High aerosol acidity despite declining atmospheric sulfate concentrations

Lessons learned from the SE US and implications for models.

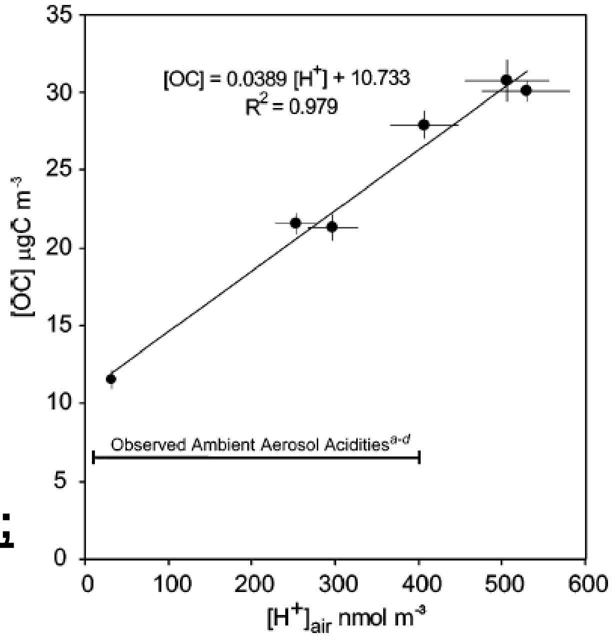
A.Nenes[1,2,3,4], R.J. Weber[1], H.Guo[1], A.Russell[5] with contributions from C. Liu[5], P. Vasilakos[2], A.Bougiatioti[1,3] and N.Mihalopoulos[3]

[1]Georgia Tech, School of Earth and Atmospheric Sciences, [2]Georgia Tech, School or Chemical & Biomolecular Engineering, [3]IERSD, National Observatory of Athens, Greece, [4]ICE-HT, Foundation for Research and Technology Hellas, Greece, [5]Georgia Tech, School of Civil & Environmental Engineering

Introduction

Particle pH:

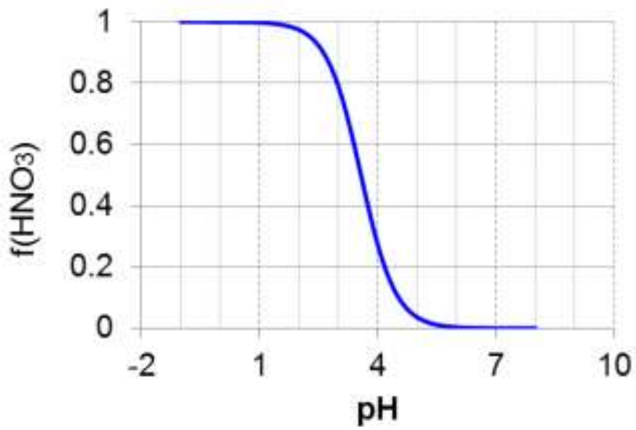
1. **Controls particle phase acid-catalyzed reactions;**
   - Isoprene (the largest VOC) → IEPOX-OA
   - Laboratory studies found that acidity enhances IEPOX-OA formation (*Surratt et al., 2007&2010*).
   - IEPOX-OA 20% of OA in SE in summer (*Xu et al., 2015*)



(*Surratt et al., 2007*)

2. **Controls acidic and basic gas-particle partitioning;**
   - e.g. Nitric acid and nitrate

$$HNO_{3(g)} + H_2O \leftrightarrow HNO_3 \cdot H_2O, \qquad K_H$$
$$HNO_3 \cdot H_2O \leftrightarrow NO_3^- + H^+, \qquad K_a$$



3. **Solubilizes mineral dust and metals;**
   - 1-2% Fe mobilized after 4 days at pH=2 → ecosystem nutrient (*Meskhidze et al., 2003*)
   - redox metals → reactive oxygen species (ROS) (*Verma et al., 2014*)

Introduction

Particle Acidity sources and evolution in atmosphere:

Acidic

SO_2(g)
NOx(g)

Oxidation

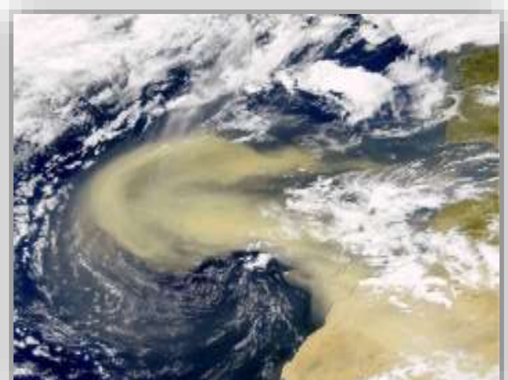
H_2SO_4(p)
HNO_3(p)

Basic

NH_3(g) + Mineral dust + seasalt (Na, K, Ca, Mg, etc.)

formation of $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, etc. that depends on particle acidity

Other sources of alkalinity



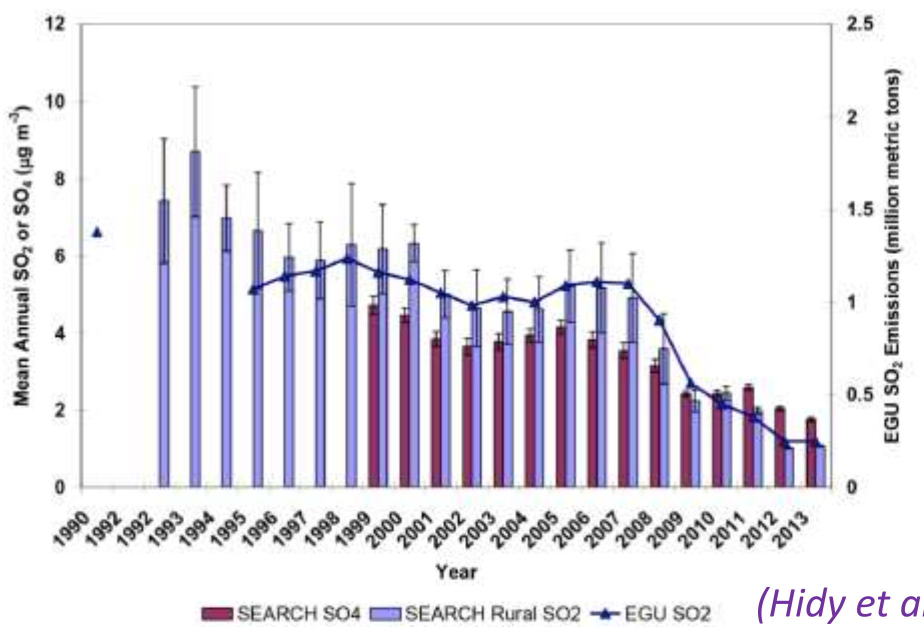
Introduction

Historical SO_2 and SO_4^{2-} trends:

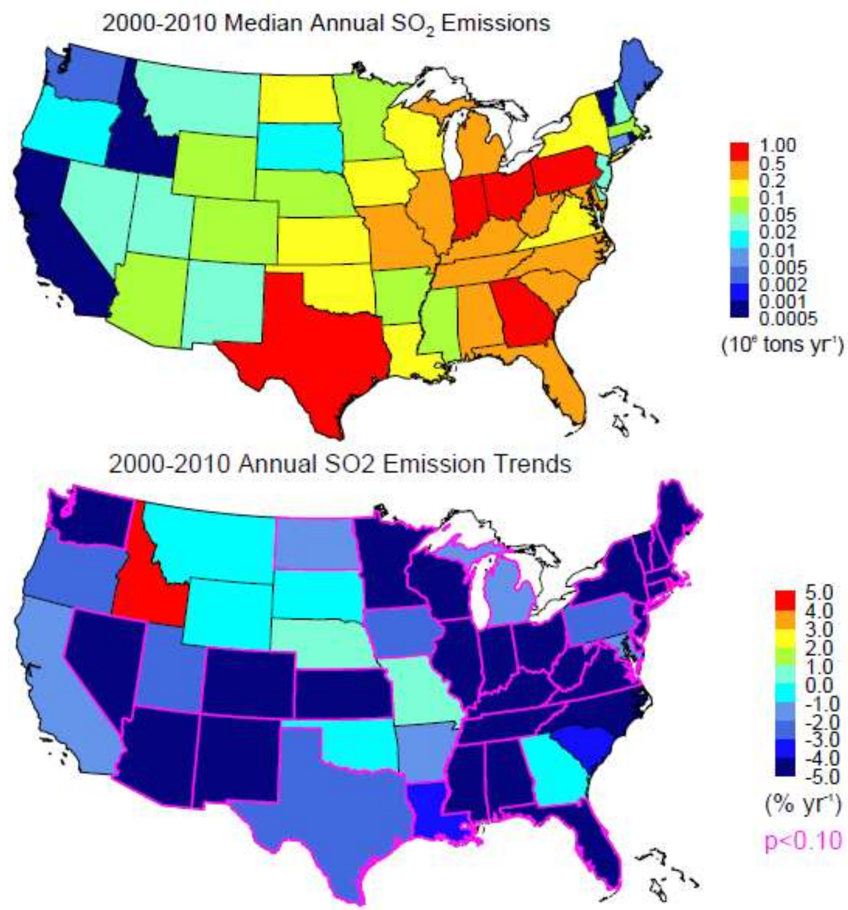
- In the past twenty years, SO_2 emissions have decreased significantly (-6.2% yr^{-1}, 2000-2010, *Hand et al. 2012*).
- SO_4^{2-} followed SO_2 reduction.

Scientific questions:

1. Are particles in southeast US becoming neutral as SO_2 emissions go down?
2. Are nitrate particles becoming dominant aerosols in southeast US?



(Hidy et al., 2014)



(Hand et al., 2012)

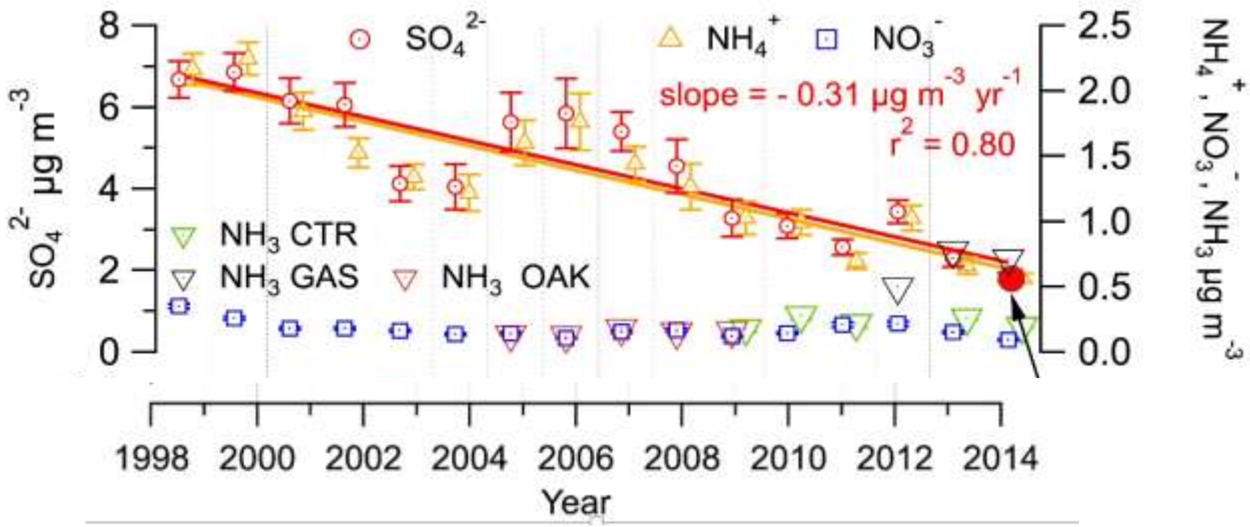
The acidity "paradox"

