Inconsistency of ammonium-sulfate aerosol ratios with thermodynamic models in the eastern US: a possible role of organic aerosol

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Great Smoky Mountains National Park, Southeast US
Sulfate aerosol forms from emissions of $\text{SO}_2$ and ammonia following thermodynamics

**Coal combustion**

- $\text{SO}_2$ → $\text{NH}_3$ → $\text{SO}_4^{2-}$

**Fertilizer & livestock**

- $\text{NH}_3$ → $\text{NO}_x$ → $\text{HNO}_3$ → $\text{NH}_4^+$

**Combustion**

- $\text{NH}_4^+$ → $\text{HNO}_3$ → $\text{NH}_3$ → $\text{SO}_4^{2-}$

**Ammonium-sulfate aerosol ratio**

$$\frac{[\text{NH}_4^+]}{[\text{S(VI)}]}, \text{ mol mol}^{-1}$$

**Graph**

- $\text{NH}_3(g)$, $\mu g \text{ m}^{-3}$
- $\text{Aerosol pH}$
- $\text{Ammonium-sulfate aerosol ratio}$

- Thermodynamic models predict the ammonium-sulfate aerosol ratio approaches 2 mol mol$^{-1}$ when ammonia is in excess.
Surface observations in the eastern US summer show that excess ammonia is available.

Emission Ratio
\( \frac{\text{NH}_3}{\text{SO}_2} \)

Wet Deposition Ammonium-sulfate Ratio
\( \frac{[\text{NH}_4^+]}{[\text{S(VI)}]} \)

Aerosol Ammonium-sulfate Ratio
\( \frac{[\text{NH}_4^+]}{[\text{S(VI)}]} \)

Data: EPA NEI & MASAGE

Data: NADP

Excess ammonia

Low observed ammonium-sulfate aerosol ratios despite the presence of excess ammonia
Long-term trends in observations show further departure from thermodynamic predictions

Averages for Southeast US summer 2003-2013

Wet Deposition Fluxes (kg ha\(^{-1}\))

CSN Aerosol Concentrations (\(\mu g m^{-3}\))

Sulfate

-6.1% a\(^{-1}\)

-8.0% a\(^{-1}\)

no trend

-8.5% a\(^{-1}\)

Ammonium

[\(NH_4^+\)/[S(VI)] (mol mol\(^{-1}\))]

+5.8% a\(^{-1}\)

-3.0% a\(^{-1}\)

Year

Ammonium-sulfate aerosol ratio decreasing despite increasing relative supply of ammonia
Uptake of ammonia by sulfate aerosol may be affected by mixing with organic aerosol (OA)

**OA increasing relative to sulfate**

SEARCH OA/S(VI) Aerosol Ratio (g g\(^{-1}\))

![](chart.png)

**Phase separation observed in laboratory and field**

You et al., 2012

**Laboratory evidence for delayed uptake of ammonia due to OA**

\[ \gamma = 5 \times 10^{-4} \]

Liggio et al., 2011

**Implement kinetic limitation for uptake of ammonia**

\[
\frac{d[NH_4^+]}{dt} = k([NH_3(g)] - [NH_3(g)]_{eq})
\]

\(\gamma\) from Liggio et al., 2011
Kinetic limitation improves agreement of modeled and observed ammonium-sulfate ratios

Kinetic limitation improves agreement of modeled and observed ammonium-sulfate ratios and reproduces observed ammonia without significant bias in the Southeast US.
Conclusions and implications

• Observations show low ammonium-sulfate aerosol ratios despite excess ammonia, at odds with thermodynamic models

• Despite declining SO\textsubscript{2} emissions and constant ammonia emissions, the ammonium-sulfate aerosol ratio decreased from 2003-2013

• Southeast US aerosol has transformed from being sulfate-dominated to OA-dominated over the same time period

• Implementation of a simple kinetic mass transfer limitation for ammonia uptake to sulfate aerosol better reproduces observed ammonium-sulfate aerosol ratios and ammonia

• The co-benefit of SO\textsubscript{2} emission reductions for suppressing secondary organic aerosol formation may not be as large as previously thought if aerosol acidity is increasing

• A mass transfer limitation may also have implications for the partitioning of semi-volatile species such as nitrate as well as water