Developing the adjoint of ISORROPIA:

Equipping CMAQ-ADJ for Comprehensive Treatment of Inorganic Aerosol

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Georgia Institute of Technology

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Overview

How would a comprehensive inorganic aerosol adjoint augment the functionality of CMAQ-ADJ?

What is the process of adjoint development?

In what sensitivity regime are Atlanta aerosol?

Regional influence of inorganic aerosols

- Aesthetic
  - Hinder visibility
  - Acid rain damage
- Ecological
  - Nitrification of ecosystems (Galloway et al., 2004)
- Epidemiological
  - Potential of inorganic fine particulate matter ($PM_{2.5}$) to degrade health (Schlesinger, 2007)

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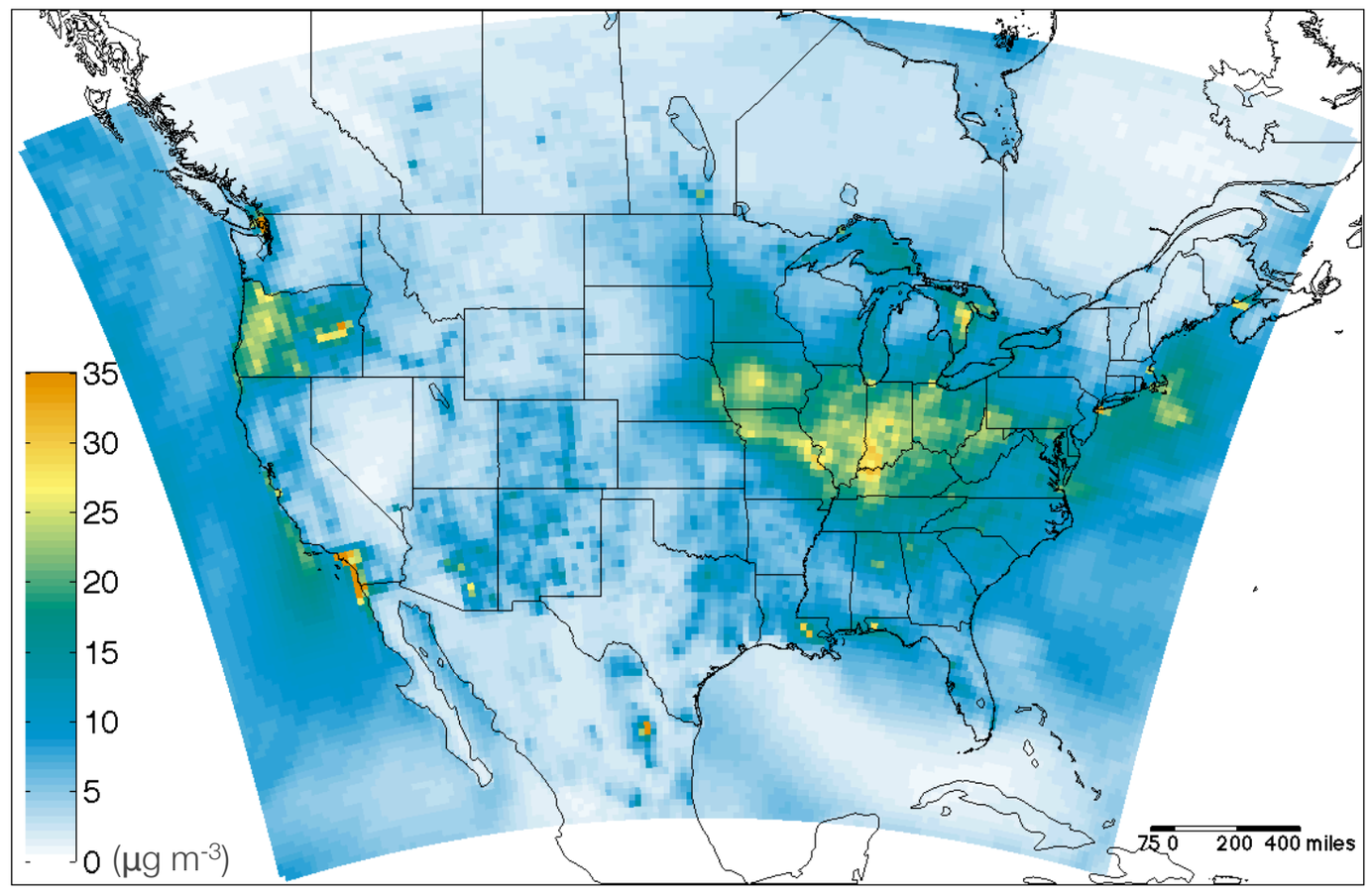
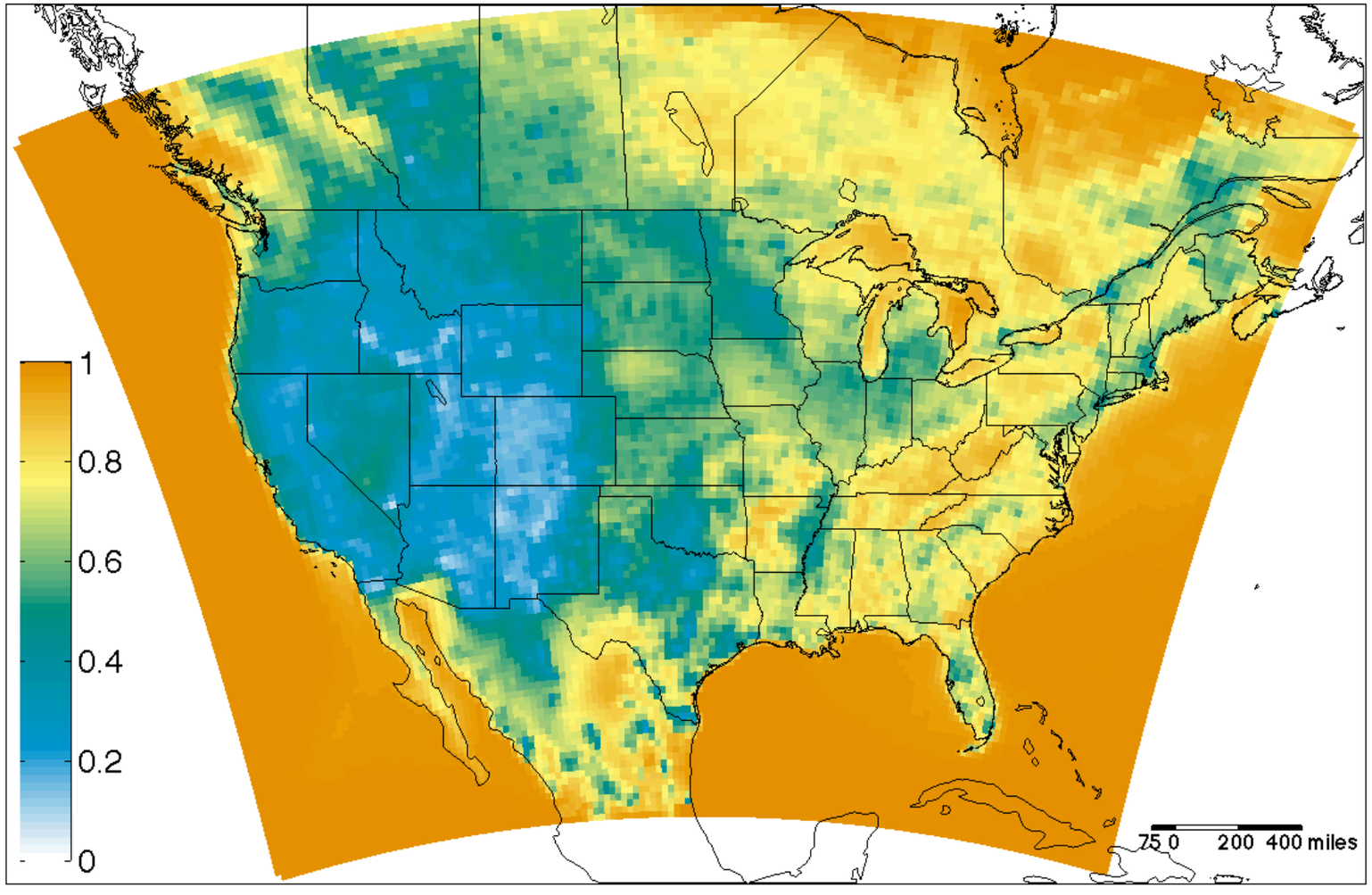
Abundance of Inorganic Aerosol

Inorganic Aerosol Mass Fraction



Total Aerosol Loading

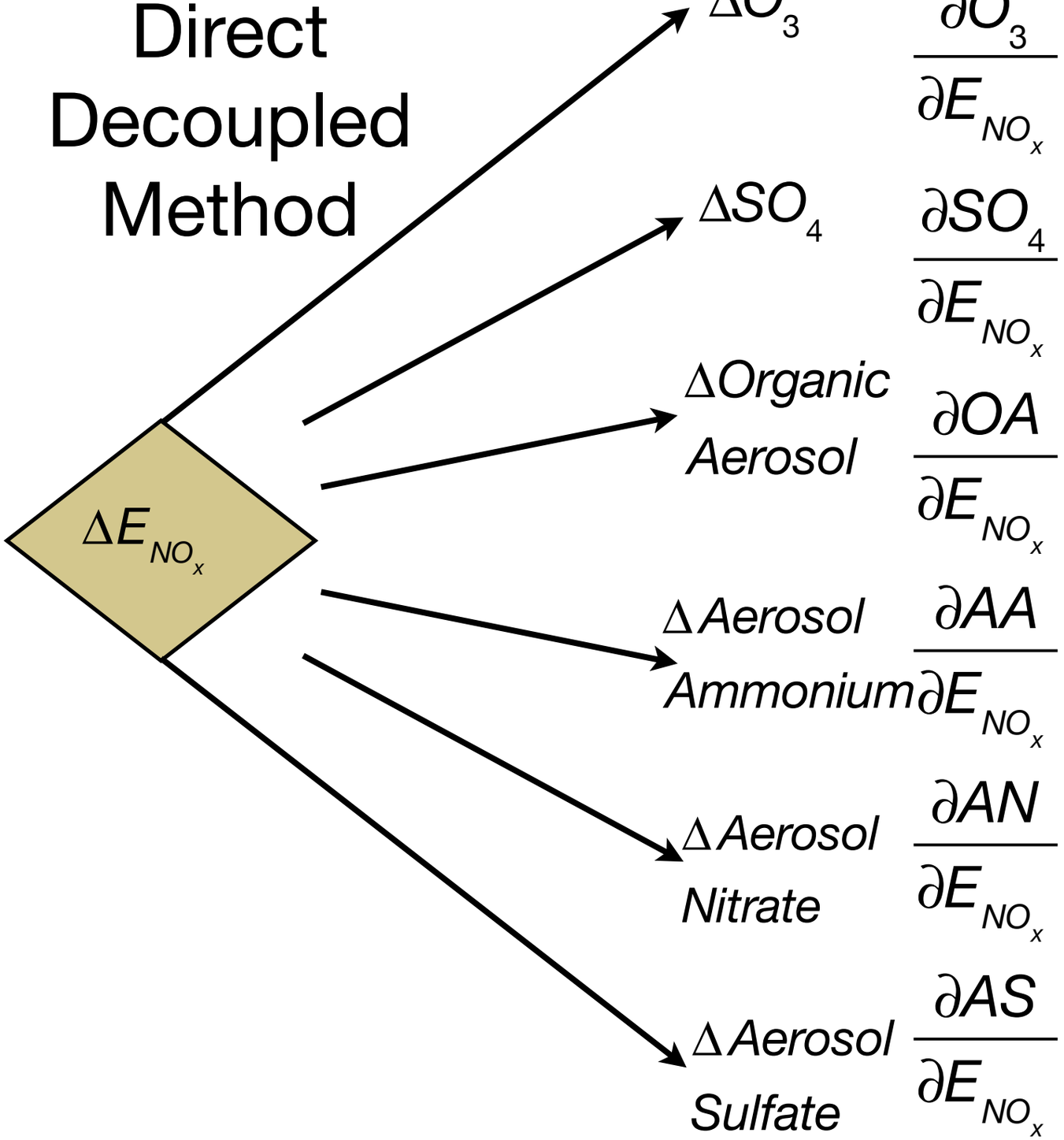


Average of CMAQ v4.6 hourly data from June 28 - July 7, 2007

Importance of sensitivity calculations:

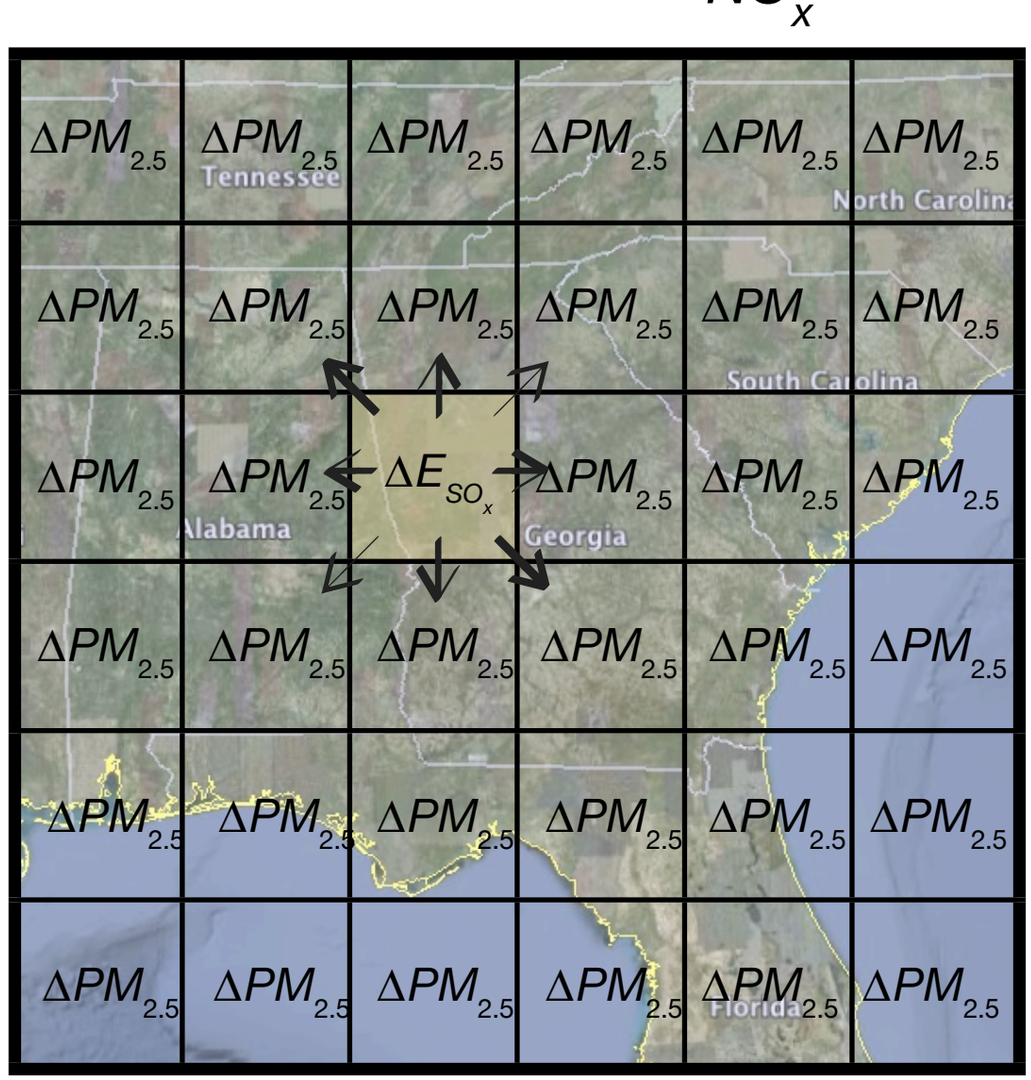
Comprehensive understanding of PM formation

Direct Decoupled Method



"Forward" Sensitivities

$$\frac{\partial(\textbf{Concentrations}_i)}{\partial(Emissions_{NO_x})}$$

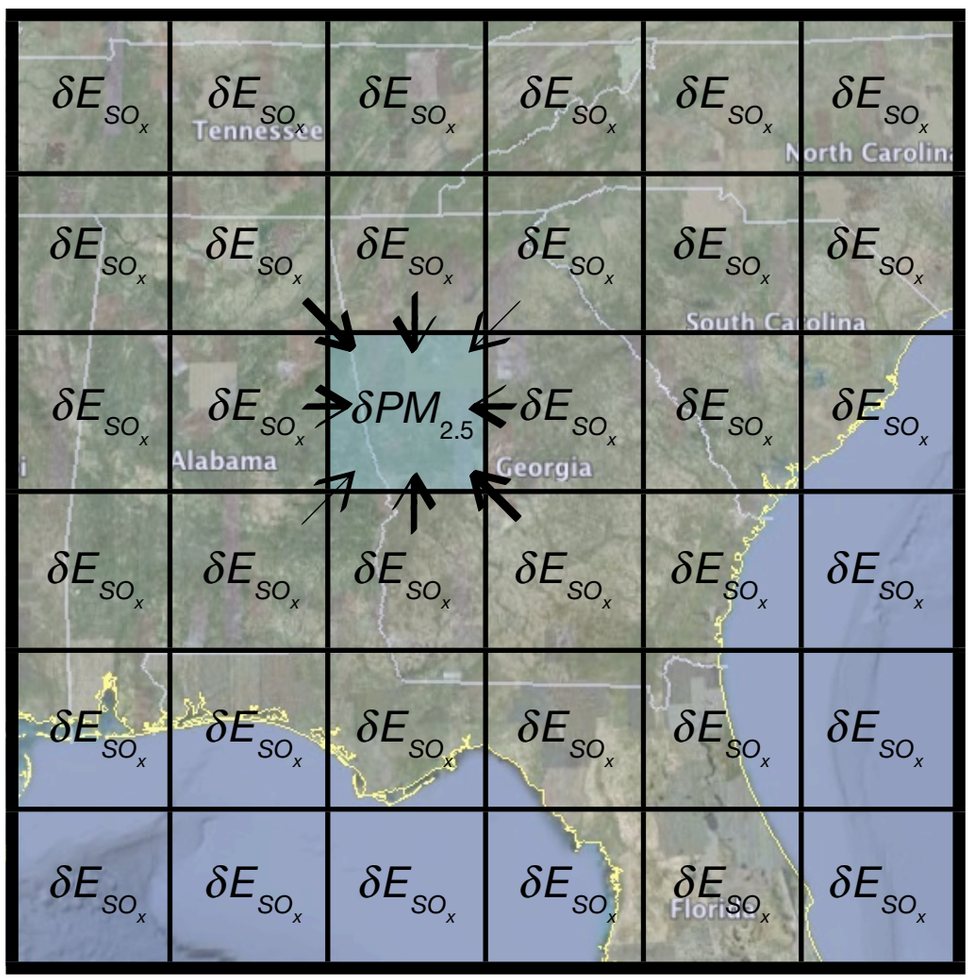


Importance of sensitivity calculations:

Comprehensive understanding of PM formation

"Reverse" Sensitivities

$$\frac{\partial(\textit{Sulfate Aerosol})}{\partial(\textbf{Emissions}_j)}$$



Adjoint Method

$$\frac{\partial SA}{\partial E_{NO_x}|_{power}}\,\delta E_{NO_x}|_{power}$$

$$\frac{\partial SA}{\partial E_{SO_x}|_{power}}\,\delta E_{SO_x}|_{power}$$

$$\frac{\partial SA}{\partial E_{ROG}|_{mobile}}\,\delta E_{ROG}|_{mobile}$$

$$\frac{\partial SA}{\partial E_{NO_x}|_{mobile}}\,\delta E_{NO_x}|_{mobile}$$

$$\frac{\partial SA}{\partial E_{NH_3}}\,\delta E_{NH_3}$$

$$\frac{\partial SA}{\partial E_{dust}}\,\delta E_{dust}$$

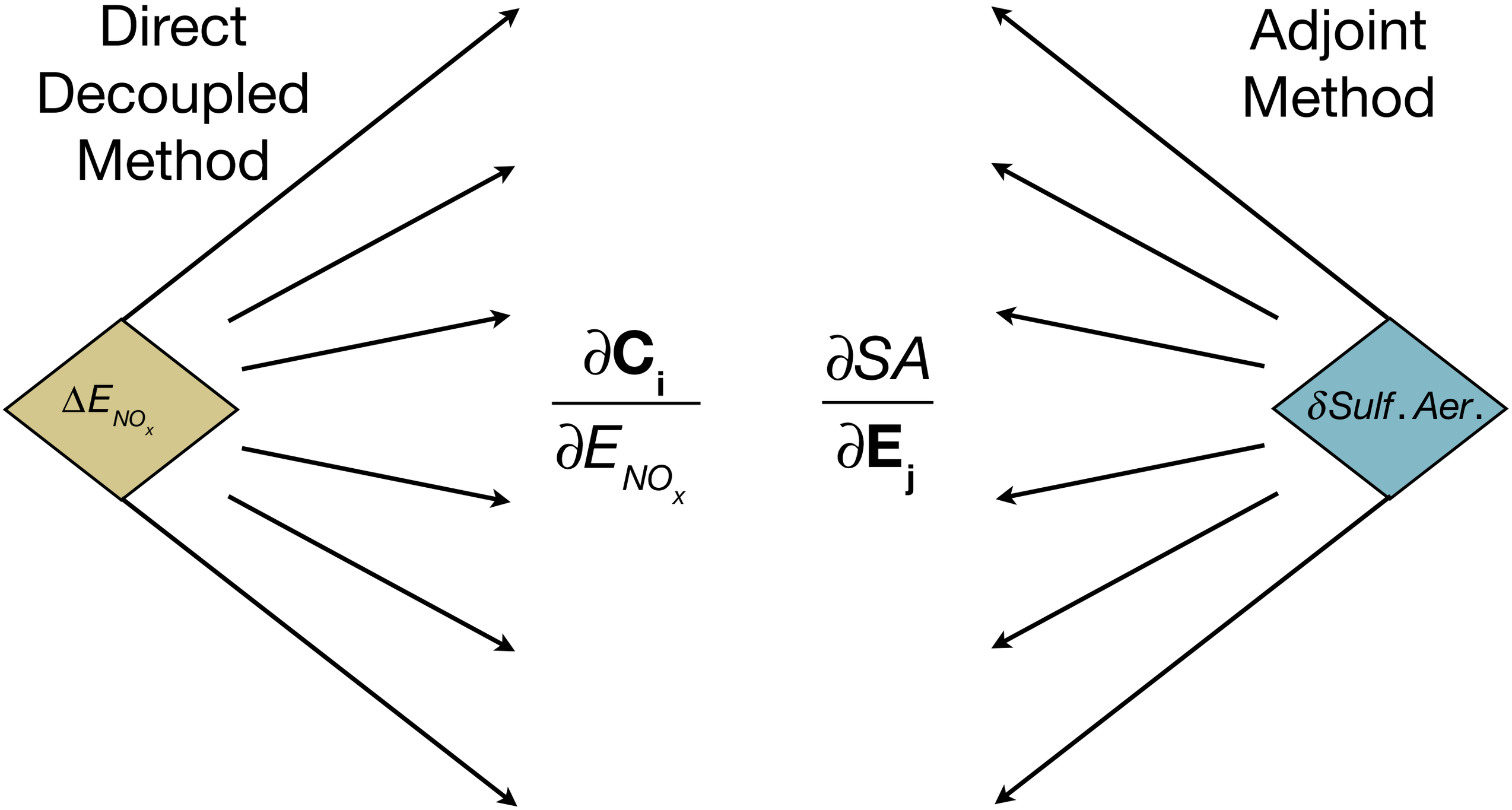
$\delta Sulf.Aer.$

Importance of sensitivity calculations:

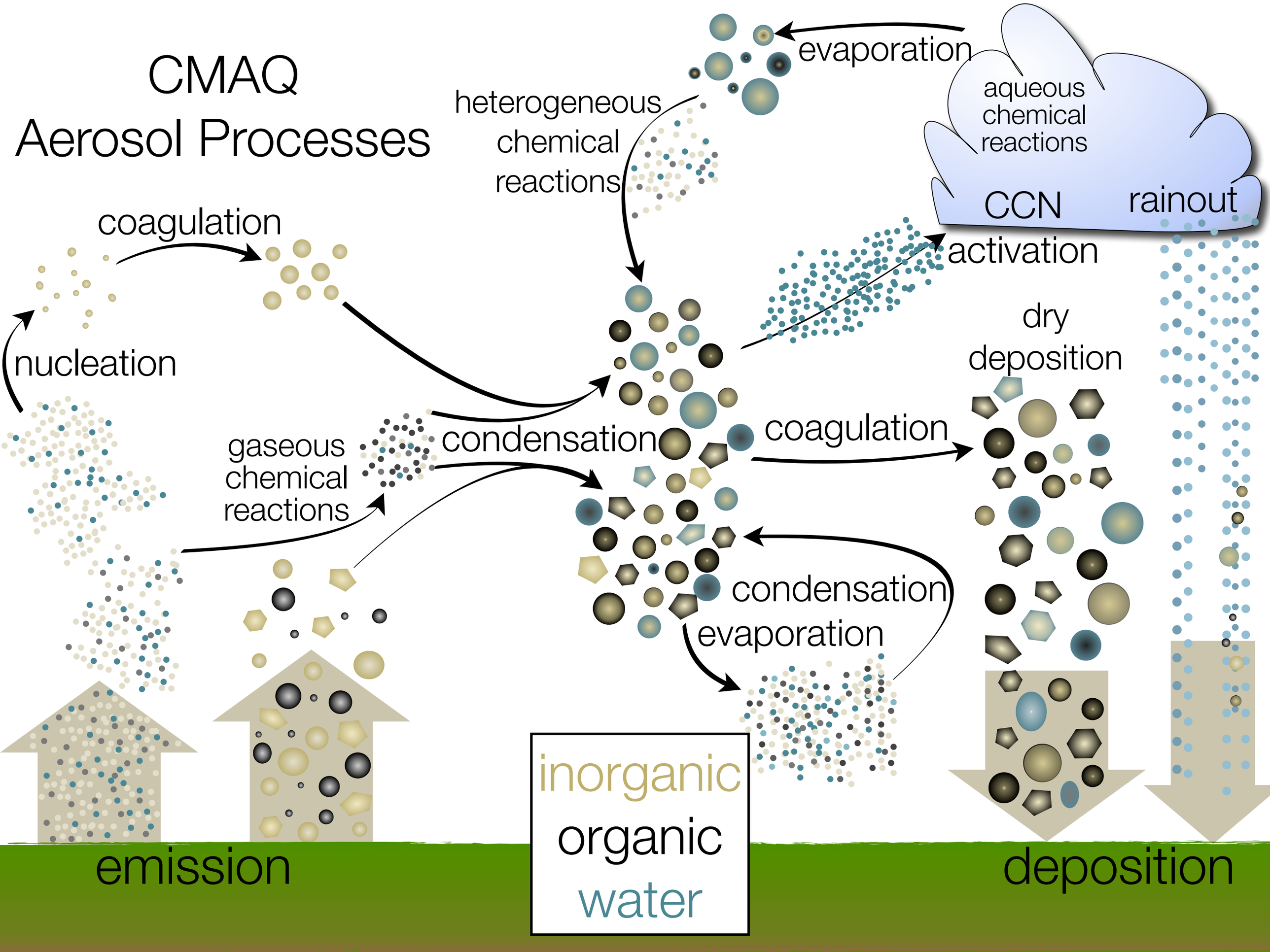
Comprehensive understanding of PM formation

Direct Decoupled Method

Adjoint Method



CMAQ Aerosol Processes



Atmospheric Aerosol Processing

heterogeneous chemical reactions

evaporation

aqueous chemical reactions

CCN

rainout

coagulation

activation

nucleation

dry deposition

gaseous chemical reactions

condensation

coagulation

condensation

evaporation

inorganic

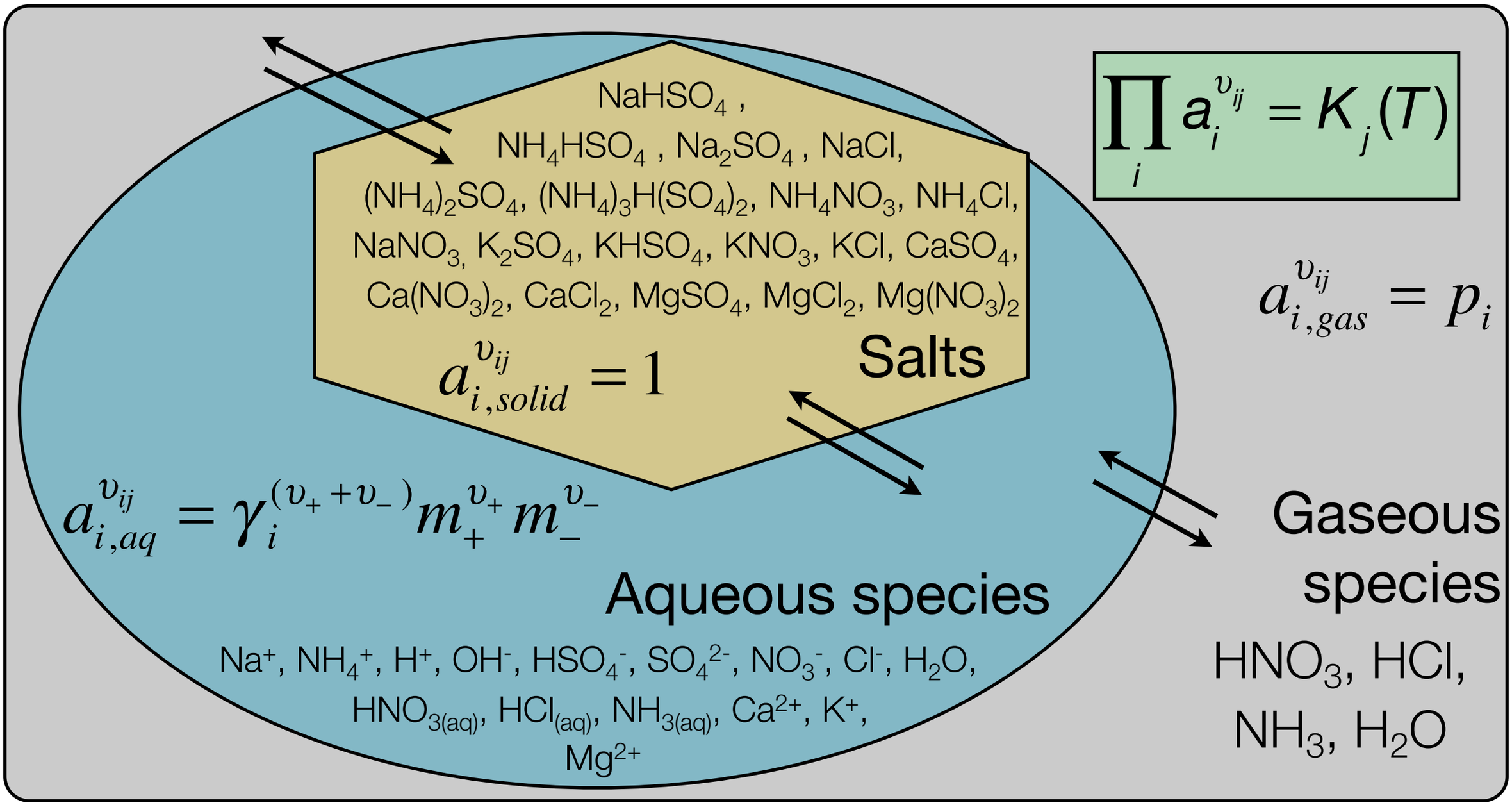
organic

water

emission

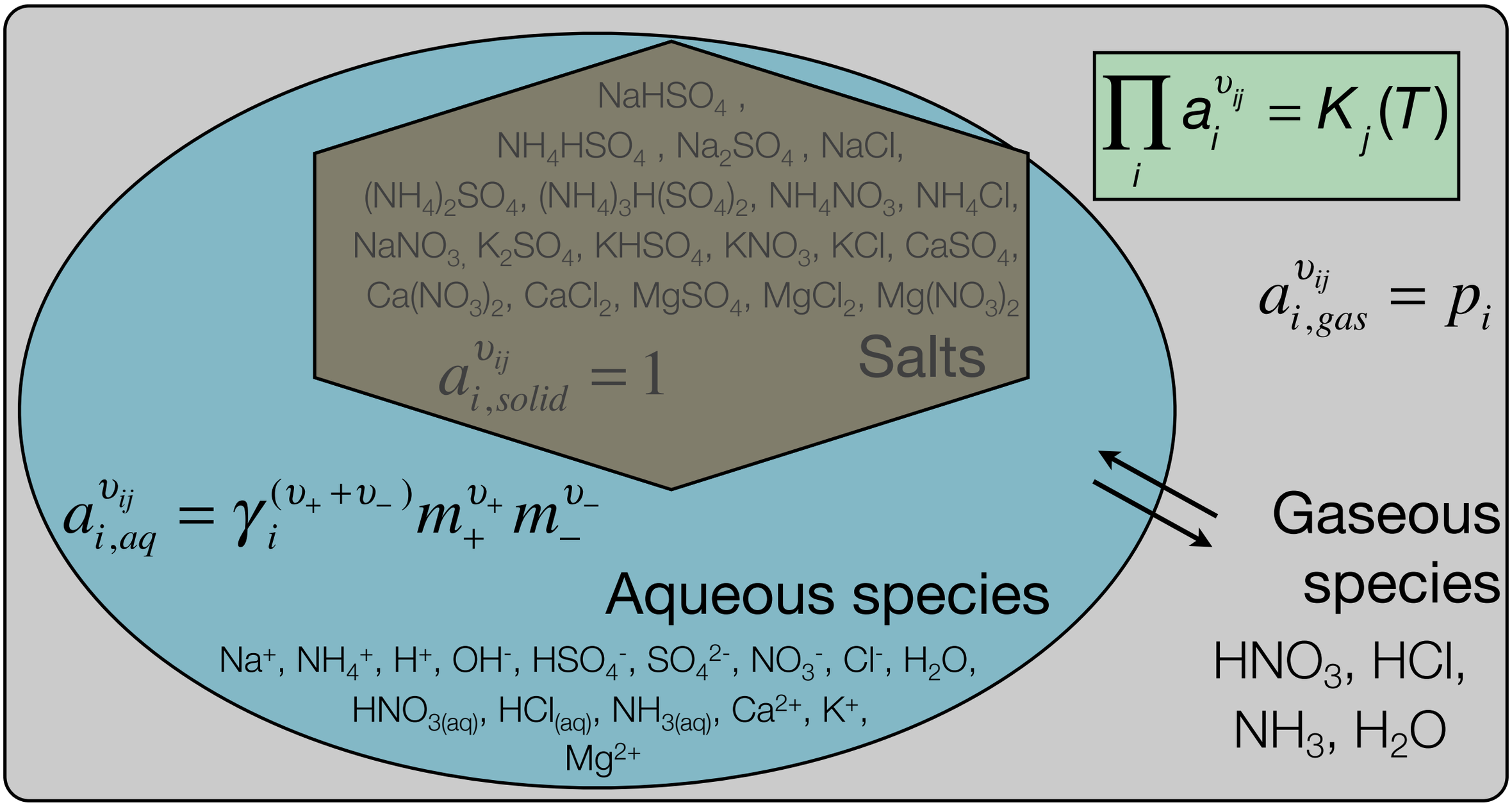
deposition

Inorganic aerosol thermodynamic equilibrium



ISORROPIA (Nenes et al., 1998)
ISORROPIA II (Fountoukis and Nenes, 2007)