Historical Data:

SO_4 is going down

NH_3 is constant

Nitrate is ~ 0

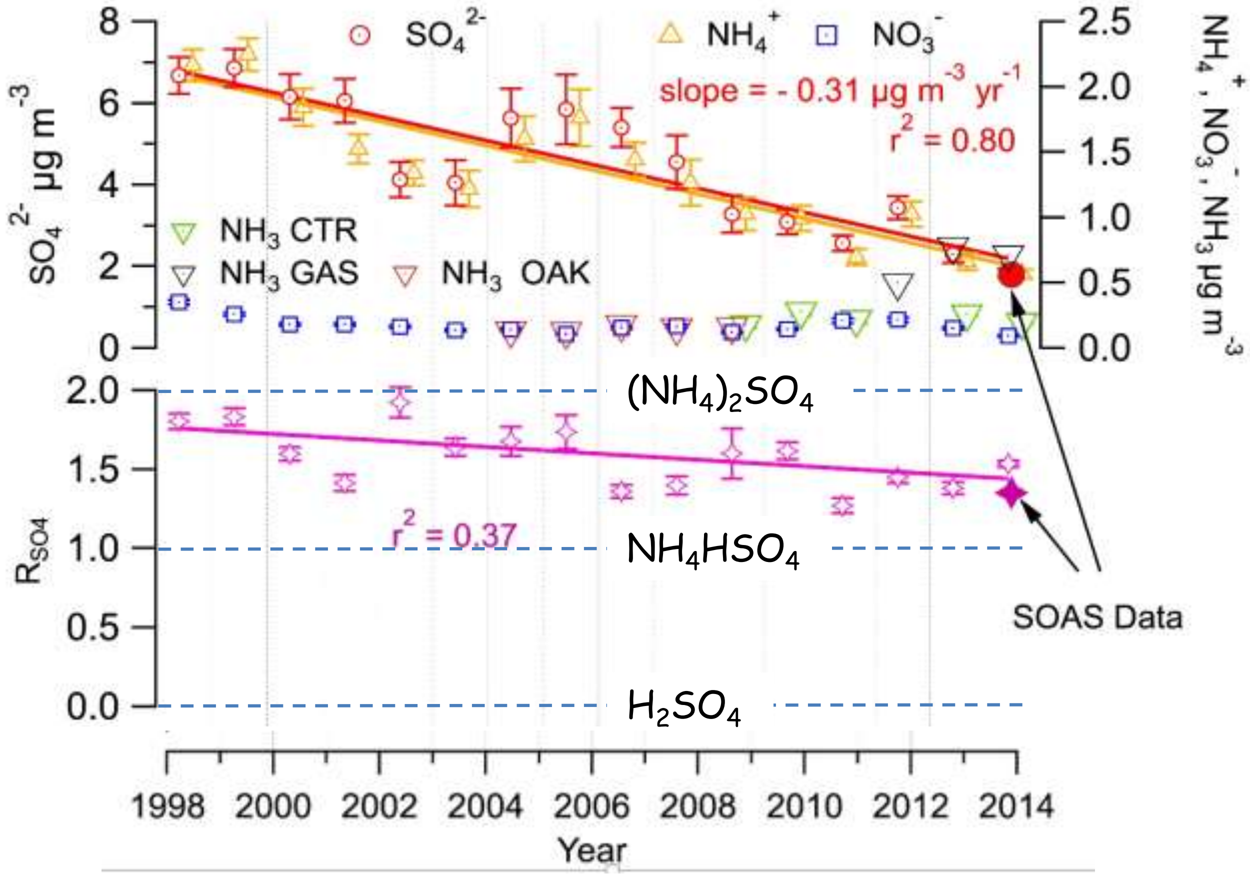


Weber et al. (2016), *Nature Geosci.*

The acidity "paradox"

Historical Data:
SO_4 is going down
NH_3 is constant
Nitrate is ~ 0

Aerosol response:
Should have become more neutralized –

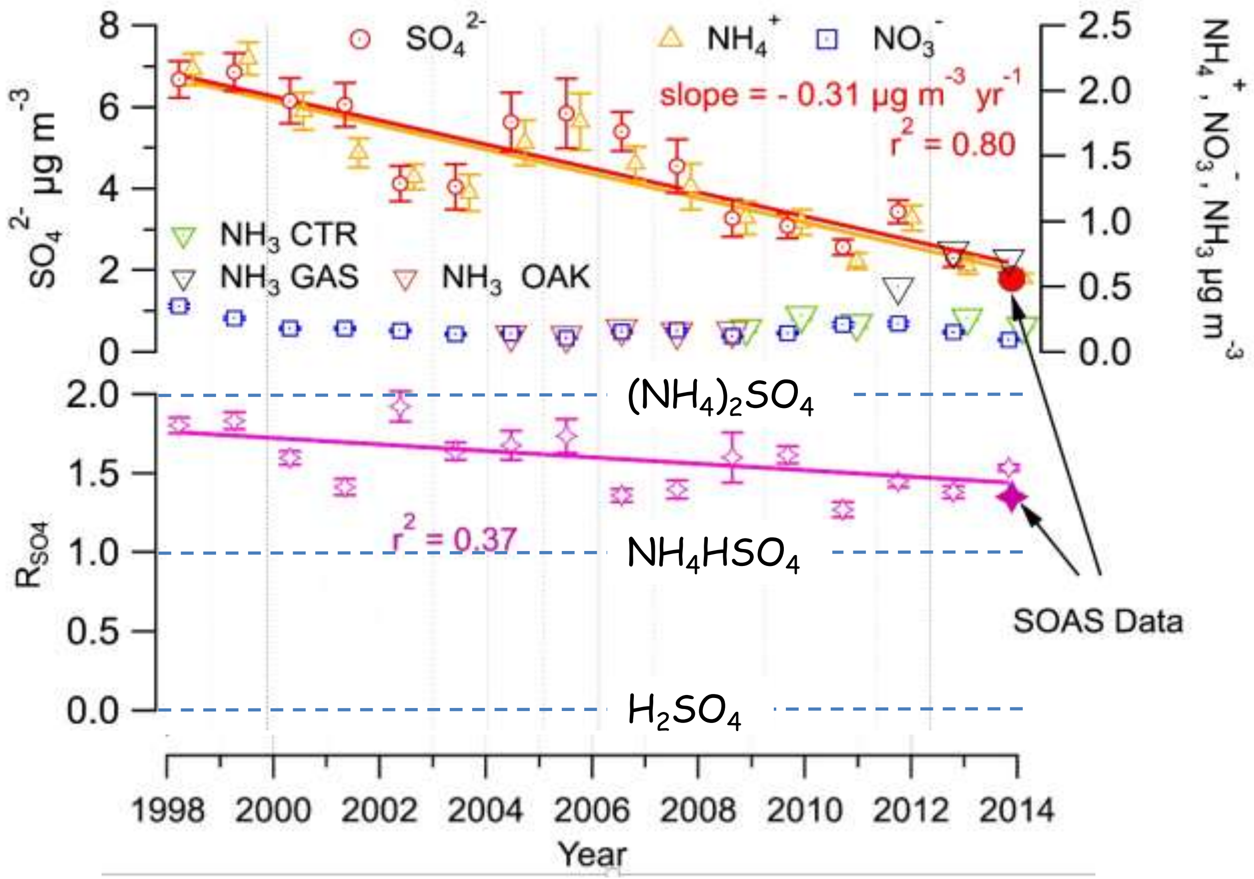


Weber et al. (2016), *Nature Geosci.*

The acidity "paradox"

Historical Data:
SO_4 is going down
NH_3 is constant
Nitrate is ~ 0

Aerosol response:
Should have become more neutralized –



… but it's NOT becoming more neutral. In fact it's "**acidifying**".

Weber et al. (2016), *Nature Geosci.*

Determining aerosol pH: The problem

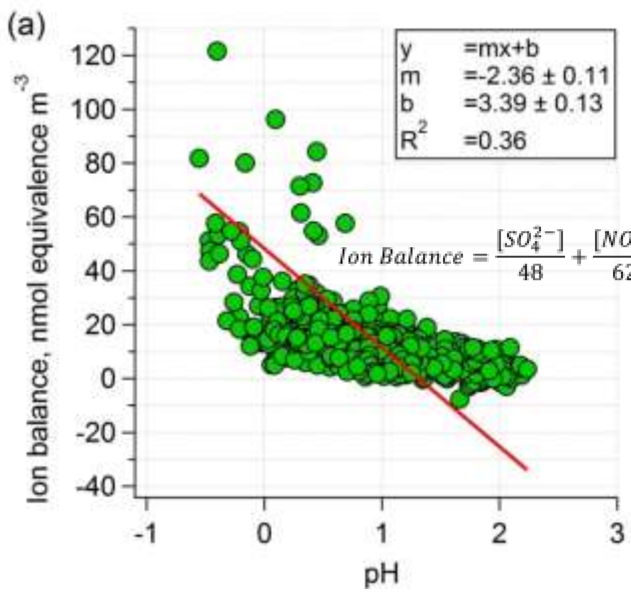
Acidity / pH definition:

$$pH = -\log_{10}[H^+] = -\log_{10}\frac{1000H^+_{air}}{LWC} \qquad H^+_{air}, LWC\ units: \mu g\ m^{-3}\ air$$

How to determine particle pH:

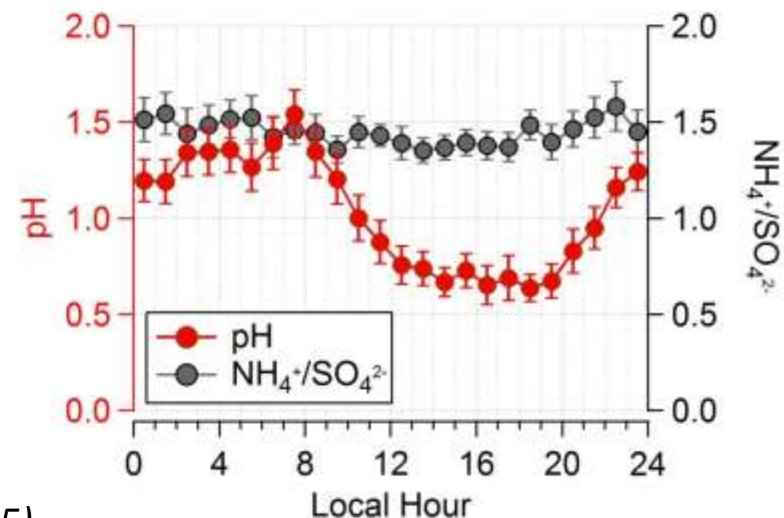
- pH cannot be measured for single particles *in-situ*.
- "pH proxies" (ion balance, molar ratios), **do not strongly correlate with pH**.
  - ✓ Ions can be in multiple forms depending on pH and p*Ka*.
  - ✓ pH depends on LWC, which can vary considerably.

