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

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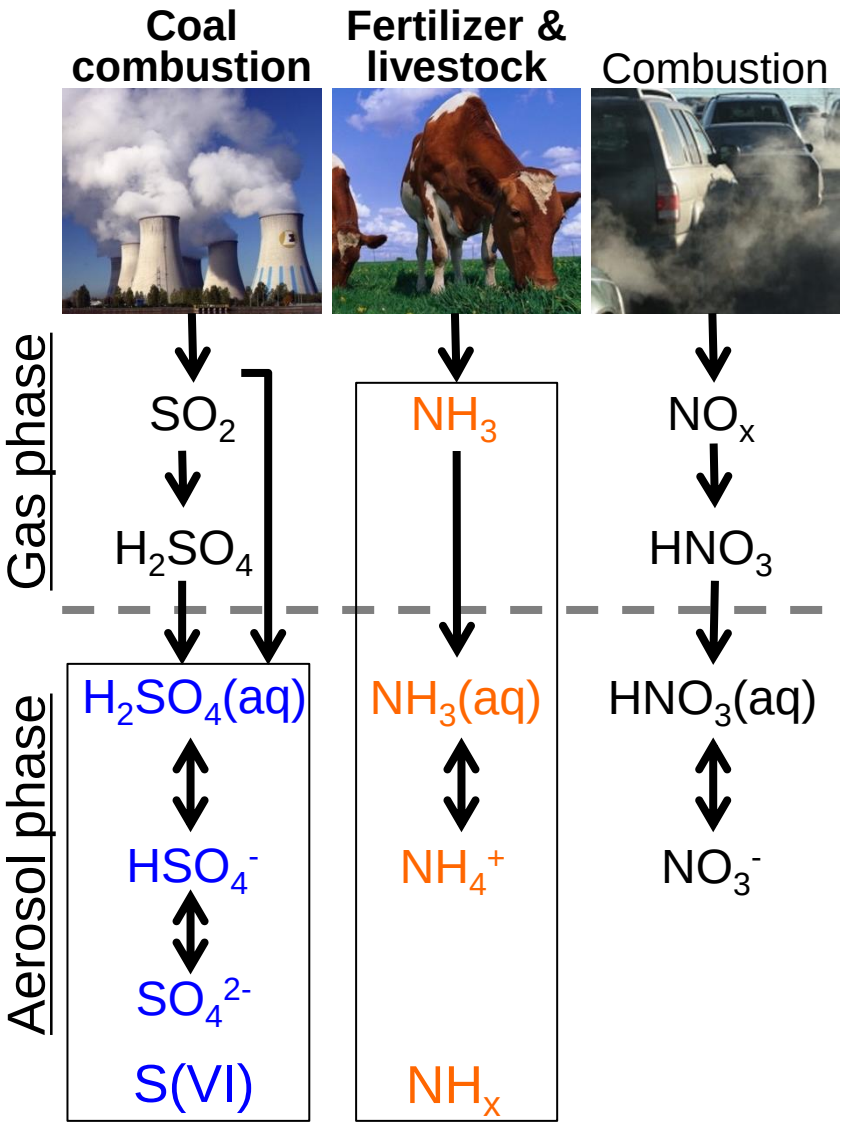
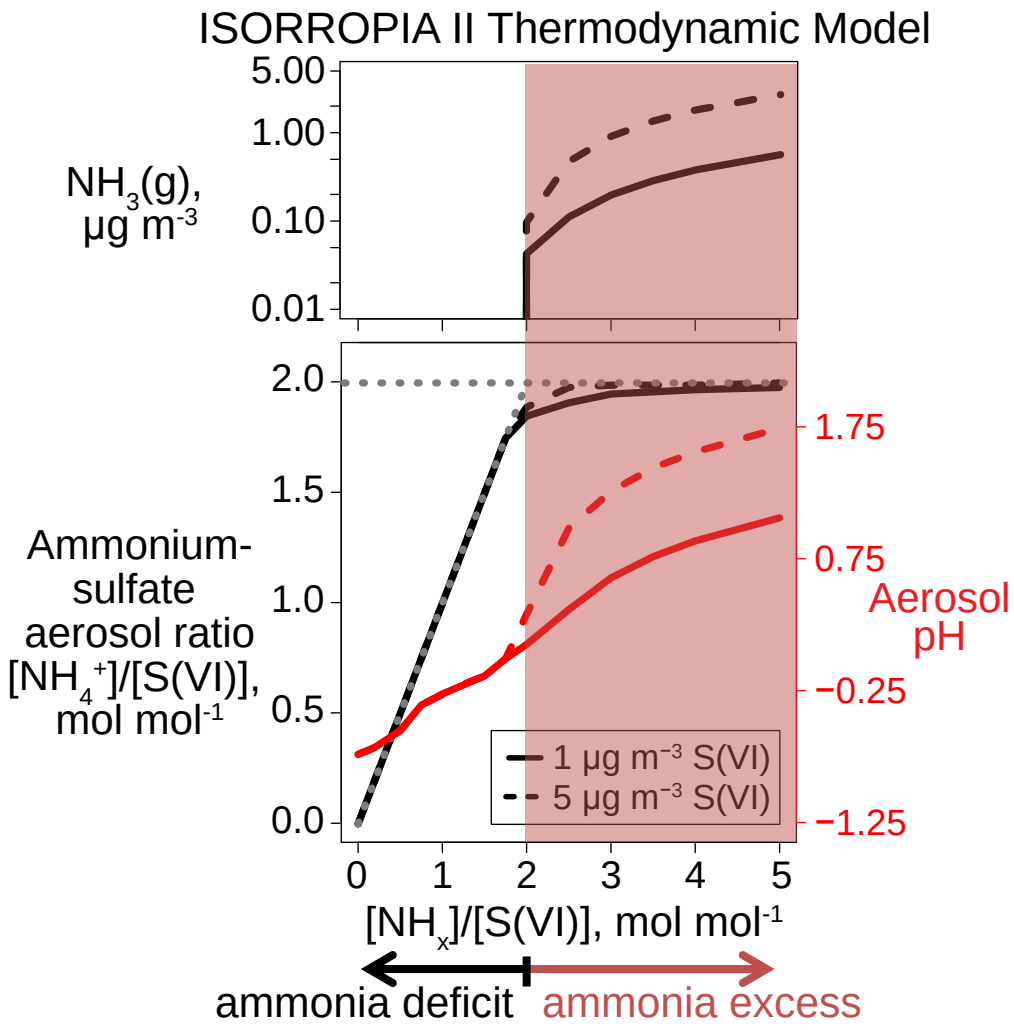
Great Smoky Mountains National Park, Southeast US