Treatment of deliquesced aerosol only in CMAQ



ISORROPIA (Nenes et al., 1998)
ISORROPIA II (Fountoukis and Nenes, 2007)

Transforming ISORROPIA into an adjoint

ISORROPIA

(Nenes et al., 1998, 1999)

$$y = F(x)$$

$$\begin{Bmatrix} \text{Aerosol Phase} \\ \text{Gas Phase} \end{Bmatrix} = F \begin{pmatrix} \text{Total Concentration} \\ \text{Relative Humidity} \\ \text{Temperature} \end{pmatrix}$$

Adjoint of ISORROPIA

$$\frac{\partial y}{\partial \mathbf{x}} = \left(\frac{\partial F}{\partial x}\right)^{T}(x, \lambda)$$

$$\begin{bmatrix} \text{Sensitivity of aerosol} \\ \text{concentration to total} \\ \text{of each species} \end{bmatrix} = \text{ISOADJ} \begin{pmatrix} \text{Total concentrations} \\ \text{RH, Temperature} \\ \text{Adjoint forcing vector} \end{pmatrix}$$

Implementation of automatic differentiation

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ISORROPIA

(Nenes et al., 1998, 1999)

$$y = F(x)$$

$$\begin{Bmatrix} \text{Aerosol Phase} \\ \text{Gas Phase} \end{Bmatrix} = F \begin{pmatrix} \text{Total Concentration} \\ \text{Relative Humidity} \\ \text{Temperature} \end{pmatrix}$$

Adjoint of ISORROPIA

$$\frac{\partial y}{\partial \mathbf{x}} = \left(\frac{\partial F}{\partial x}\right)^T (x, \lambda)$$

$$\begin{bmatrix} \text{Sensitivity of aerosol or} \\ \text{gas phase concentration} \\ \text{to total of each species} \end{bmatrix} = \text{ISOADJ} \begin{pmatrix} \text{Total concentrations} \\ \text{RH, Temperature} \\ \text{Adjoint forcing vector} \end{pmatrix}$$

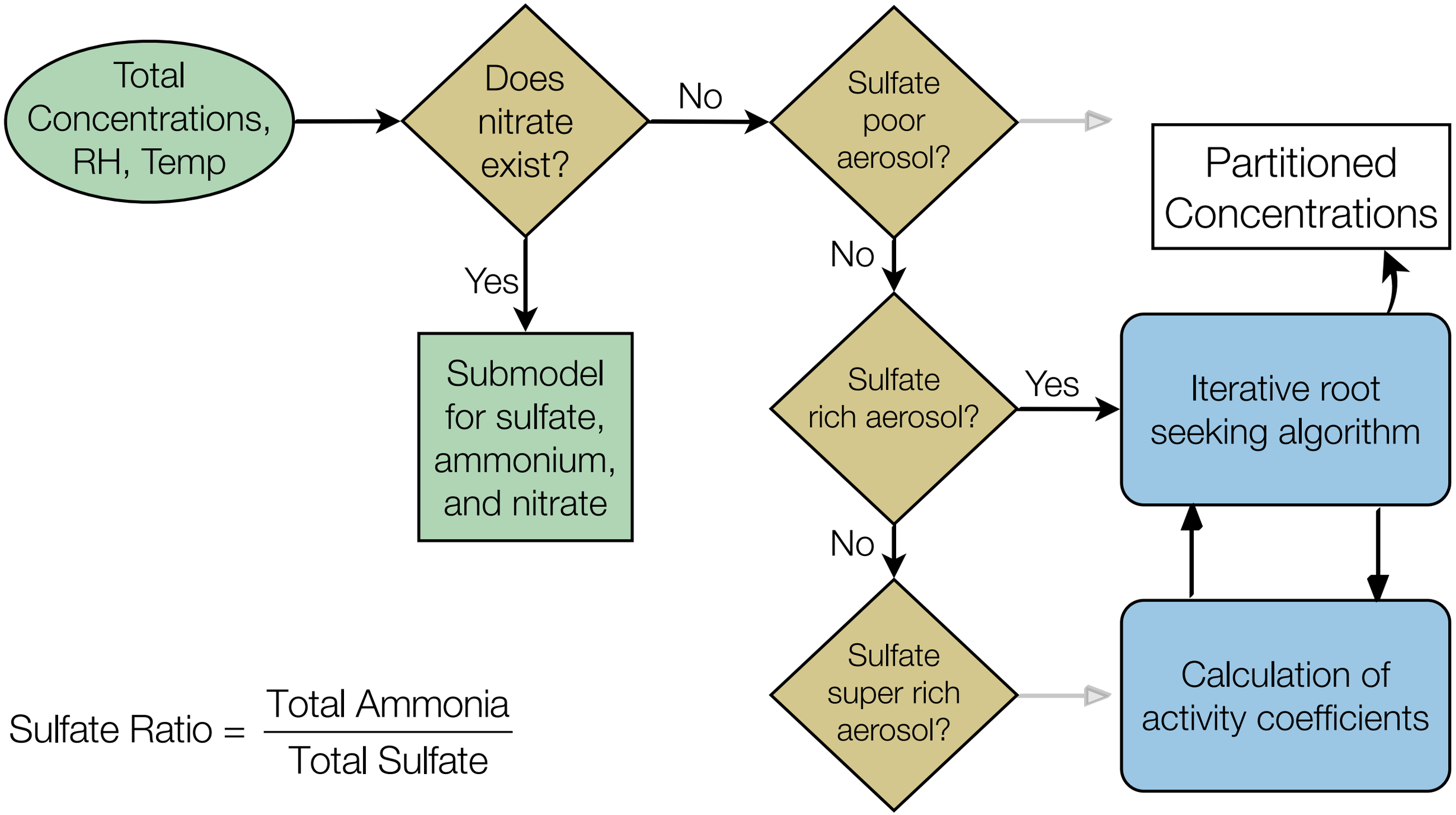
TAPENADE

(Hascoet et al., 2004)

$$\left(\frac{\partial F}{\partial x}\right)^T = Q(F, x, y)$$

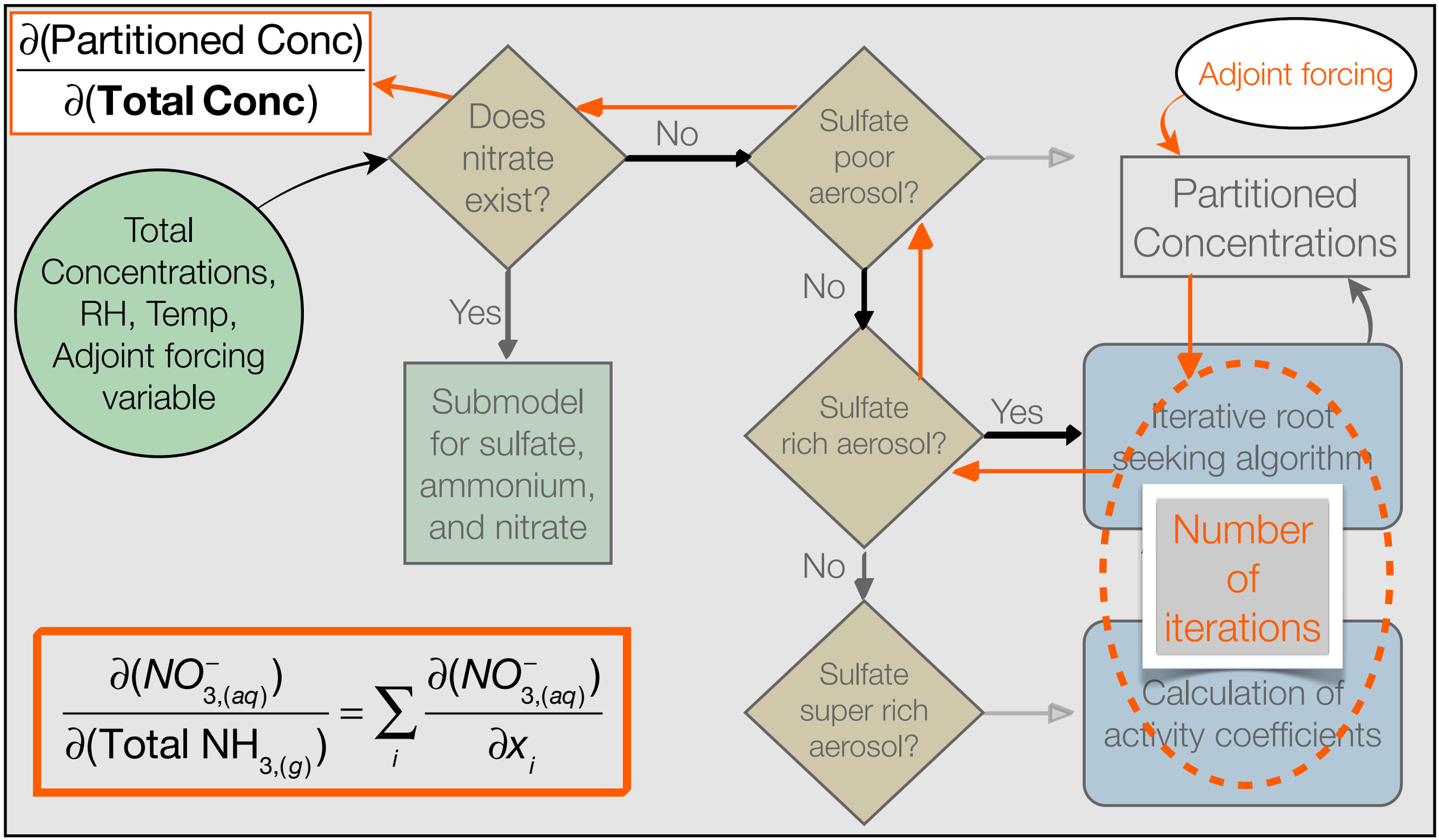
Adjoint of ISORROPIA = Q(ISORROPIA)

Forward execution of ISORROPIA



$$\text{Sulfate Ratio} = \frac{\text{Total Ammonia}}{\text{Total Sulfate}}$$

Augmentation of ISORROPIA by TAPENADE



Verification of adjoint performance

- **Method**
  - Finite difference sensitivity

$$\frac{\Delta[\mathrm{NO}^-_{3,(aq)}]}{\Delta[\text{Total NH}_3]} = \frac{[\mathrm{NO}^-_{3,(aq)}]_{(\text{Total NH}_3 + \frac{1}{2}h)} - [\mathrm{NO}^-_{3,(aq)}]_{(\text{Total NH}_3 - \frac{1}{2}h)}}{(\text{Total NH}_3 + \frac{1}{2}h) - (\text{Total NH}_3 - \frac{1}{2}h)}$$