Ion balance:



$$Ion\ Balance = \frac{[SO_4^{2-}]}{48} + \frac{[NO_3^-]}{62} + \frac{[Cl^-]}{35.5} - \frac{[NH_4^+]}{18} - \frac{[Na^+]}{23}$$

NH_4^+/SO_4^{2-} Molar ratio:

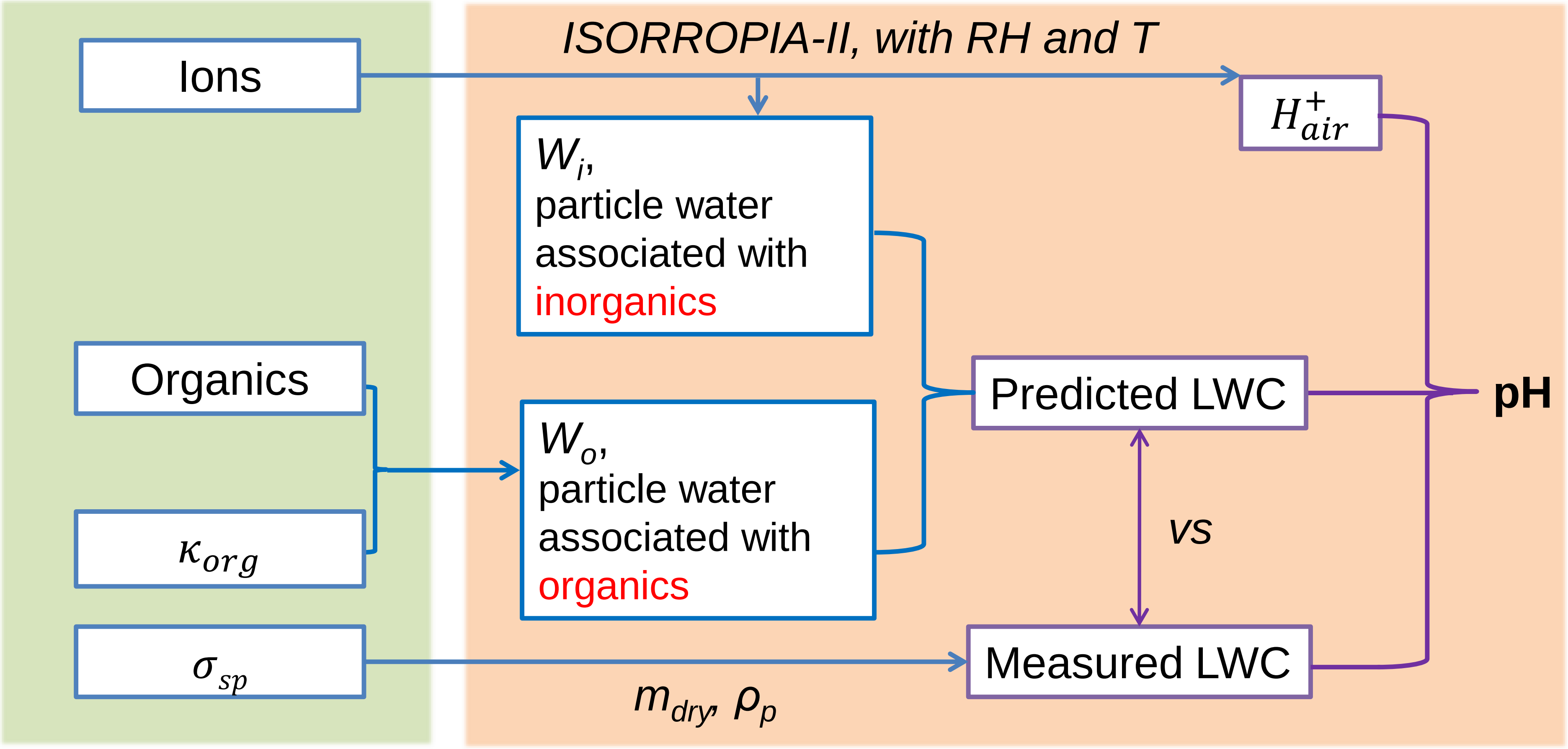


(Guo et al., 2015)

Determining aerosol pH: How we do it (model+obs)

Follow the approach of Guo et al. (2015):

- *Particle ions (**SO_4^{2-}, NH_4^+,** NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^2);*
- *Gas (**NH_3**);*
- *Particle water or **total organics & κ_{org};***
- ***RH** and T;*

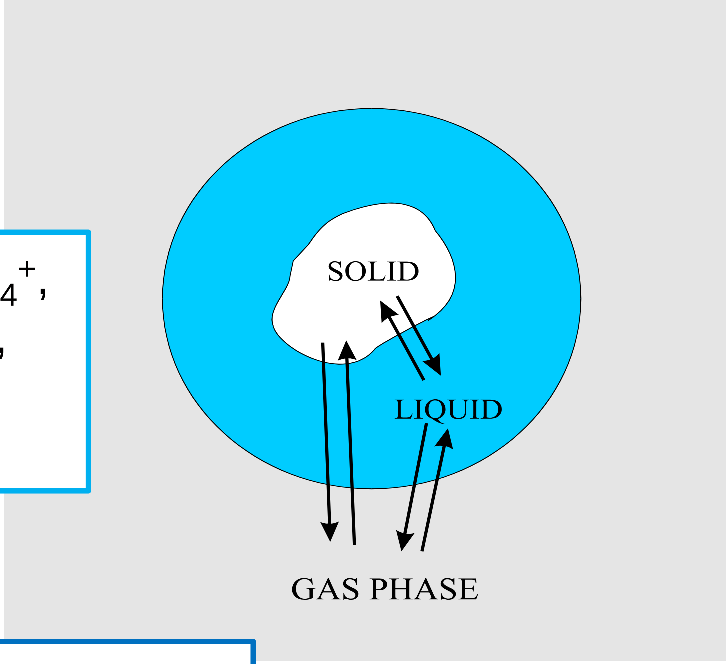


Lu et al. (2015) PNAS; Guo et al., (2015) ACP; Cerully et al., (2015) ACP

Determining aerosol pH: The "heart" of it

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, $CaSO_4$, $Ca(NO_3)_2$, $CaCl_2$, $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$**

Species in **bold** were introduced in ISORROPIA II (Fountoukis and Nenes, 2007)



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

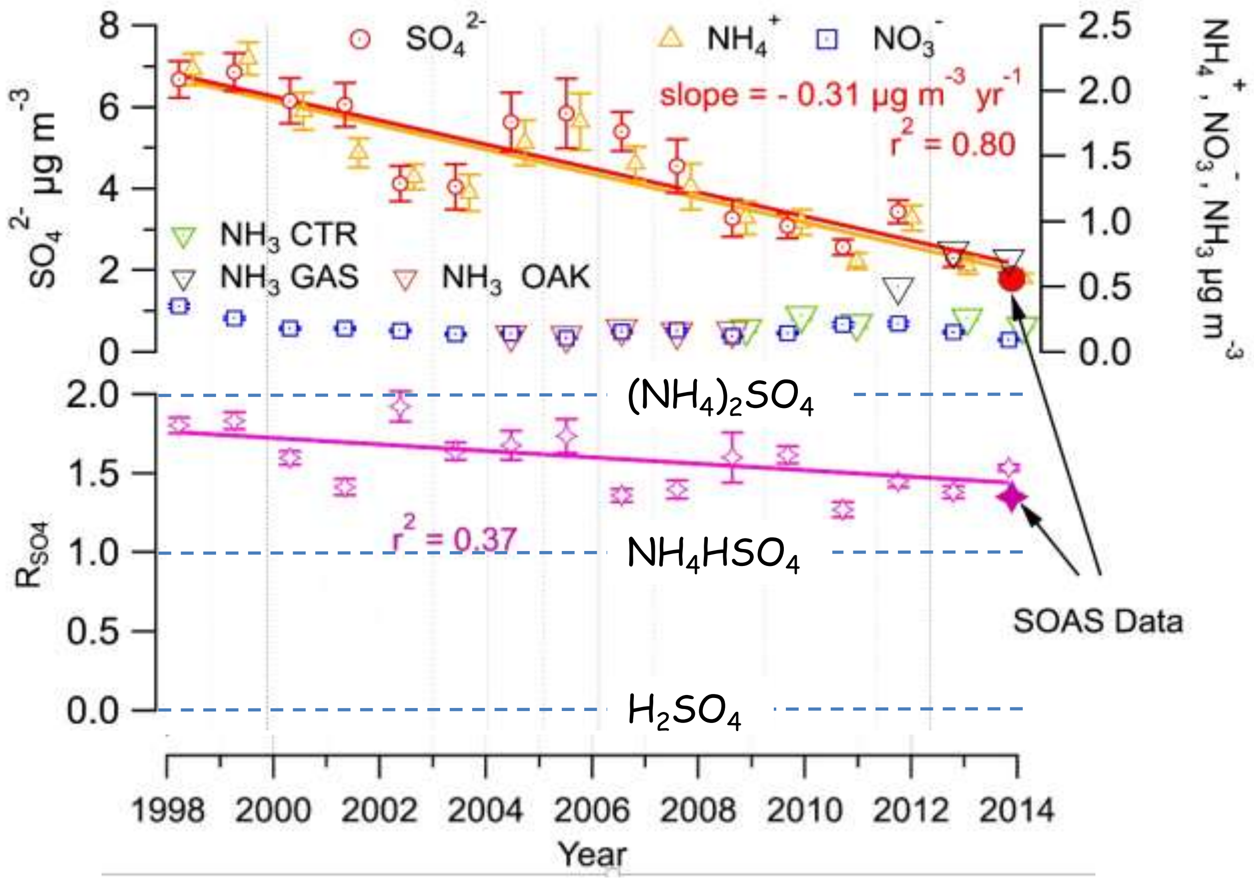
In this study, ISORROPIA-II was run in "**Forward mode**", which calculates equilibrium partitioning given total concentration of species (gas + particle).

http://isorropia.eas.gatech.edu

The acidity paradox

Historical Data:
SO_4 is going down
NH_3 is constant
Nitrate is ~ 0

Aerosol response:
Should have become more neutralized – It's "acidifying".