Sulfate aerosol forms from emissions of SO_2 and ammonia following thermodynamics





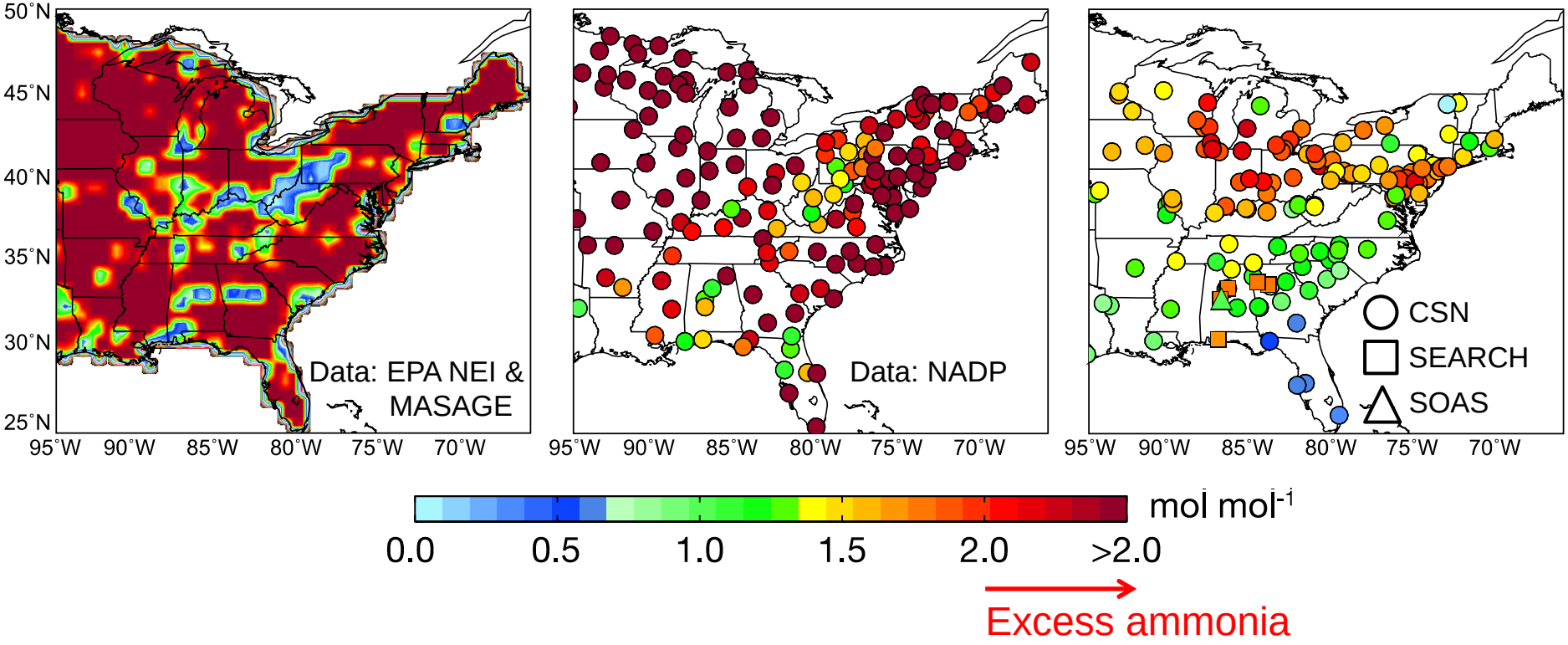
Thermodynamic models predict the ammonium-sulfate aerosol ratio approaches 2 mol mol^{-1} when ammonia is in excess

Surface observations in the eastern US summer show that excess ammonia is available