  - Adjoint-produced sensitivity

$$\frac{\partial([\mathrm{NO}^-_{3,(aq)}])}{\partial([\text{Total NH}_3])} = \left(\frac{\partial F}{\partial x}\right)^T \left(x, \lambda_{[\mathrm{NO}^-_{3,(aq)}]}\right)$$

- **Range**
  - Ammonium-sulfate-nitrate systems
  - 5 - 95% relative humidity

Total Sulfate | **Total Ammonia** | **Total Nitrate**

H^+

1E-3+1.002*x | 4E-4+1.0007*x | -1.1E-3+1.025*x

NH_4^+

-2E-4+0.9998*x | 9E-4+0.9992*x | -1.5E-4+0.9996*x

SO_4^{2-}

2E-4+1.0002*x | 8E-5+0.9999*x | -2E-5+0.9979*x

HSO_4^-

-4E-4+1.0002*x | -8E-5+0.9999*x | 2E-5+0.9979*x

NO_3^-

7E-3+1.024*x | -2.5E-3+1.031*x | -9E-4+1.0074*x

Adjoint-produced sensitivities *(mol/mol)*

Finite difference sensitivities *(mol/mol)* (Capps et al., *manuscript in preparation*)

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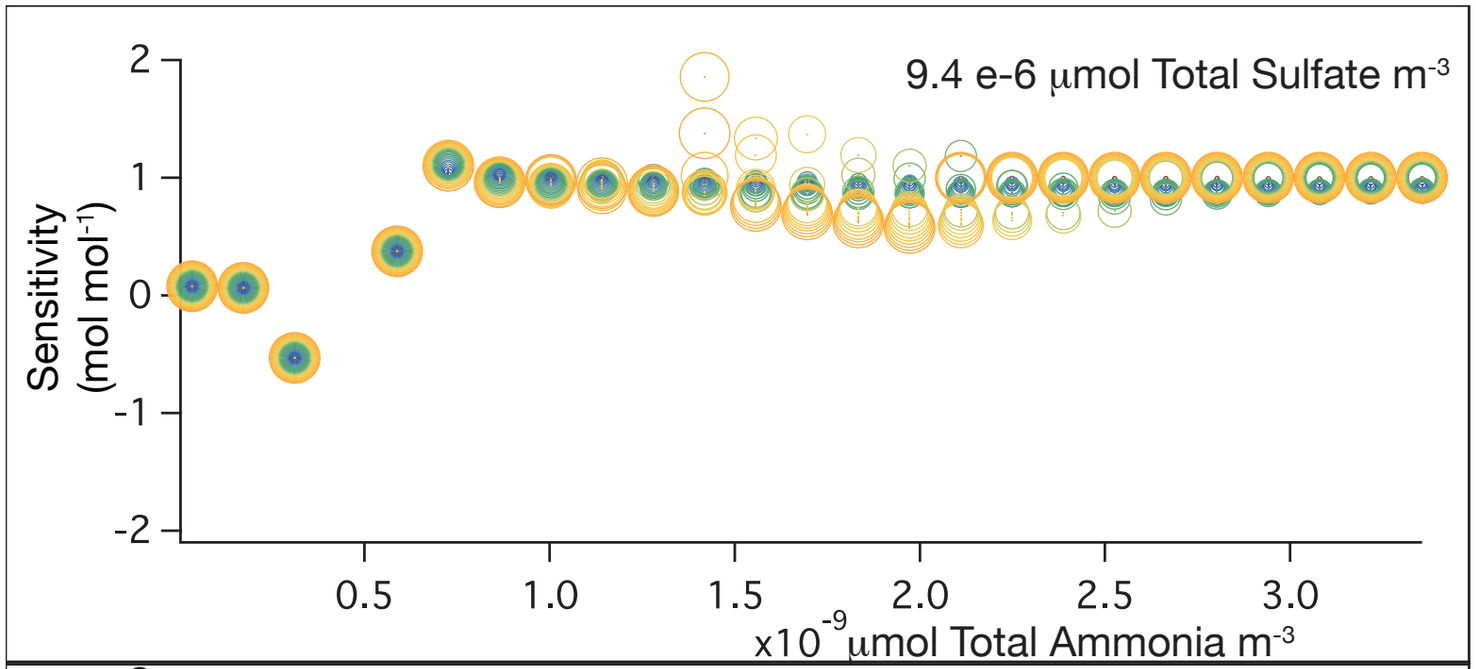
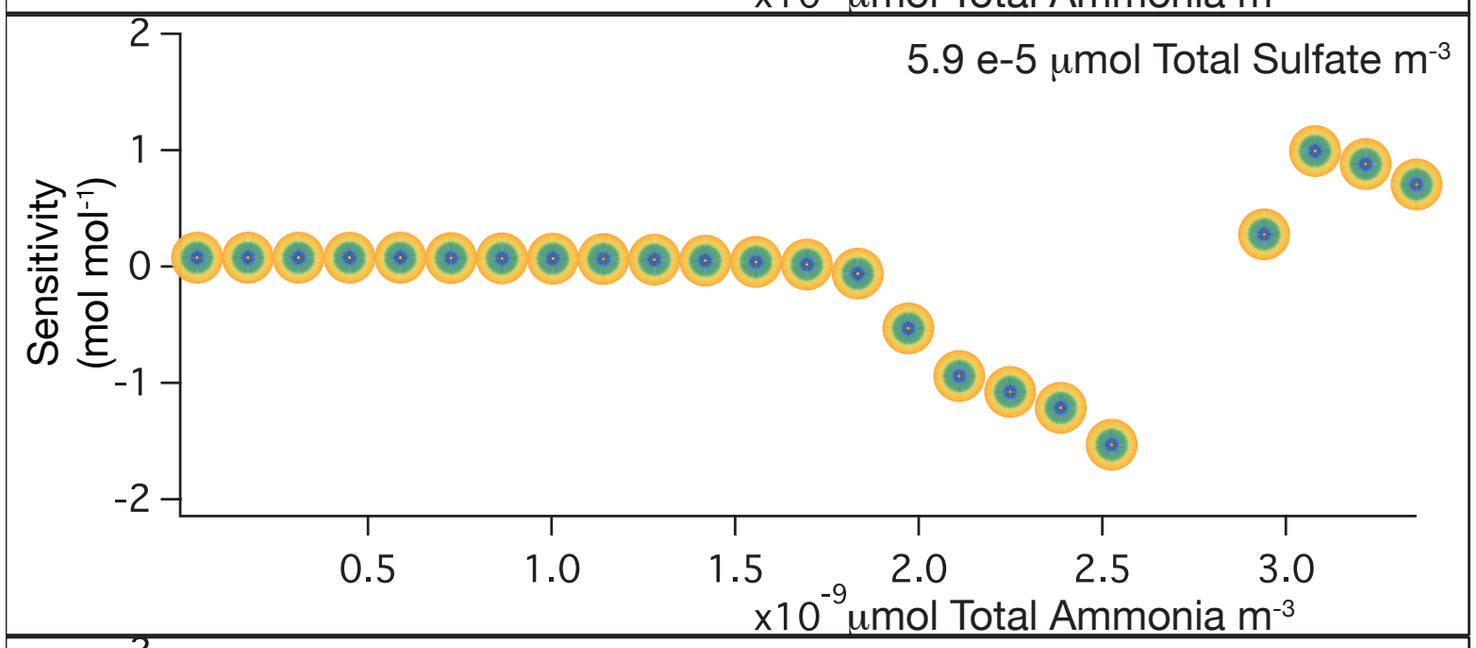
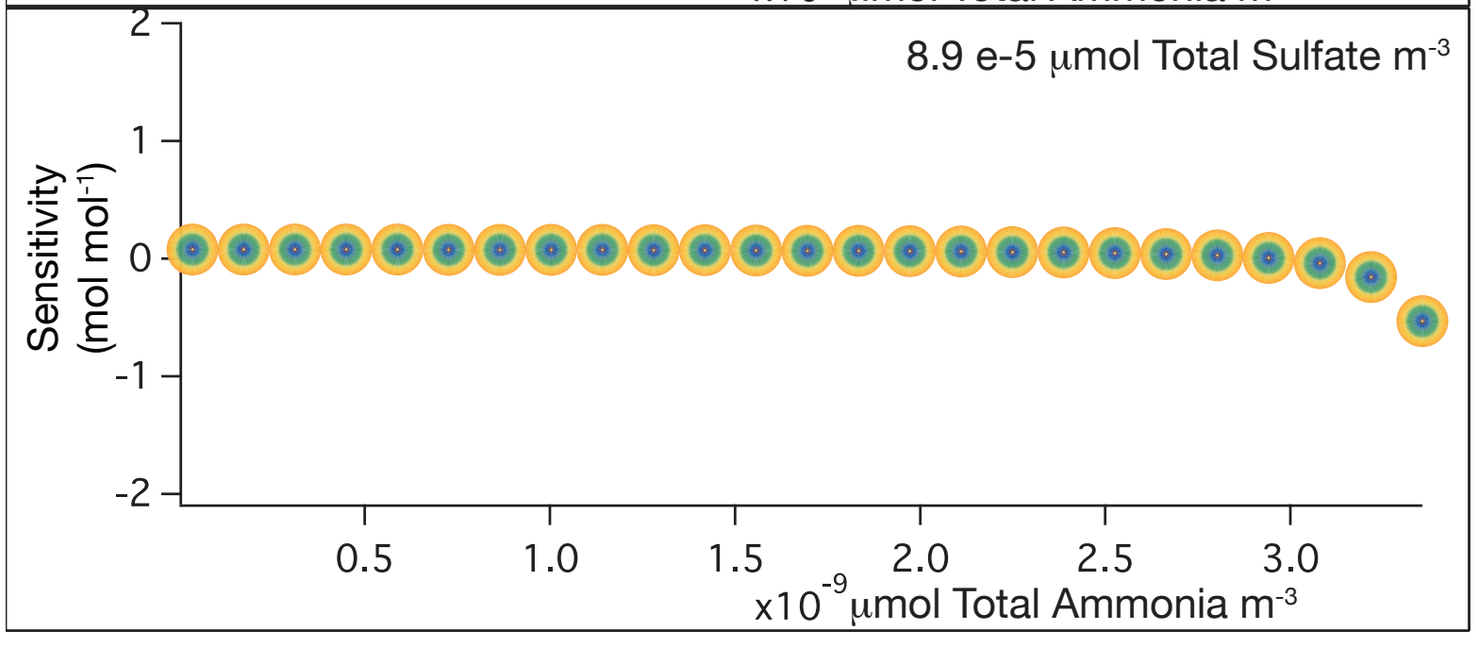
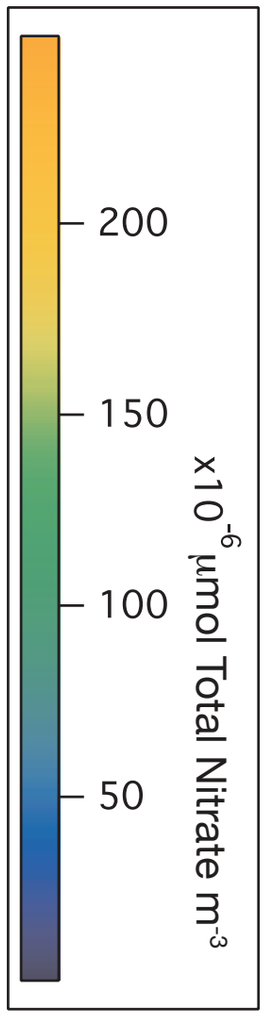
Elucidating the physical system:

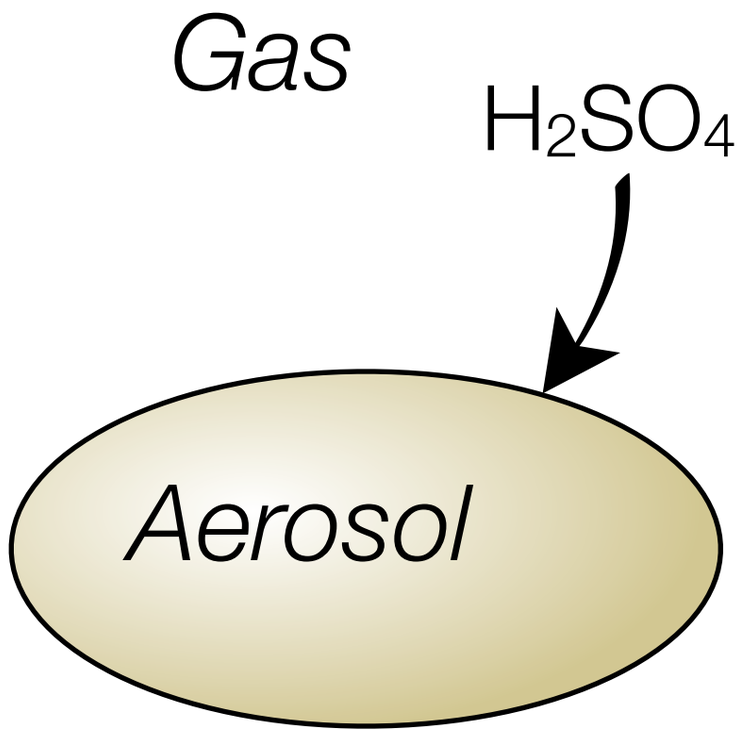
Sensitivity of sulfate ion (SO_4^{2-}) to total sulfate











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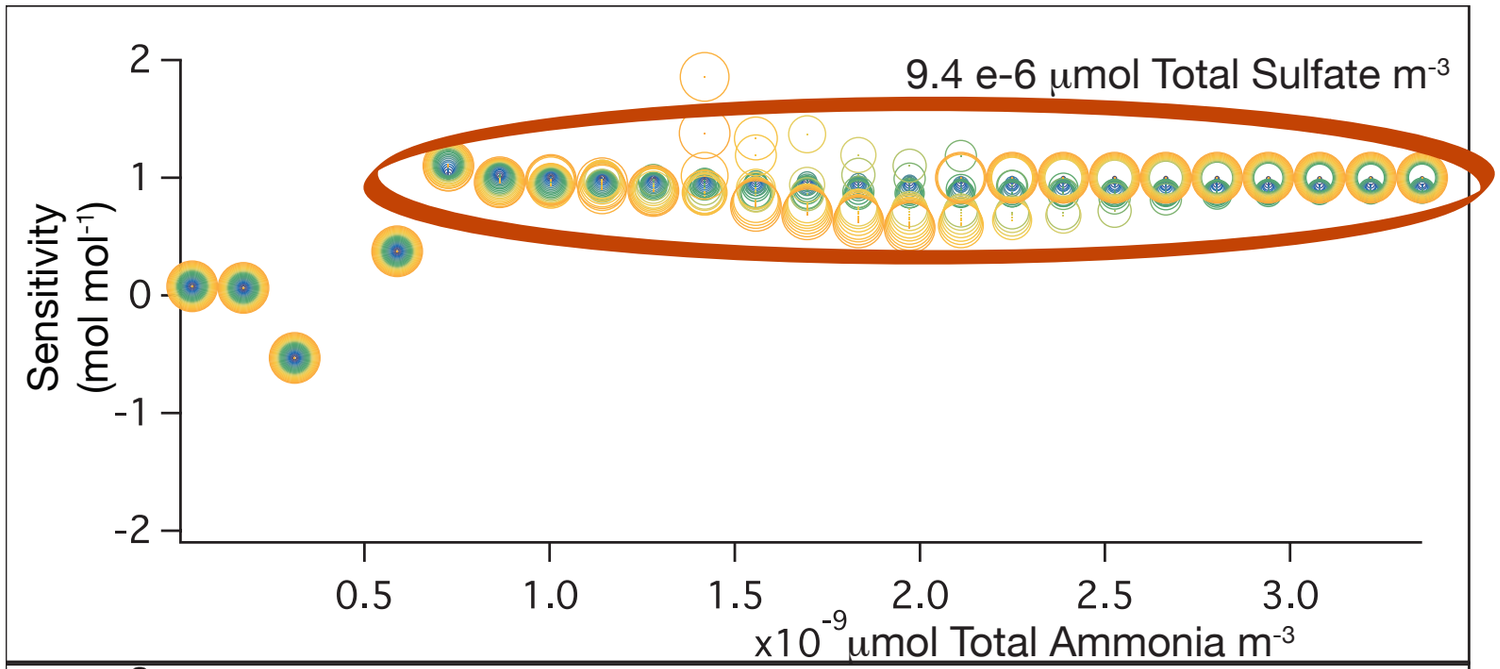