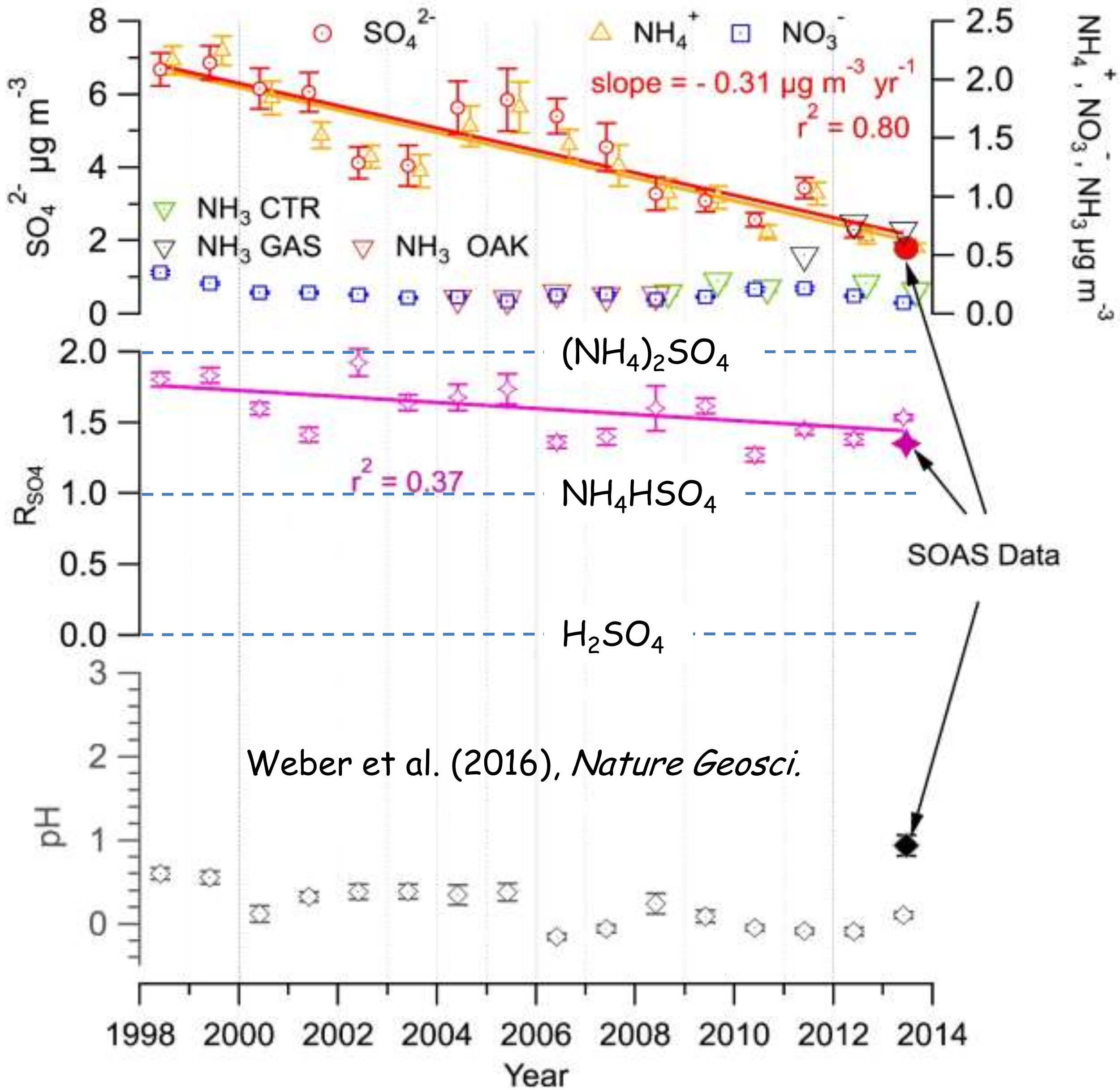
Weber et al. (2016), *Nature Geosci.*

The acidity paradox

Historical Data:
SO_4 is going down
NH_3 is constant
Nitrate is ~ 0

Aerosol response:
Should have become more neutralized – it hasn't.

pH calculations:
Confirm that this is the case for SE US.

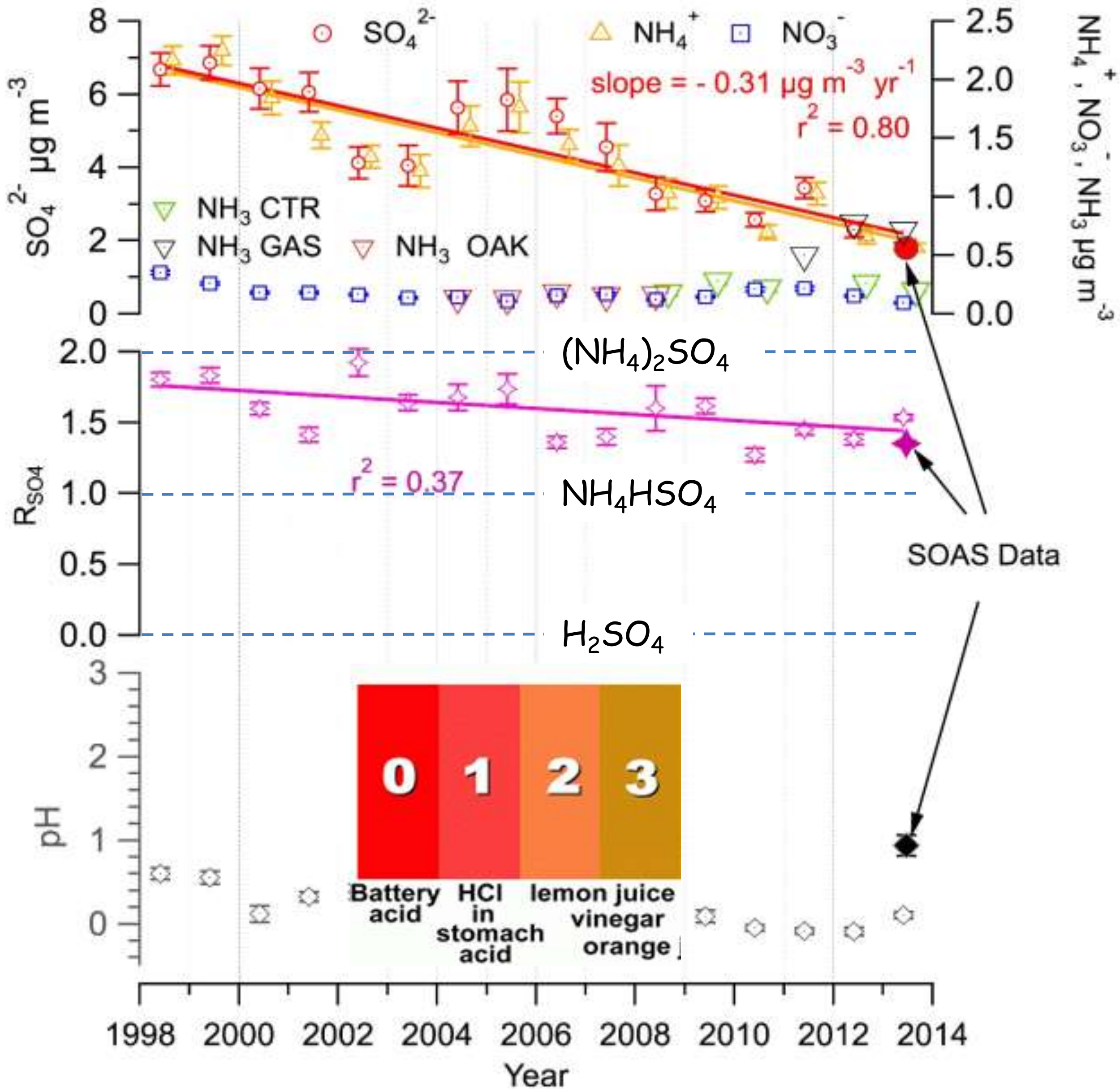


SE US: pH is very low despite large reductions in SO_2

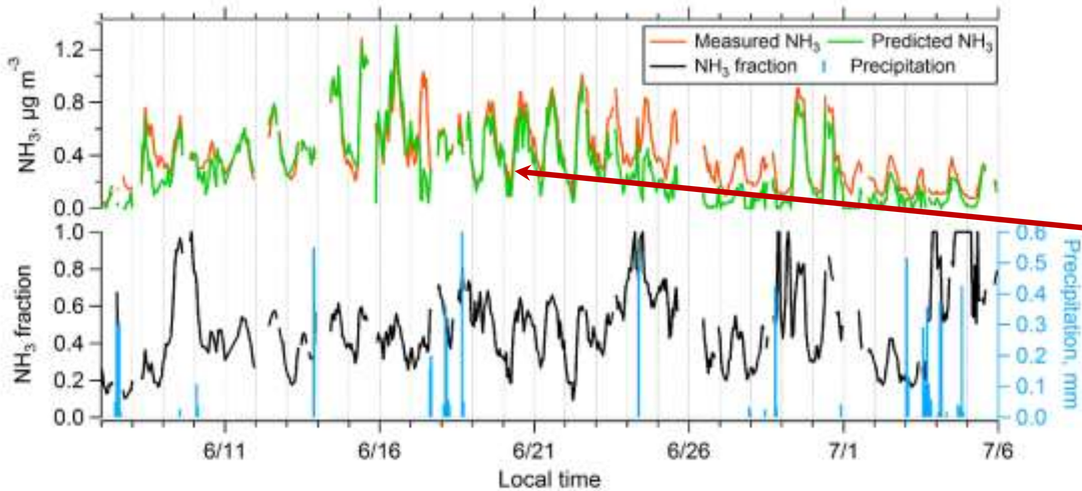
Historical Data:
SO_4 is going down
NH_3 is constant
Nitrate is ~ 0

Aerosol response:
Should have become more neutralized – it hasn't.

pH calculations:
Confirm that this is the case for SE US.

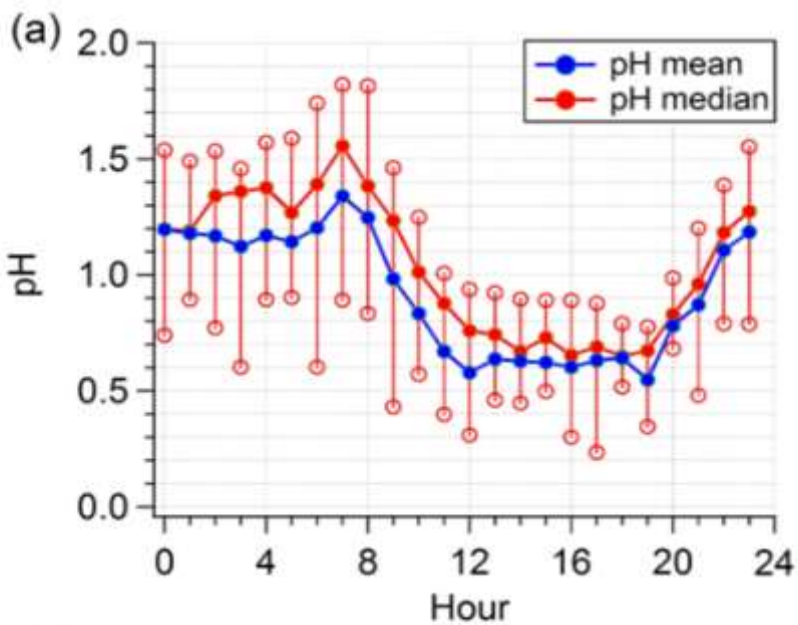


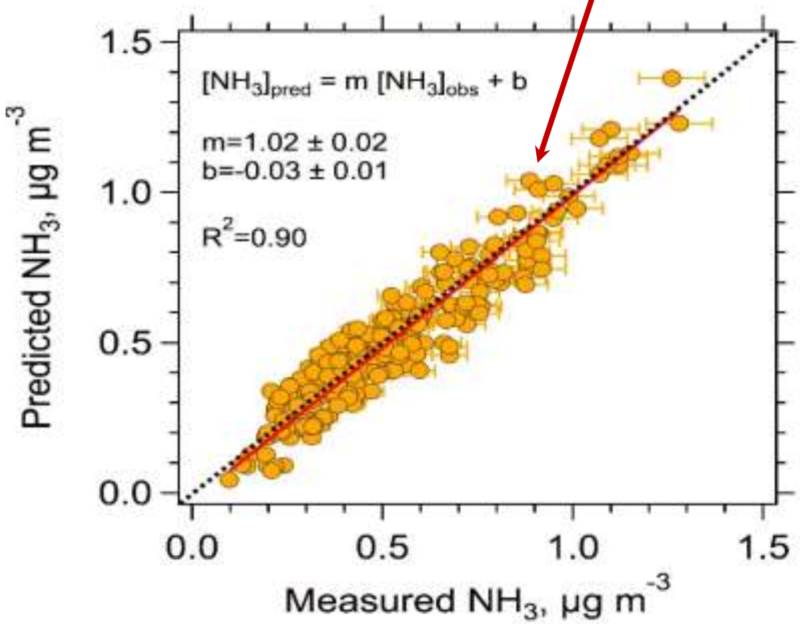
SOAS Data analysis confirms pH calculations



Guo et al., ACP, 2015.

