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

$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- \rightarrow \text{SO}_4^{2-}$

Fertilizer & livestock

Ammonia excess

$\text{NH}_3 \rightarrow \text{NH}_3(aq) \rightarrow \text{NH}_4^+ \rightarrow \text{NH}_x$

Combustion

Ammonia deficit

$\text{NO}_x \rightarrow \text{HNO}_3 \rightarrow \text{HNO}_3(aq) \rightarrow \text{NH}_3(aq)$

Thermodynamic models predict the ammonium-sulfate aerosol ratio approaches 2 mol mol$^{-1}$ when ammonia is in excess

$\text{NH}_3(g), \mu g \text{ m}^{-3}$

$\text{NH}_3(aq)$

Ammonium-sulfate aerosol ratio

$[\text{NH}_4^+]/[\text{S(VI)}]$, mol mol$^{-1}$
Surface observations in the eastern US summer show that excess ammonia is available. Data: EPA NEI & MASAGE. A low observed ammonium-sulfate aerosol ratios despite the presence of excess ammonia.
Surface observations in the Southeast US do not follow thermodynamic predictions.

Collocated Observations

Observed ammonium-sulfate aerosol ratios are not sensitive to increasing wet deposition ratio.
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 (\(\mu g \text{ m}^{-3}\))

Sulfate

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

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

Ammonium

no trend

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

Ammonium-sulfate Ratio

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

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

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

Year

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

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 now present in excess of sulfate in Southeast US**

- Dust
- Black Carbon
- Nitrate
- Ammonium
- Sulfate

Mean aerosol composition, summer 2013

**Phase separation observed in laboratory and field**

- Organic aerosol coating
- Inorganic core \((\text{NH}_4^+, \text{SO}_4^{2-})\)

You et al., 2012

**OA increasing relative to sulfate**

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

- Year: '03, '06, '09, '12
- OA/S(VI) increasing by +9.8% a\(^{-1}\)

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

- \(y = 5 \times 10^{-4}\)

Liggio et al., 2011
GEOS-Chem simulations of Southeast US summer 2013 – 0.25°×0.3125° resolution, detailed oxidant-aerosol chemistry

GEOS-Chem can reproduce sulfate and OA surface observations

Model overestimates aerosol ammonium compared to aircraft observations

Data: AMS, Jose Jimenez

Sulfate

Organic Carbon

Implement kinetic limitation for uptake of ammonia

Net uptake Local Equilibrium

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

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

GEOS-Chem Aerosol Ratio

Standard model
Kinetic limitation

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

Gas-phase ammonia

Kinetic limitation captures low observed ammonium-sulfate aerosol 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$_2$ 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$_2$ 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