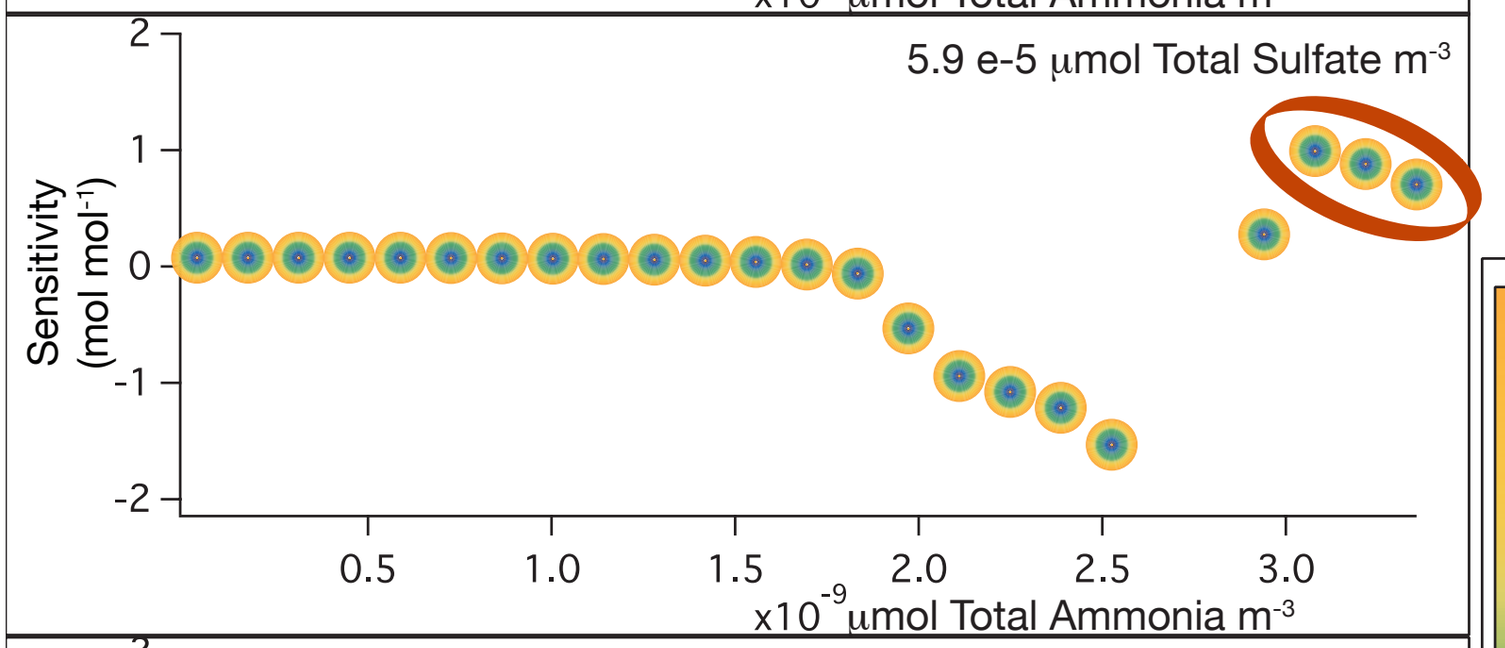

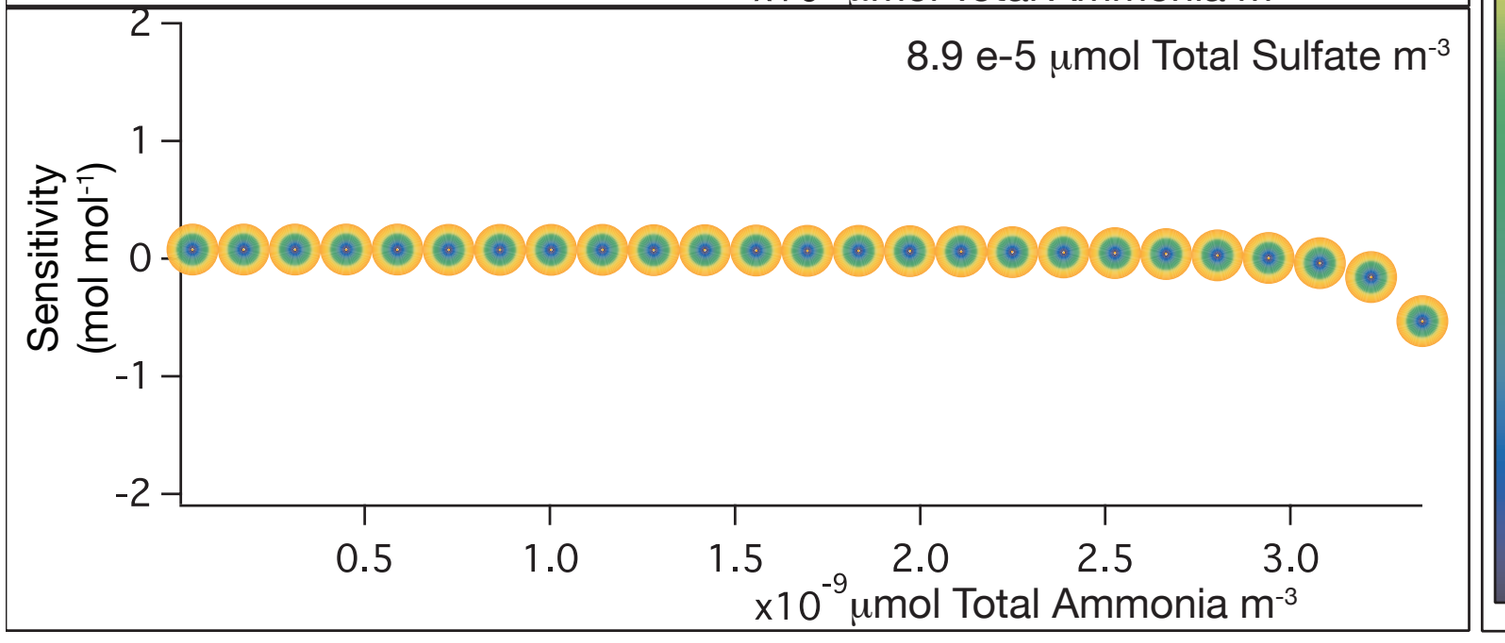

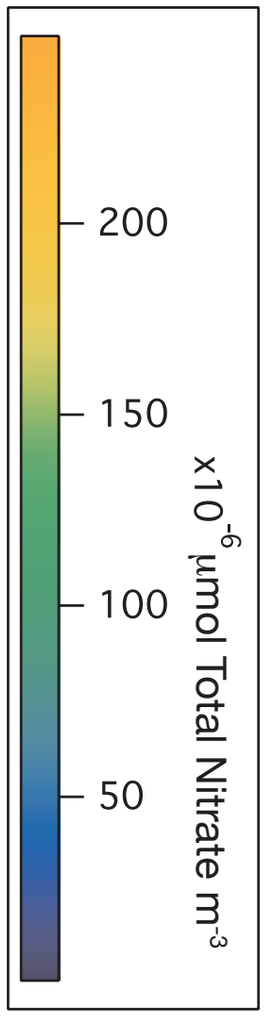

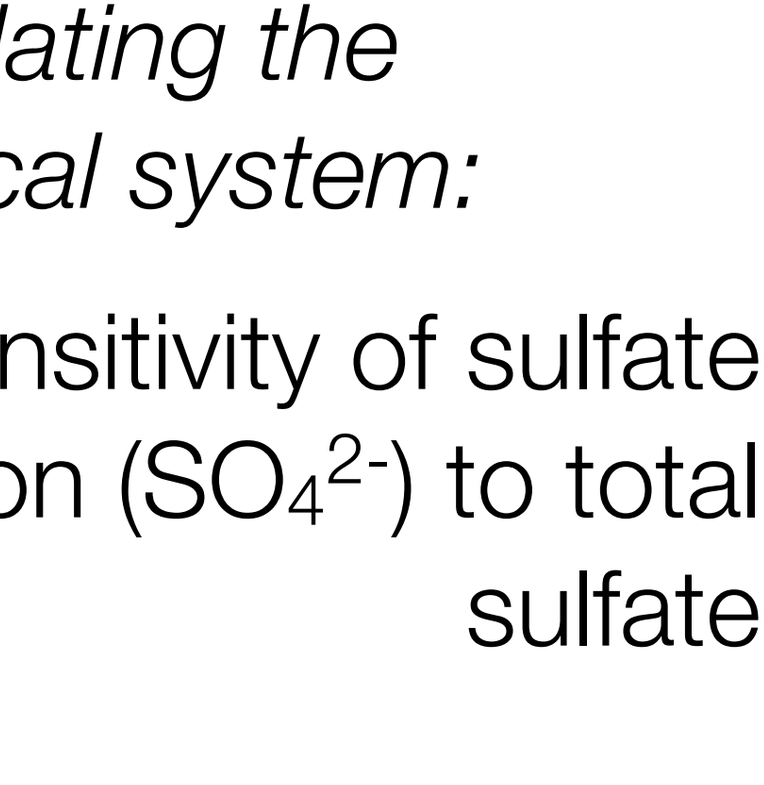

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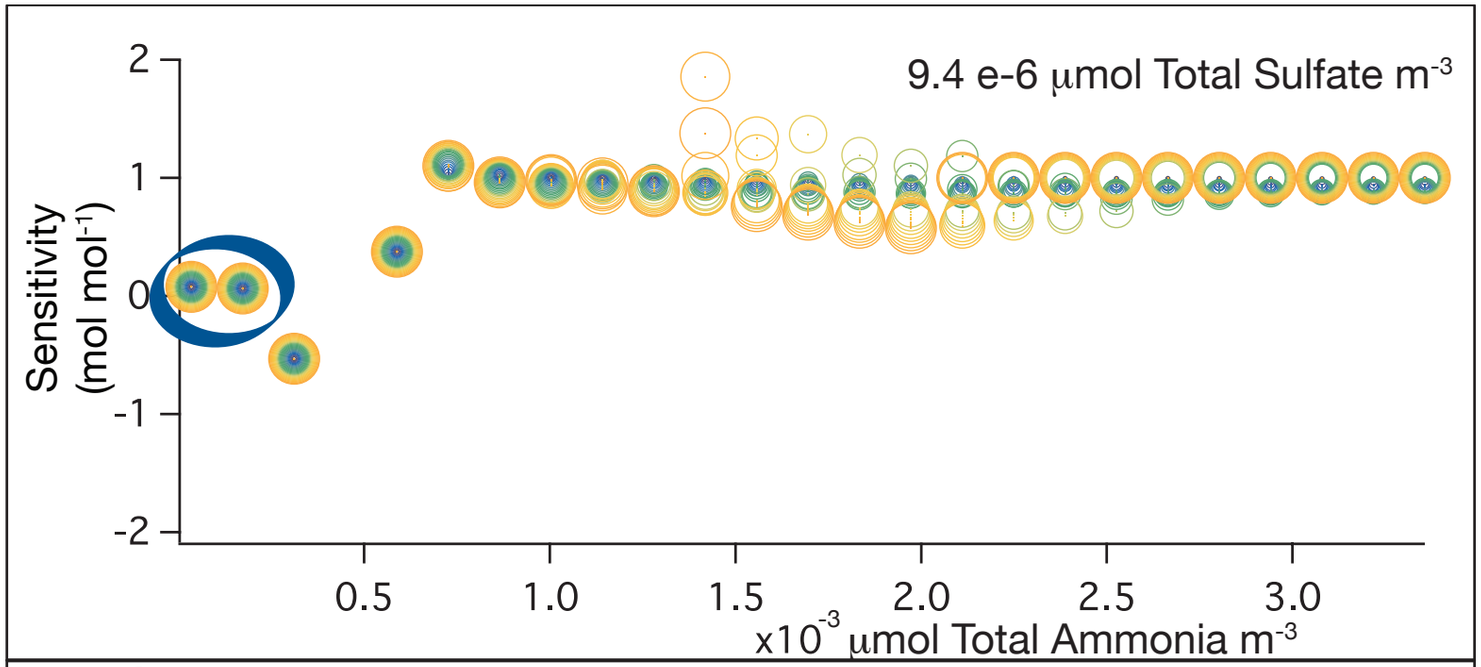
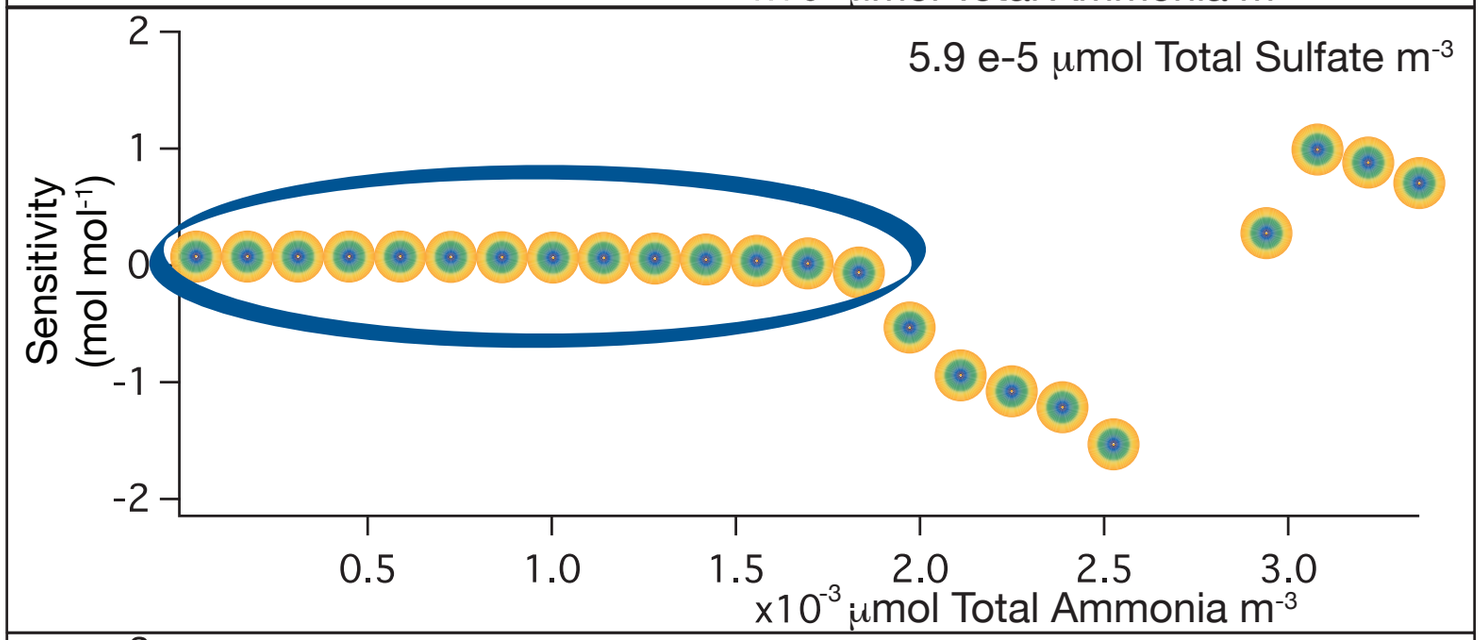
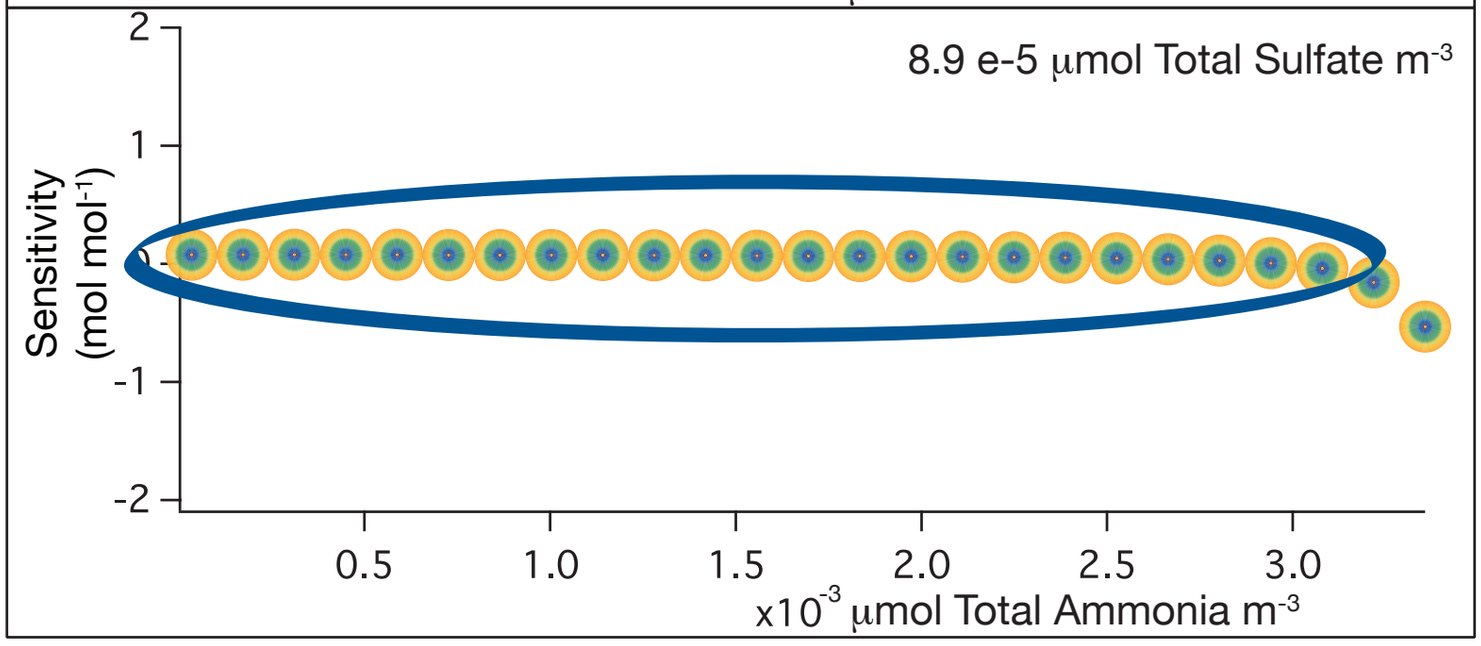
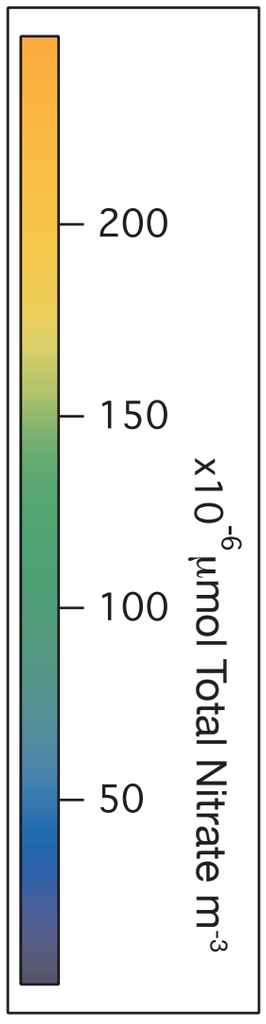
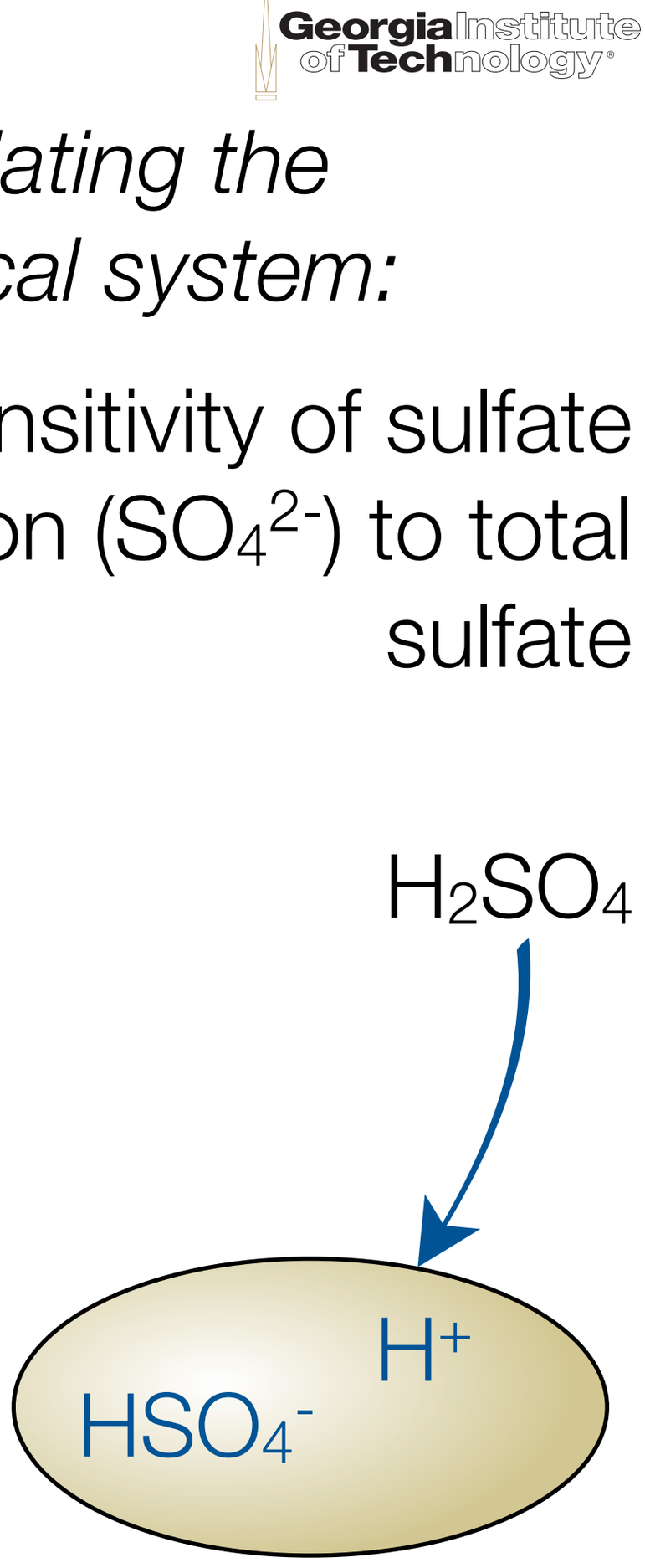


