High aerosol acidity despite declining atmospheric sulfate concentrations

Lessons learned from the SE US and implications for models.

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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*)

2. **Controls acidic and basic gas-particle partitioning:**
   - e.g. Nitric acid and nitrate
     \[
     HNO_3(g) + H_2O \leftrightarrow HNO_3 \cdot H_2O, \quad K_H
     \]
     \[
     HNO_3 \cdot H_2O \leftrightarrow NO_3^- + H^+, \quad K_a
     \]
     (Surratt et al., 2007)

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

SO₂(g) → Oxidation → H₂SO₄(p)
NOₓ(g) → HNO₃(p)

Basic

NH₃(g) + Mineral dust + seasalt (Na, K, Ca, Mg, etc.)

formation of (NH₄)₂SO₄, NH₄HSO₄, NH₄NO₃, etc. that depends on particle acidity

Other sources of alkalinity
Introduction

**Historical SO₂ and SO₄²⁻ trends:**

- In the past twenty years, SO₂ emissions have decreased significantly (-6.2% yr⁻¹, 2000-2010, *Hand et al. 2012*).
- SO₄²⁻ followed SO₂ reduction.

**Scientific questions:**

1. Are particles in southeast US becoming neutral as SO₂ 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 $\sim 0$

**Historical Data:**
SO$_4$ is going down
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**Aerosol response:**
Should have become more neutralized -

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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:**

\[
pH = -\log_{10}[H^+] = -\log_{10}\left(\frac{1000H^+_{air}}{LWC}\right)
\]

\(H^+_{air}, LWC\) 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 pKa.
  - pH depends on LWC, which can vary considerably.

**Ion balance:**

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

**NH}_4^+\text{/SO}_4^{2-} \text{ 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 & $\kappa_{org}$;
- RH and $T$;

\[ W_i, \text{ particle water associated with inorganics} \]
\[ W_o, \text{ particle water associated with organics} \]

"Determining aerosol pH: The “heart” of it"

1. **Solid phase:** NaHSO₄, NH₄HSO₄, Na₂SO₄, NaCl, (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂, NH₄NO₃, NH₄Cl, NaNO₃, K₂SO₄, KH₂SO₄, KNO₃, KCl, CaSO₄, Ca(NO₃)₂, CaCl₂, MgSO₄, MgCl₂, Mg(NO₃)₂

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

2. **Liquid phase:** Na⁺, NH₄⁺, H⁺, OH⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, Cl⁻, H₂O, HNO₃(aq), HCl(aq), NH₃(aq), Ca²⁺, K⁺, Mg²⁺

3. **Gas phase:** HNO₃, HCl, NH₃, H₂O

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:
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Aerosol response:
Should have become more neutralized
It’s “acidifying”.

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Aerosol response:
Should have become more neutralized - it hasn’t.

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

Weber et al. (2016), Nature Geosci.
**SE US: pH is very low despite large reductions in SO₂**

**Historical Data:**
SO₄ is going down
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Nitrate is ~ 0

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

**pH calculations:**
Confirm that this is the case for SE US.
Comparison of predicted vs. observed gas-phase NH$_3$. Guo et al., ACP, 2015.

SOAS Data analysis confirms pH calculations
SOAS Data analysis confirms pH calculations

The volatilization fraction 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.
NH₃ has and probably will remain the same

Proof from observation: 3 years (AMoN sites)

Summary:
In the past, NH₃ has been fairly constant.
In the future, NH₃ will probably stay at current level or increase slightly.
(Erisman et al., 2008)

Weber et al. (2016), Nature Geosci.
**NH₃ has and probably will remain the same**

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![Graph showing NH₃ emissions over time](image)

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**Proof from mass balance (in the boundary layer):**

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

- \(E_{NH_3}\): gas phase \(NH_3\) emission rate;
- \(v_{d}^{NH_3}\): gas phase deposition velocity;
- \(v_{d}^{NH_4^+}\): particle phase deposition velocity;
- \(h\): boundary layer mixed depth

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\text{emissions} \quad \text{gas} \quad \text{deposition rate} \\
\]

\[
E_{NH_3} : \text{gas phase NH}_3 \text{ emission rate;} \\
\frac{v_{d}^{NH_3}}{h} : \text{gas phase deposition velocity;} \\
\frac{v_{d}^{NH_4}}{h} : \text{particle phase deposition velocity;} \\
h : \text{boundary layer mixed depth} \\
\]

but \( v_{d}^{NH_3} \gg v_{d}^{NH_4} \)

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[NH₃] ≈ \frac{hE_{NH₃}}{v_d^{NH₃}}
\]

- \(E_{NH₃}\): gas phase NH₃ emission rate;
- \(v_d^{NH₃}\): gas phase deposition velocity;
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\(E_{NH₃}\) increased slightly (~10%) during the last decade globally. *(Erisman et al., 2008)*

**NH₃ has and probably will remain the same**

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?

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

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

**initially:** a lot of $(NH_4)_2SO_4$
but no $NH_3(g)$

**at equilibrium:** some $NH_4$ volatilizes.
particles become acidic

$NH_3(g)$
Why this behavior? $NH_3$ is semi-volatile, buffers system

Initially: a lot of $(NH_4)_2SO_4$
No $NH_3(g)$

At equilibrium: some $NH_4$ volatilizes.
Particles become acidic

Initially: less $(NH_4)_2SO_4$
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)

Summary/implications:
• $\text{NH}_3$ vs $\text{SO}_4$ is like in SE US, aerosol is quite acidic.
• Most of the time, very low $\text{NO}_3$ levels on fine mode aerosol (Surprise!!).
Finokalia, Crete pH distributions

Airmass type: Continental aerosol (fine)

Summary/implications:
• NH₃ vs SO₄ is like in SE US, aerosol is quite acidic.
• Most of the time, low levels of NO₃ on fine mode aerosol.
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.
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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.
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- Particle pH is low (-0.5 to 1.5) and NH₃ varied little in the SE US. Very low acidity seen in dusty regions too (E.Med; Bougiatioti et al., 2016).
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Models have never been evaluated for their ability to predict pH – and presents a unique opportunity for understanding predictive biases.
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