal ions (Cu^+/Cu^{2+}, Fe^{2+}/Fe^{3+}, may be others of importance)

Measurements that need to be made to predict and assess particle acidity and effects

1. Particle phase
   - Anions: SO_4^{2-}, NO_3^-, Cl^-, organic acids (?)
   - Cations: NH_4^+, NVCs: Na^+, Ca^{2+}, K^+, Mg^{2+}
   - PM_1 vs $PM_{2.5}$, also $PM_{2.5-10}$?
   - Particle water content (LWC)
   - Maybe OA for estimating OA contribution to water
   - Size resolved is useful
   - Ideally ions, not AMS "measured" ions, which also lacks NVCs
2. Gas species
   - HNO_3, HCl, NH_3, organic acids (?)
3. Meteorological
   - T, RH