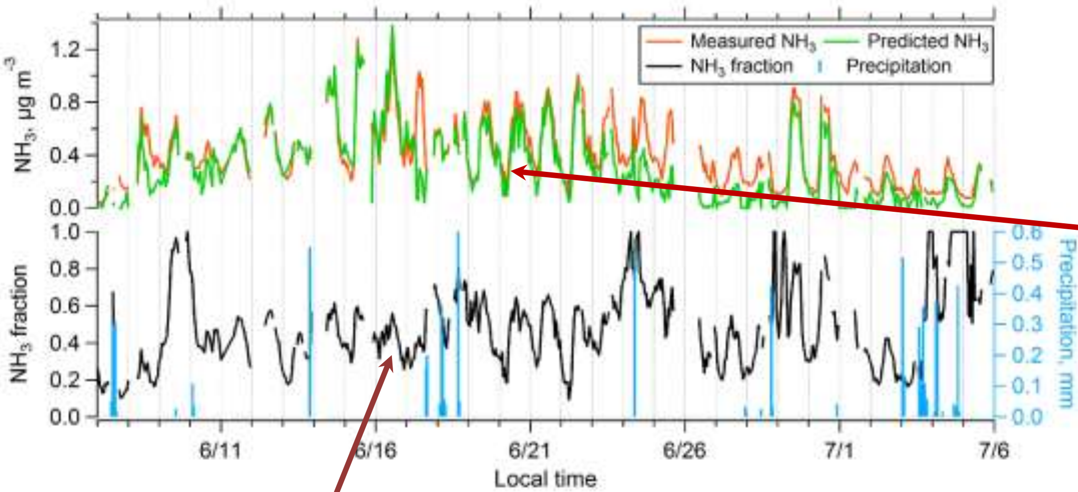
Comparison of <u>predicted vs. observed</u> gas-phase NH_3.





SOAS Data analysis confirms pH calculations

Guo et al., ACP



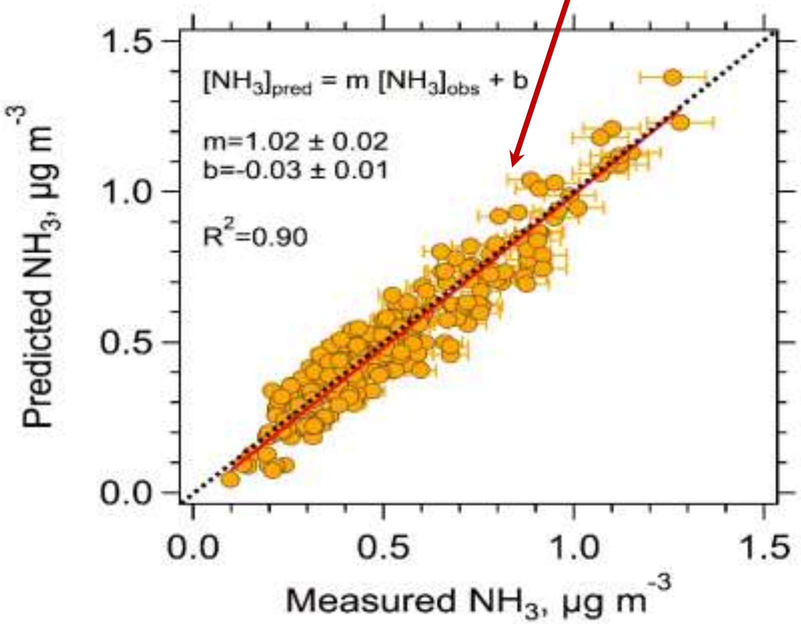
Guo et al., ACP, 2015.

Comparison of <u>predicted vs. observed</u> gas-phase NH_3.

The <u>volatilization fraction</u> fluctuates around 0.5.

This means that prediction biases in pH would result in appreciable biases in the $NH_{3(g)}$ fraction.

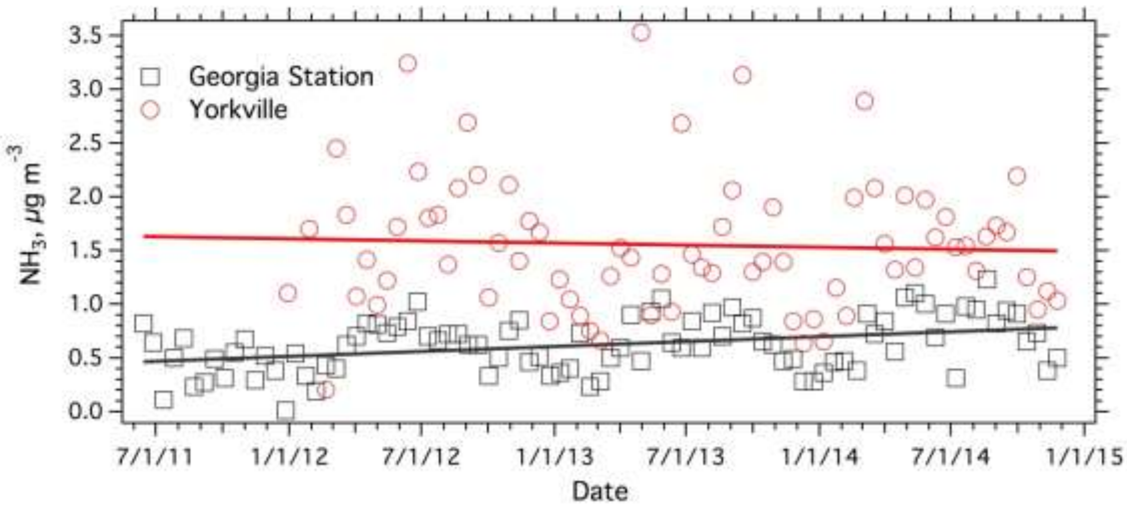
pH 0.5-1.5 is indeed likely for the SE US.



Weber et al. (2016), *Nature Geosci.*

NH_3 has and probably will remain the same

Proof from observation: 3 years (AMoN sites)



Summary:

In the past, NH_3 has been fairly constant.

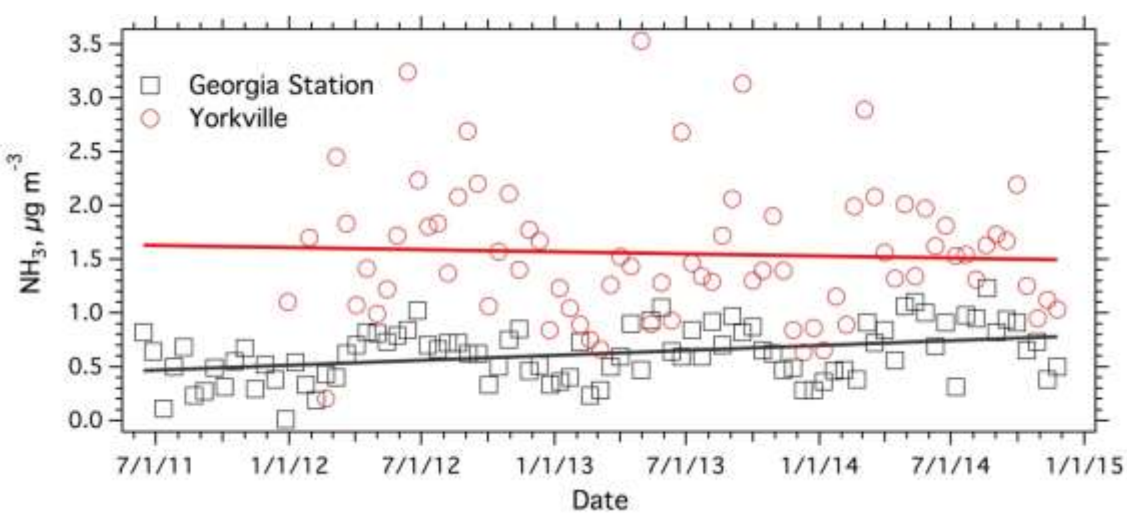
In the future, NH_3 will probably stay at current level or increase slightly.

(*Erisman et al., 2008*)

Weber et al. (2016), *Nature Geosci.*

NH_3 has and probably will remain the same

Proof from observation: 3 years (AMoN sites)



Summary:

In the past, NH_3 has been fairly constant.

In the future, NH_3 will probably stay at current level or increase slightly.

(*Erisman et al., 2008*)

Proof from mass balance (in the boundary layer):

$$\frac{d[NH_3]}{dt} = E_{NH_3} - \frac{v_d^{NH3}}{h}[NH_3] - \frac{v_d^{NH_4^+}}{h}[NH_4^+]$$

emissions *gas* *aerosol*

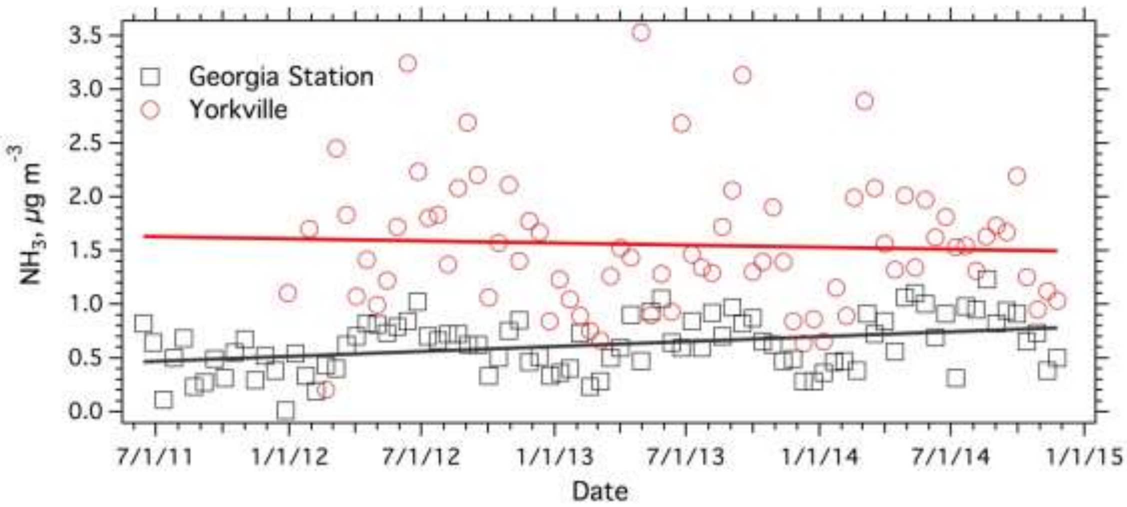
deposition rate

E_{NH_3}: *gas phase* NH_3 *emission rate*;
v_d^{NH3}: *gas phase deposition velocity*;
$v_d^{NH_4^+}$: *particle phase deposition velocity*;
h: *boundary layer mixed depth*

Weber et al. (2016), *Nature Geosci.*

NH_3 has and probably will remain the same

Proof from observation: 3 years (AMoN sites)



Summary:

In the past, NH_3 has been fairly constant.