Emission Ratio
NH_3 / SO_2

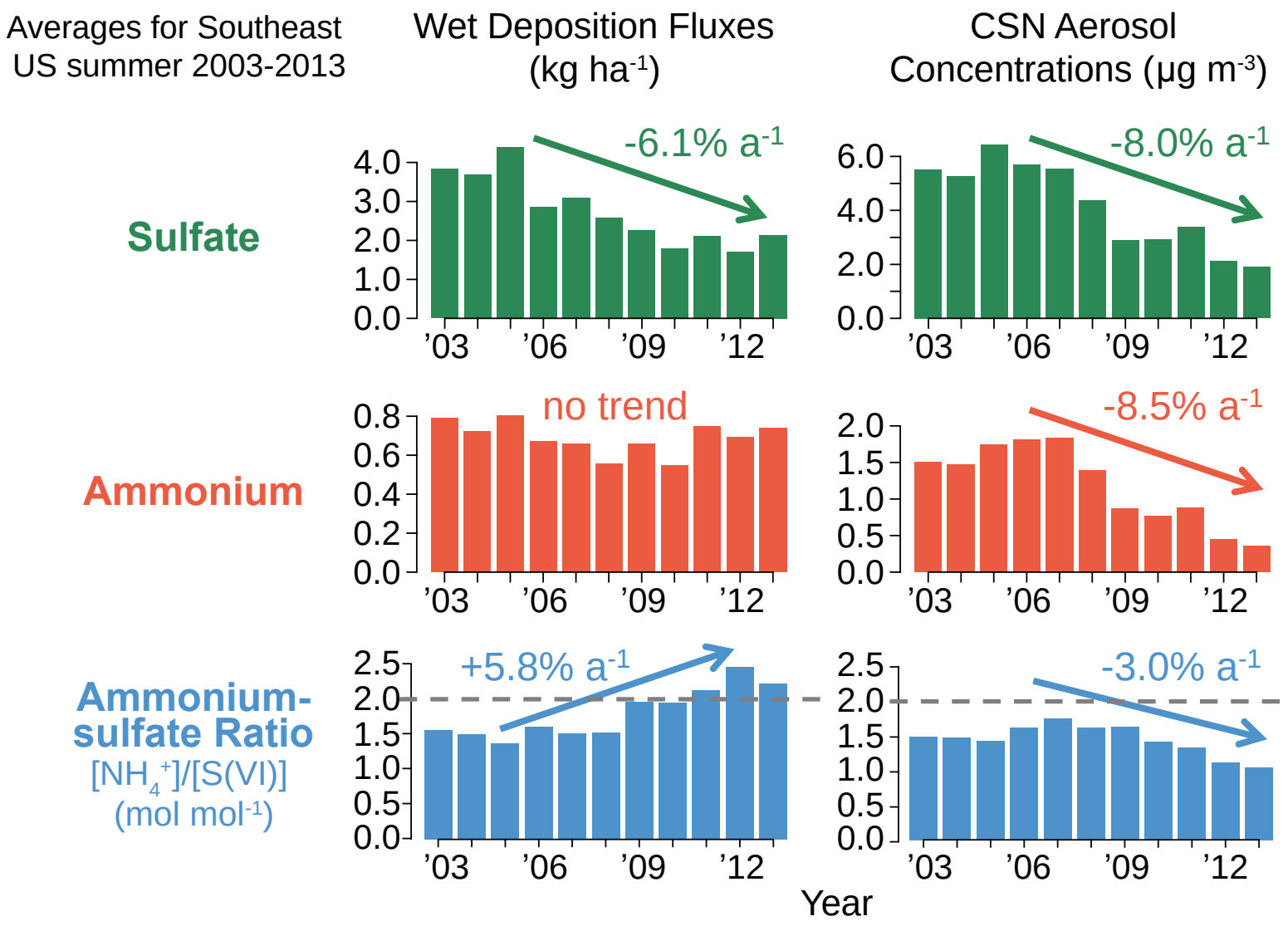
Wet Deposition
Ammonium-sulfate Ratio
$[NH_4^+] / [S(VI)]$

Aerosol
Ammonium-sulfate Ratio
$[NH_4^+] / [S(VI)]$



Low observed ammonium-sulfate aerosol ratios despite the presence of excess ammonia

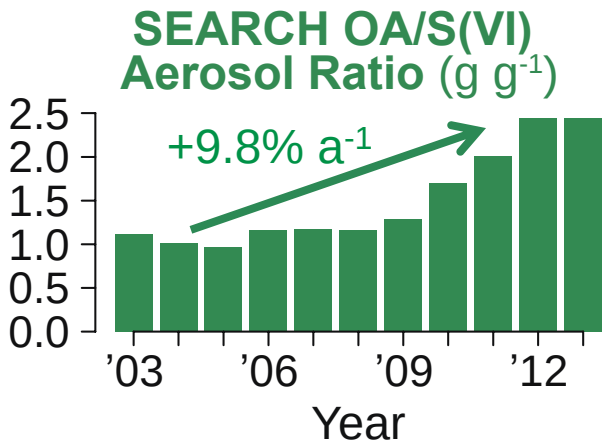
Long-term trends in observations show further departure from thermodynamic predictions