In the future, NH_3 will probably stay at current level or increase slightly.

(*Erisman et al., 2008*)

Proof from mass balance (in the boundary layer):

$$\frac{d[NH_3]}{dt} = E_{NH_3} - \frac{v_d^{NH3}}{h}[NH_3] - \frac{v_d^{NH_4^+}}{h}[NH_4^+]$$

emissions — *gas* — *aerosol*

deposition rate

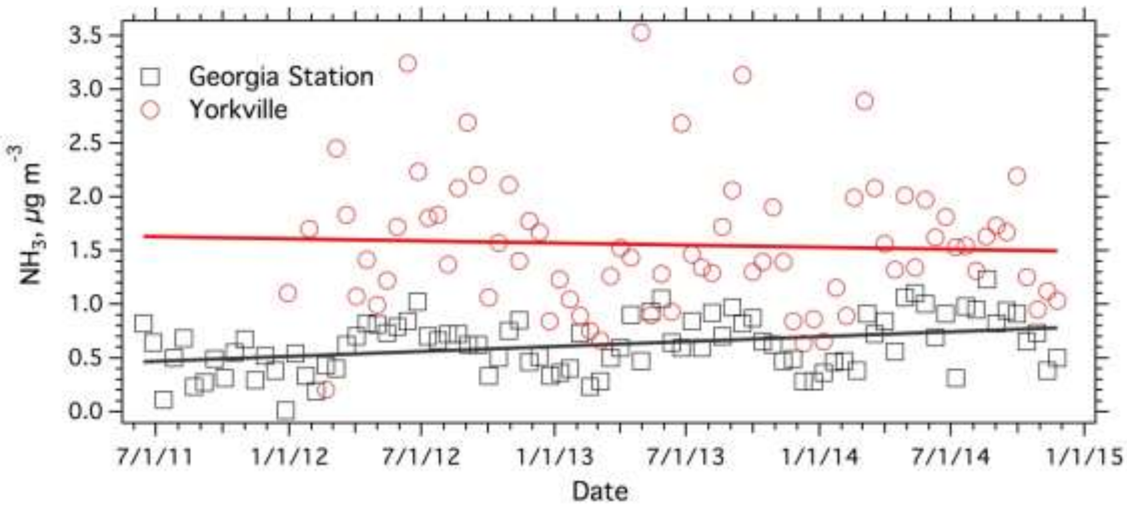
E_{NH_3}: *gas phase* NH_3 *emission rate*;
v_d^{NH3}: *gas phase deposition velocity*;
$v_d^{NH_4^+}$: *particle phase deposition velocity*;
h: *boundary layer mixed depth*

$$but\ v_d^{NH3} \gg v_d^{NH_4^+}$$

Weber et al. (2016), *Nature Geosci.*

NH_3 has and probably will remain the same

Proof from observation: 3 years (AMoN sites)



Summary:

In the past, NH_3 has been fairly constant.

In the future, NH_3 will probably stay at current level or increase slightly.

(*Erisman et al., 2008*)

Proof from mass balance (in the boundary layer):

$$[NH_3] \cong \frac{hE_{NH_3}}{v_d^{NH3}}$$

E_{NH_3}: *gas phase NH_3 emission rate*;
v_d^{NH3}: *gas phase deposition velocity*;
h: *boundary layer mixed depth*

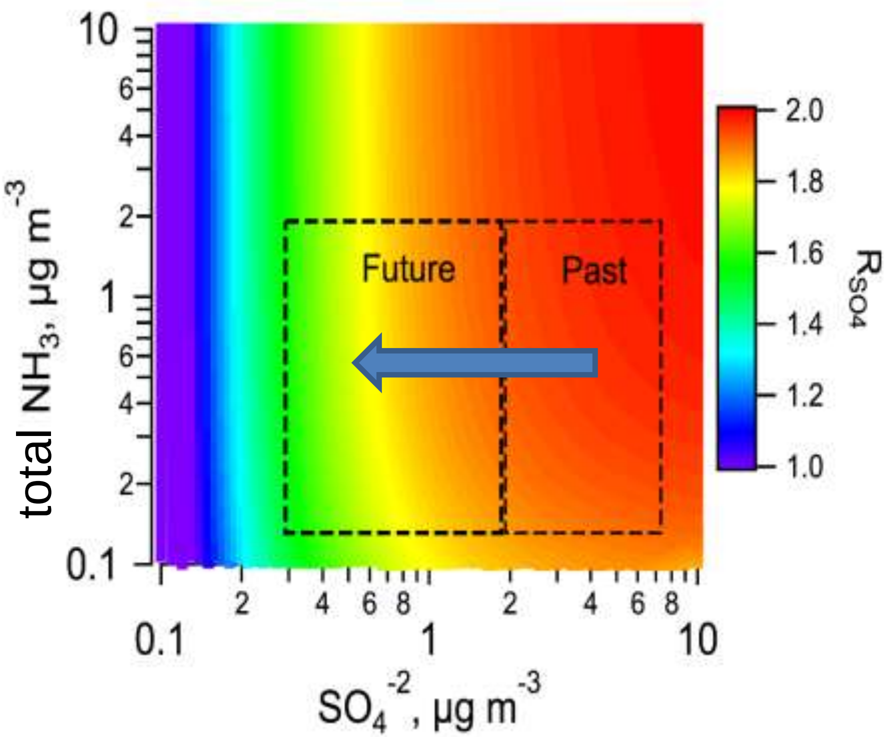
E_{NH_3} increased slightly (~10%) during the last decade globally. (*Erisman et al., 2008*)

NH_3 has and probably will remain the same

Weber et al. (2016), *Nature Geosci.*

Looking into the future: how will acidity respond?

Reference state: average SOAS conditions (RH=75%, T=25°C)



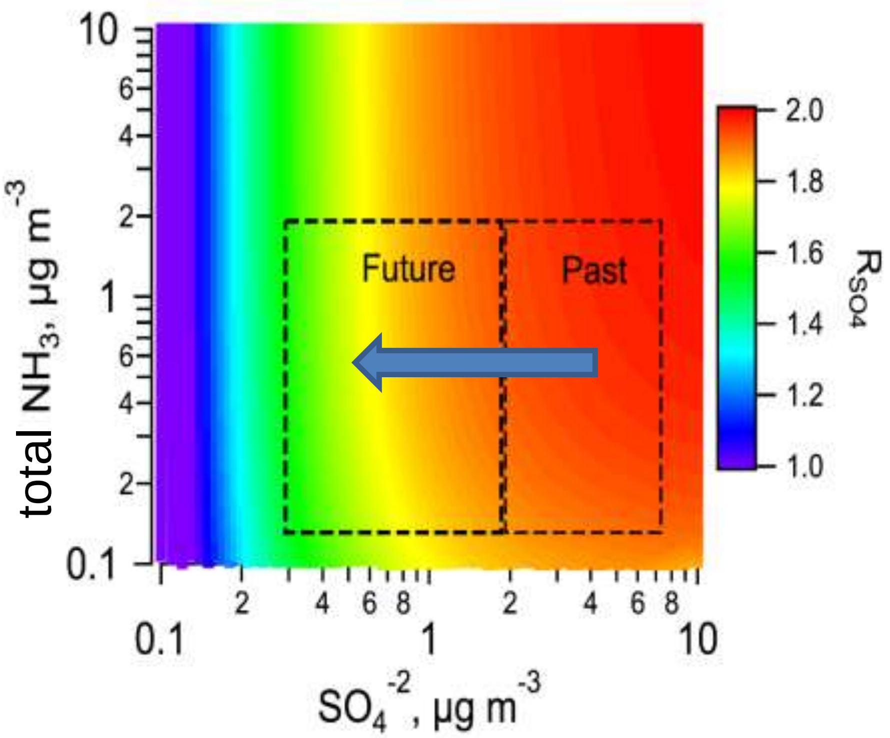
For constant total NH_3, R_{SO4} goes *down* as SO_4 drops.

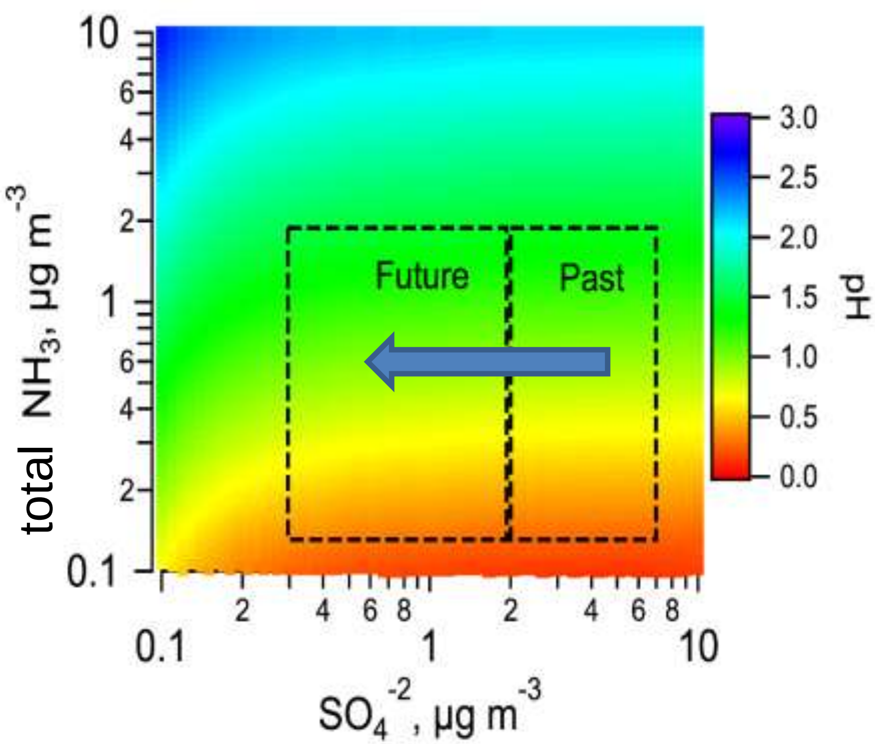
This is seen in the data too.

Weber et al. (2016), *Nature Geosci.*

Looking into the future: how will acidity respond?

Reference state: average SOAS conditions (RH=75%, T=25°C)





For constant total NH_3, R_{SO4} goes *down* as SO_4 drops.

This is seen in the data too.

The pH levels remain insensitive to SO_4 changes in the SE US.

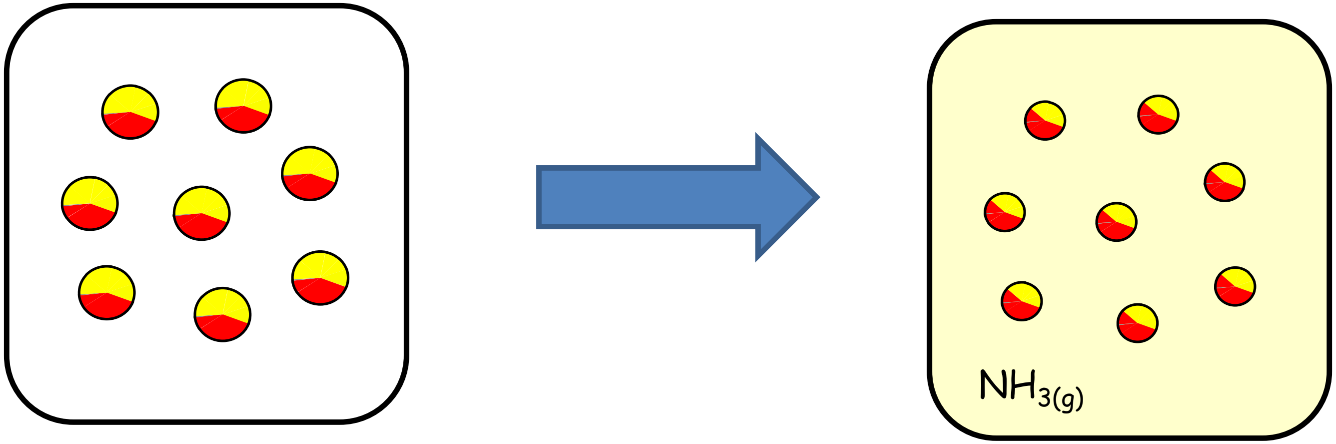
Huge changes in NH_3 (which won't happen) are needed to increase pH

Weber et al. (2016), *Nature Geosci.*

Why this behavior? NH_3 is semi-volatile, buffers system

initially: a lot of $(NH_4)_2SO4$ but no $NH_{3(g)}$

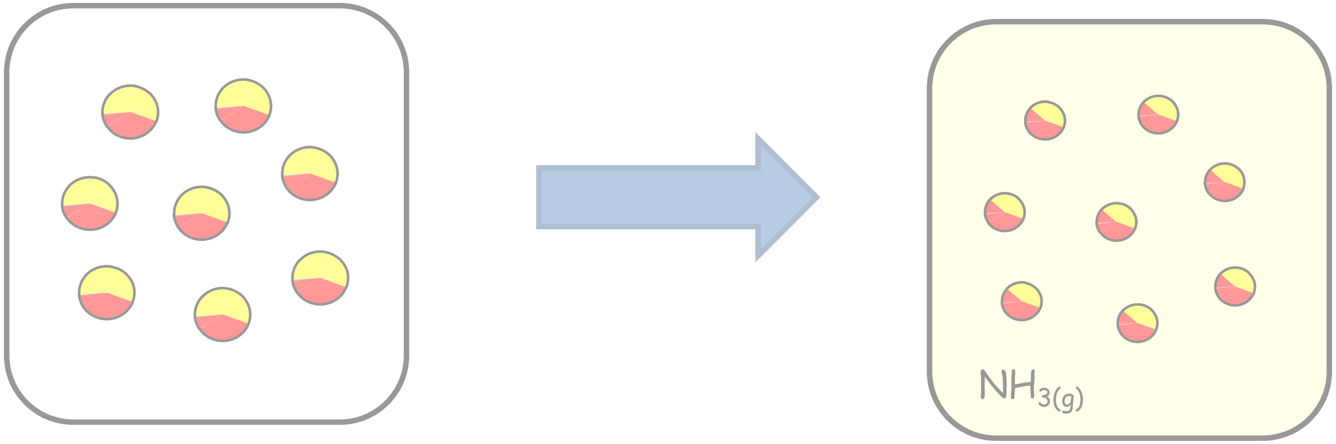
at equilibrium: some NH_4 volatilizes. particles become acidic



Why this behavior? NH_3 is semi-volatile, buffers system

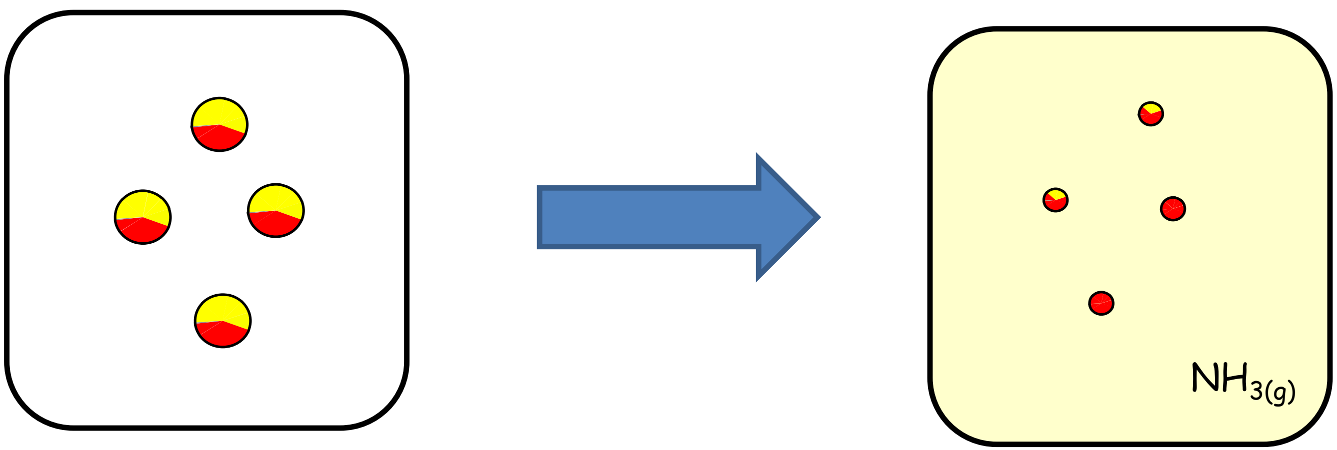
initially: a lot of $(NH_4)_2SO4$
no $NH_{3(g)}$

at equilibrium: some NH_4 volatilizes.
particles become acidic

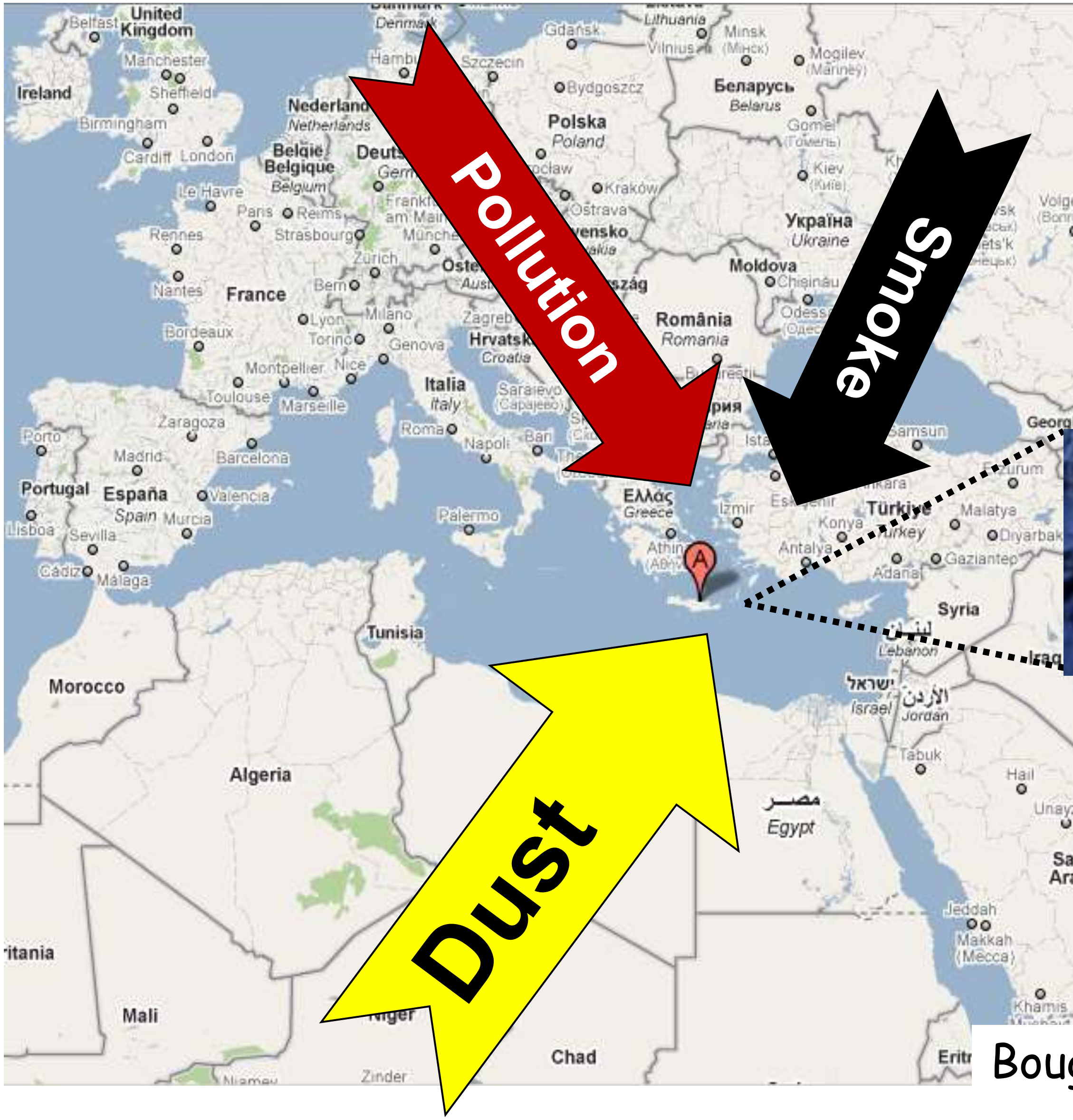


initially: *less* $(NH_4)_2SO4$
no $NH_{3(g)}$

at equilibrium: *more* NH_4 volatilizes.
particles may become a little *more* acidic



Low acidities are found everywhere



Summertime data (2013)

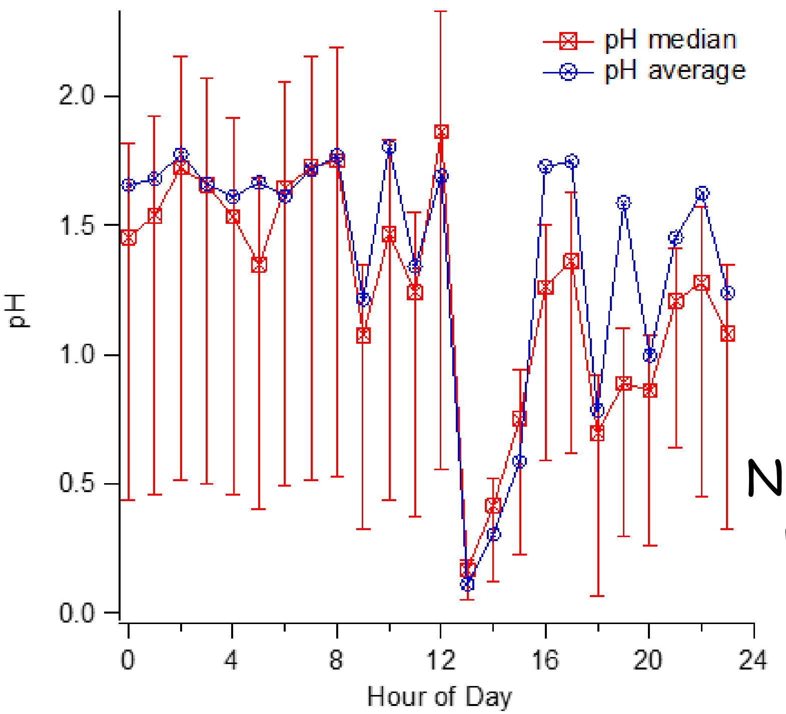
- ACSM/WAD (comp.)
- Nephelometer (LWC)
- pH analysis