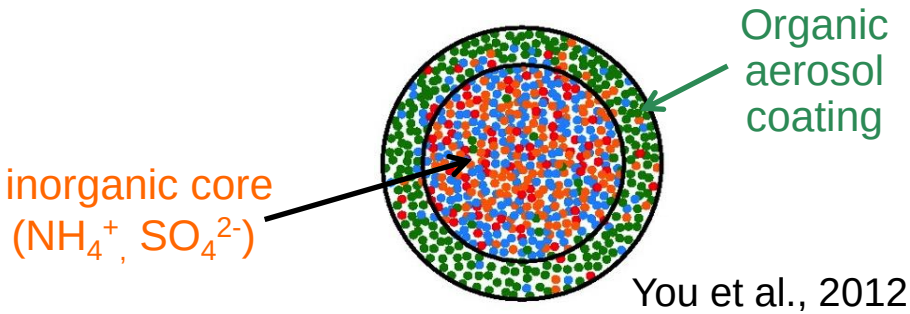
Ammonium-sulfate aerosol ratio decreasing despite increasing relative supply of ammonia

Uptake of ammonia by sulfate aerosol may be affected by mixing with organic aerosol (OA)

OA increasing relative to sulfate

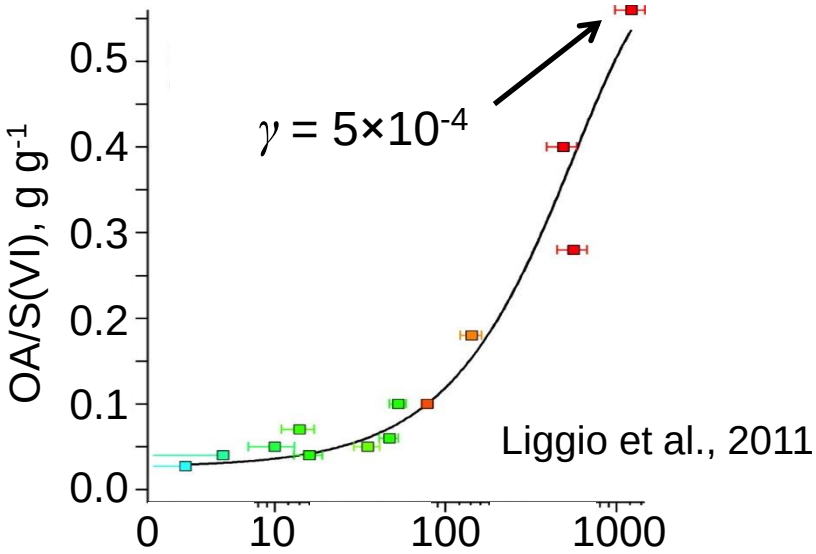


Phase separation observed in laboratory and field



You et al., 2012

Laboratory evidence for delayed uptake of ammonia due to OA



Liggio et al., 2011

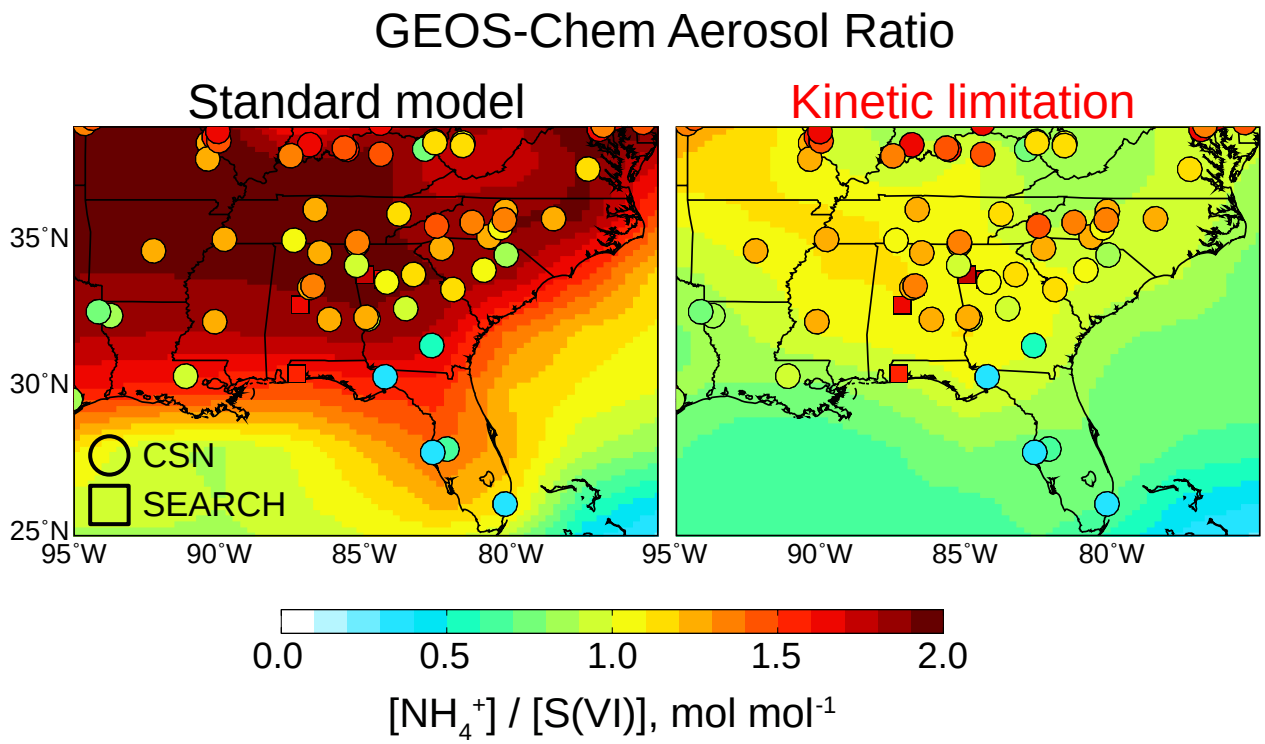
Implement kinetic limitation for uptake of ammonia

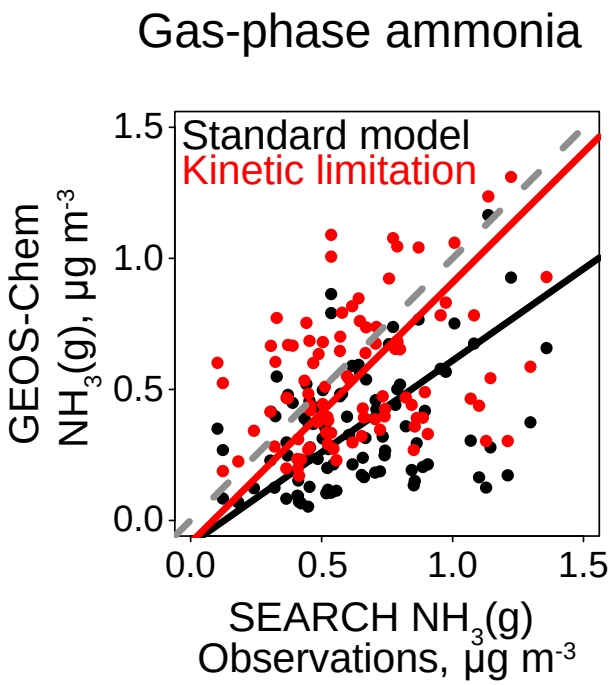
Net uptake Local Equilibrium

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

γ from Liggio et al., 2011

Kinetic limitation improves agreement of modeled and observed ammonium-sulfate ratios





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