Look at average and each airmass type sampled

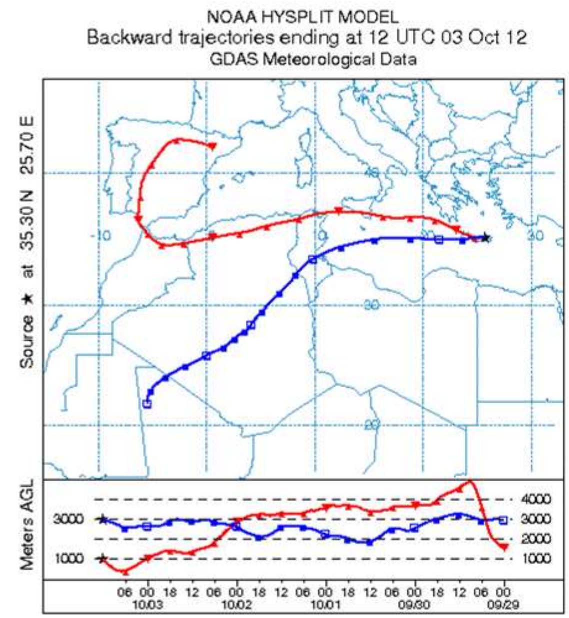
Bougiatioti et al., ACPD (2016)

Finokalia, Crete pH distributions

Airmass type: Mineral dust aerosol (fine)



Nitrate formation pH "threshold"

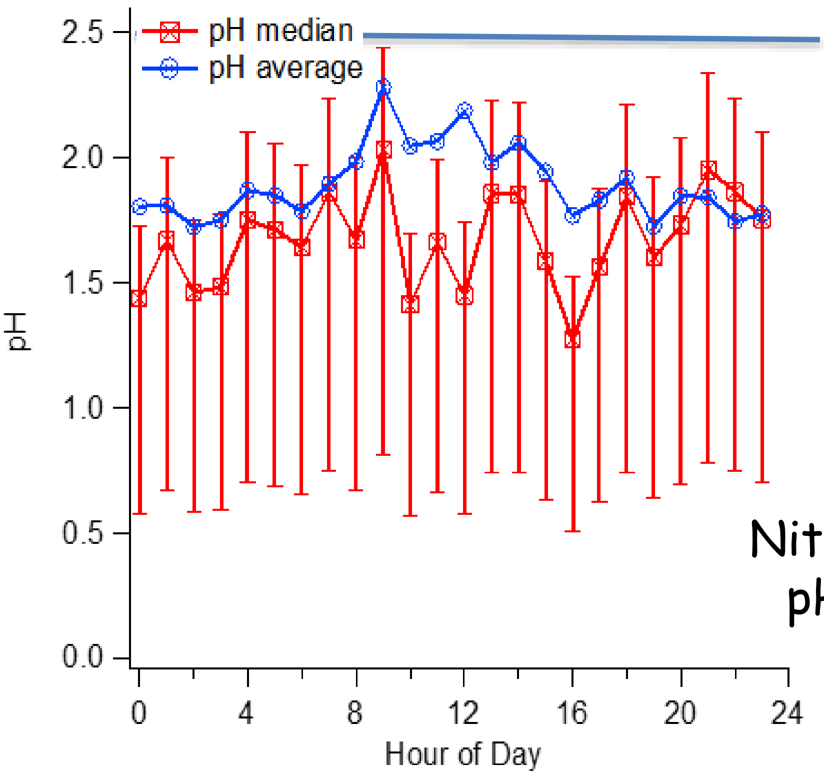


Summary/implications:

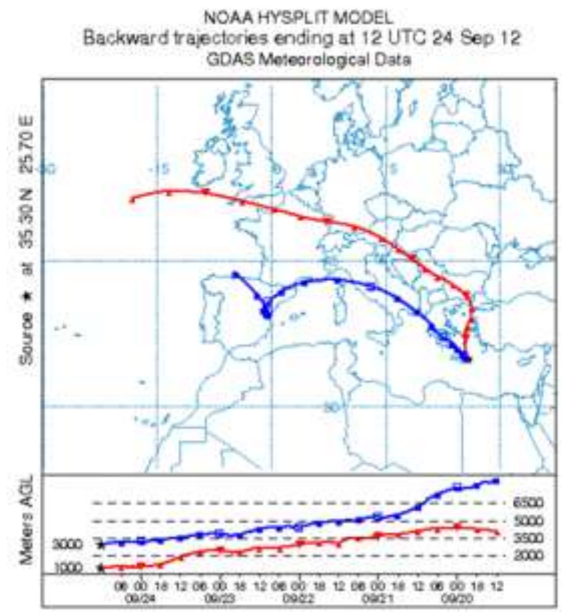
- NH_3 vs SO_4 is like in SE US, aerosol is quite acidic.
- Most of the time, very low NO_3 levels on fine mode aerosol (Surprise!!).

Finokalia, Crete pH distributions

Airmass type: Continental aerosol (fine)



Nitrate formation pH "threshold"

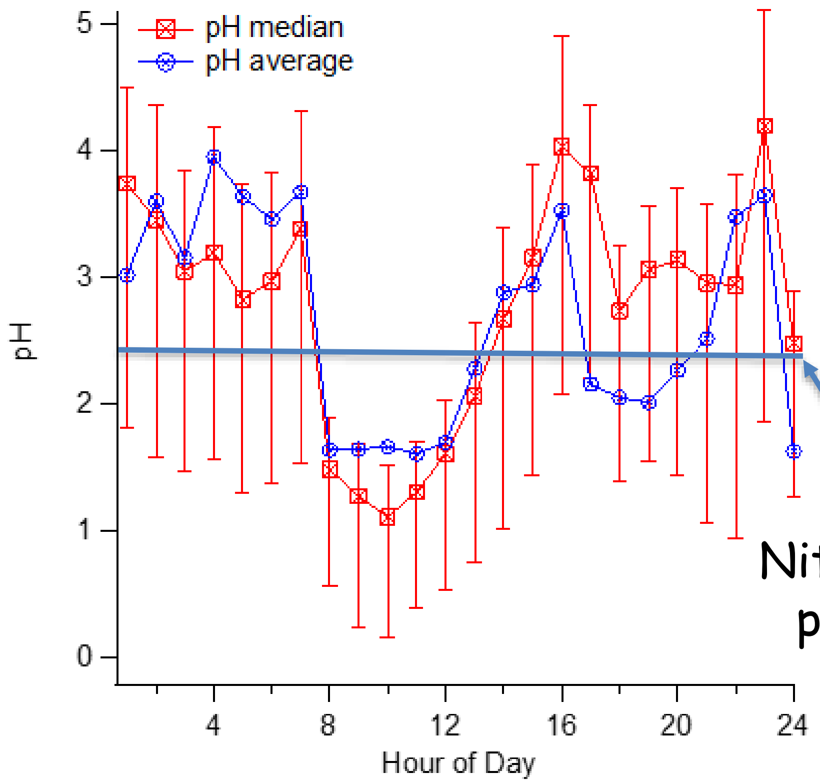


Summary/implications:

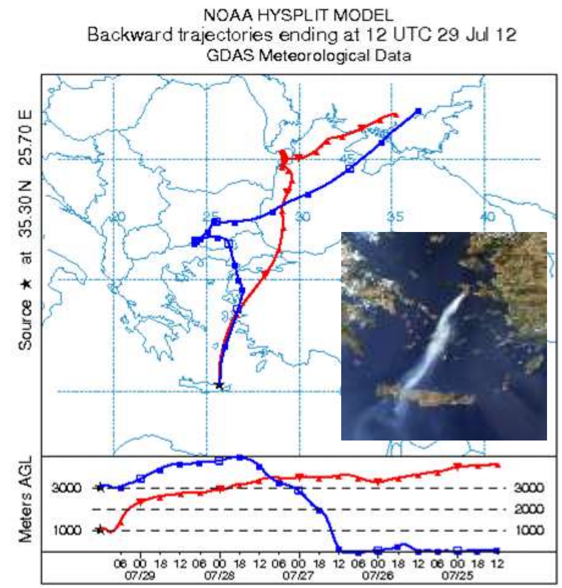
- NH_3 vs SO_4 is like in SE US, aerosol is quite acidic.
- Most of the time, low levels of NO_3 on fine mode aerosol.

Finokalia, Crete pH distributions

Airmass type: Smoke/Biomass burning



Nitrate formation
pH "threshold"



Summary/implications:

- NH_3 is very high (vs SO_4) and that leads to neutralization of aerosol.
- Most of the time, a lot (almost all) HNO_3/NO_3 partitions to aerosol.

Some take home messages

Findings:

- Particle pH is low (-0.5 to 1.5) and NH_3 varied little in the SE US. Very low acidity seen in dusty regions too (E.Med; Bougiatioti et al., 2016).
- Future particle pH may remain low even if SO_4 goes down. pH is **insensitive** to shifts in NH_3 and SO_4 levels because NH_4 is volatile.
- You can have very acidic aerosol **even if $NH_4/SO_4 > 2$**.

Some take home messages

Findings:

- Particle pH is low (-0.5 to 1.5) and NH_3 varied little in the SE US. Very low acidity seen in dusty regions too (E.Med; Bougiatioti et al., 2016).
- Future particle pH may remain low even if SO_4 goes down. pH is **insensitive** to shifts in NH_3 and SO_4 levels because NH_4 is volatile.
- You can have very acidic aerosol **even if $NH_4/SO_4 > 2$**.

Implications:

- pH proxies used for decades do **not** work well and should be **avoided**.
- Aerosol nitrate, contrary to current belief and policy, may **not** be a major component of the regional aerosol as sulfate levels drop.
- Acid-mediated process may continue to remain unchanged.
- Mineral dust (land use change)/seasalt emissions very important.

Some take home messages

Findings:

- Particle pH is low (-0.5 to 1.5) and NH_3 varied little in the SE US. Very low acidity seen in dusty regions too (E.Med; Bougiatioti et al., 2016).
- Future particle pH may remain low even if SO_4 goes down. pH is **insensitive** to shifts in NH_3 and SO_4 levels because NH_4 is volatile.
- You can have very acidic aerosol **even if NH_4/SO_4 > 2**.

Implications:

- pH proxies used for decades do **not** work well and should be **avoided**.
- Aerosol nitrate, contrary to current belief and policy, may **not** be a major component of the regional aerosol as sulfate levels drop.
- Acid-mediated process may continue to remain unchanged.
- Mineral dust (land use change)/seasalt emissions very important.

Models have *never* been evaluated for their ability to predict pH – and presents a unique opportunity for understanding predictive biases.

Acknowledgements

THANK YOU!

NSF

United States Environmental Protection Agency

NASA

National Oceanic and Atmospheric Administration, U.S. Department of Commerce, NOAA

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R834799

Health Effects Institute

NOAA CPO Award NA10OAR4310102

SOAS
Southern Aerosol Oxidant Study

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R835410

This publication was made possible by US EPA grant R834799 and R835410. This publication's contents are solely the responsibility of the grantee and do not necessarily represent the official views of the US EPA. Further, US EPA does not endorse the purchase of any commercial products or services mentioned in the publication.