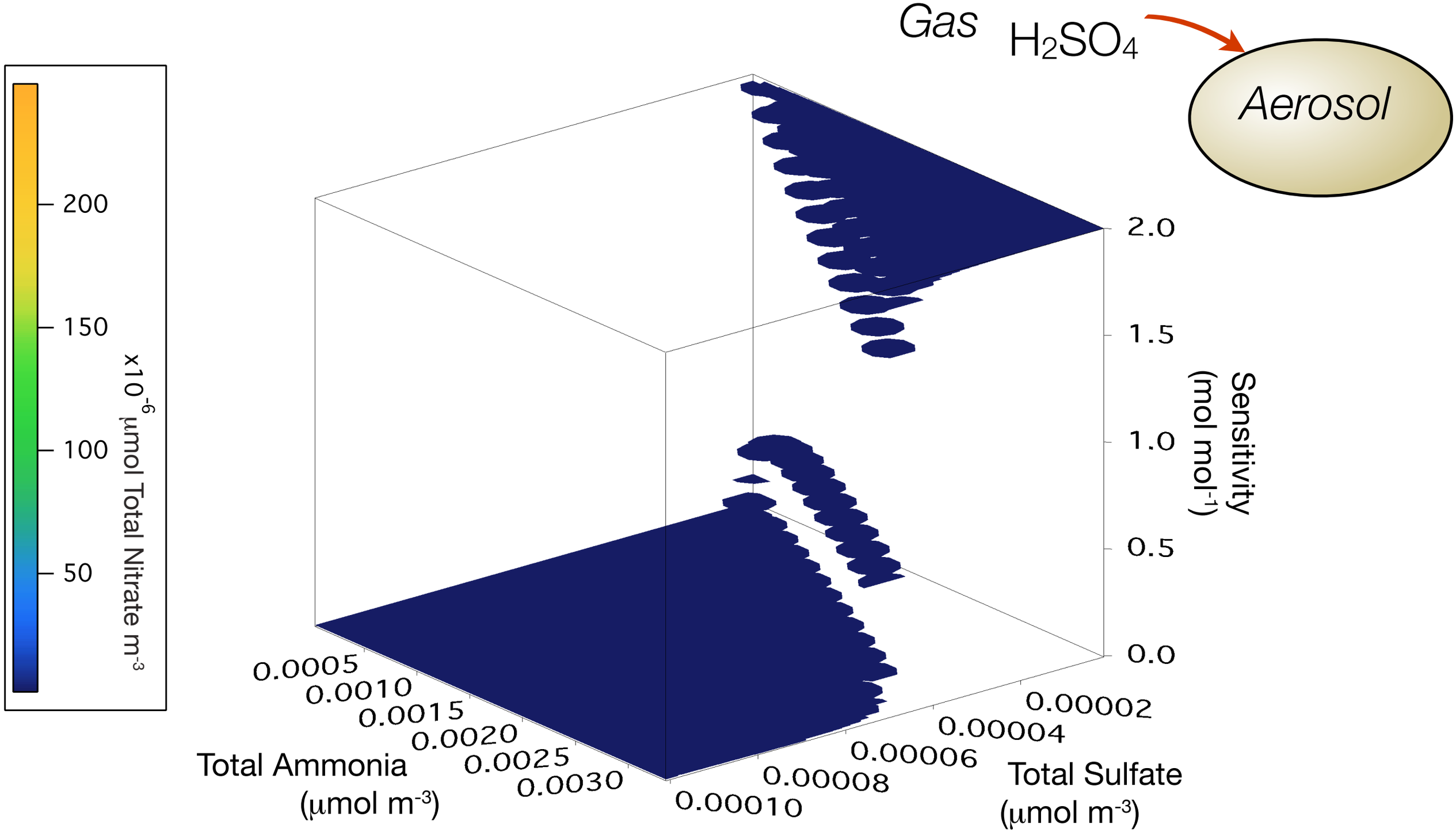








Elucidation of the physical system:
Sensitivity of ammonium ion (NH_4^+) to total sulfate



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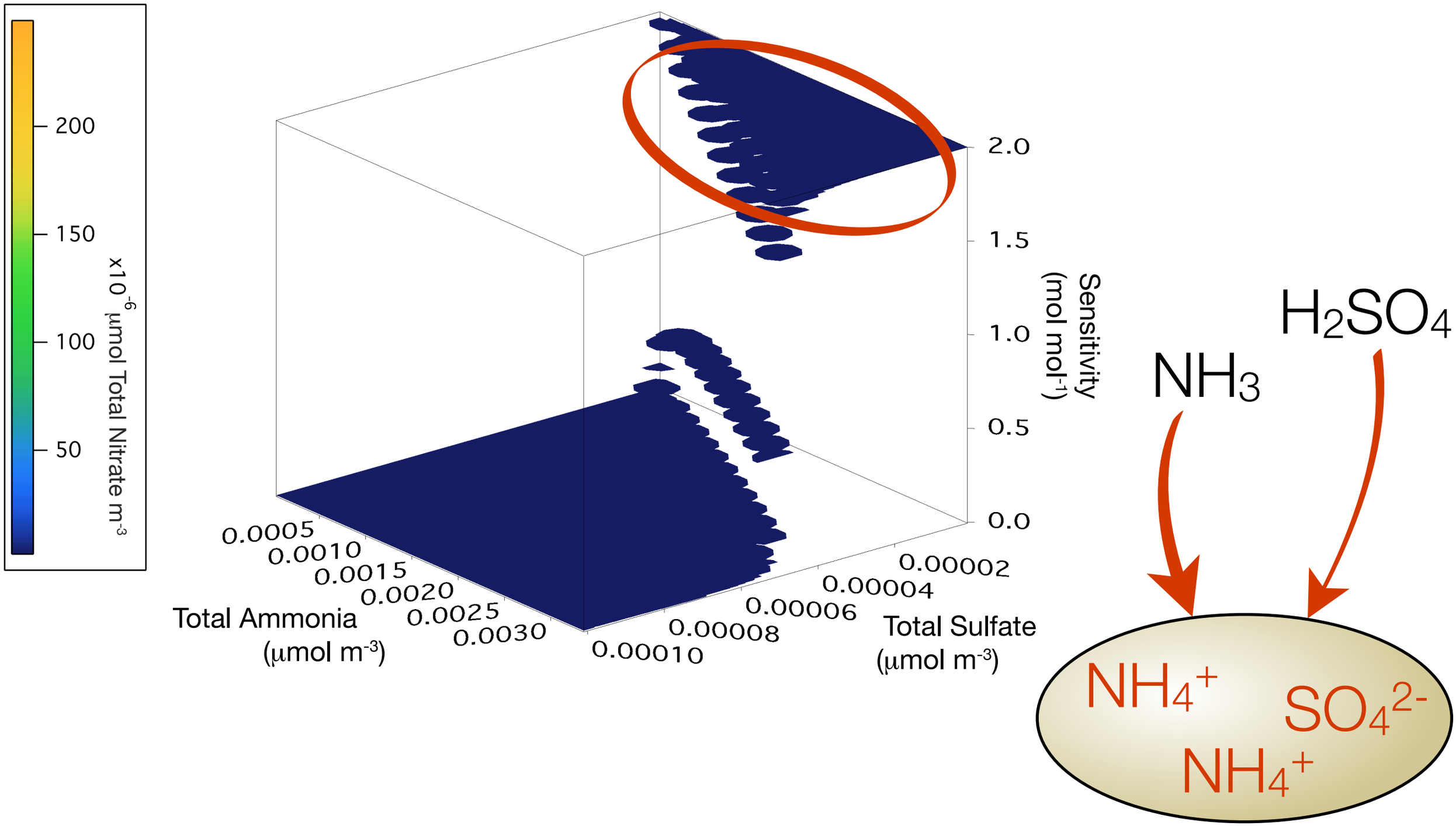

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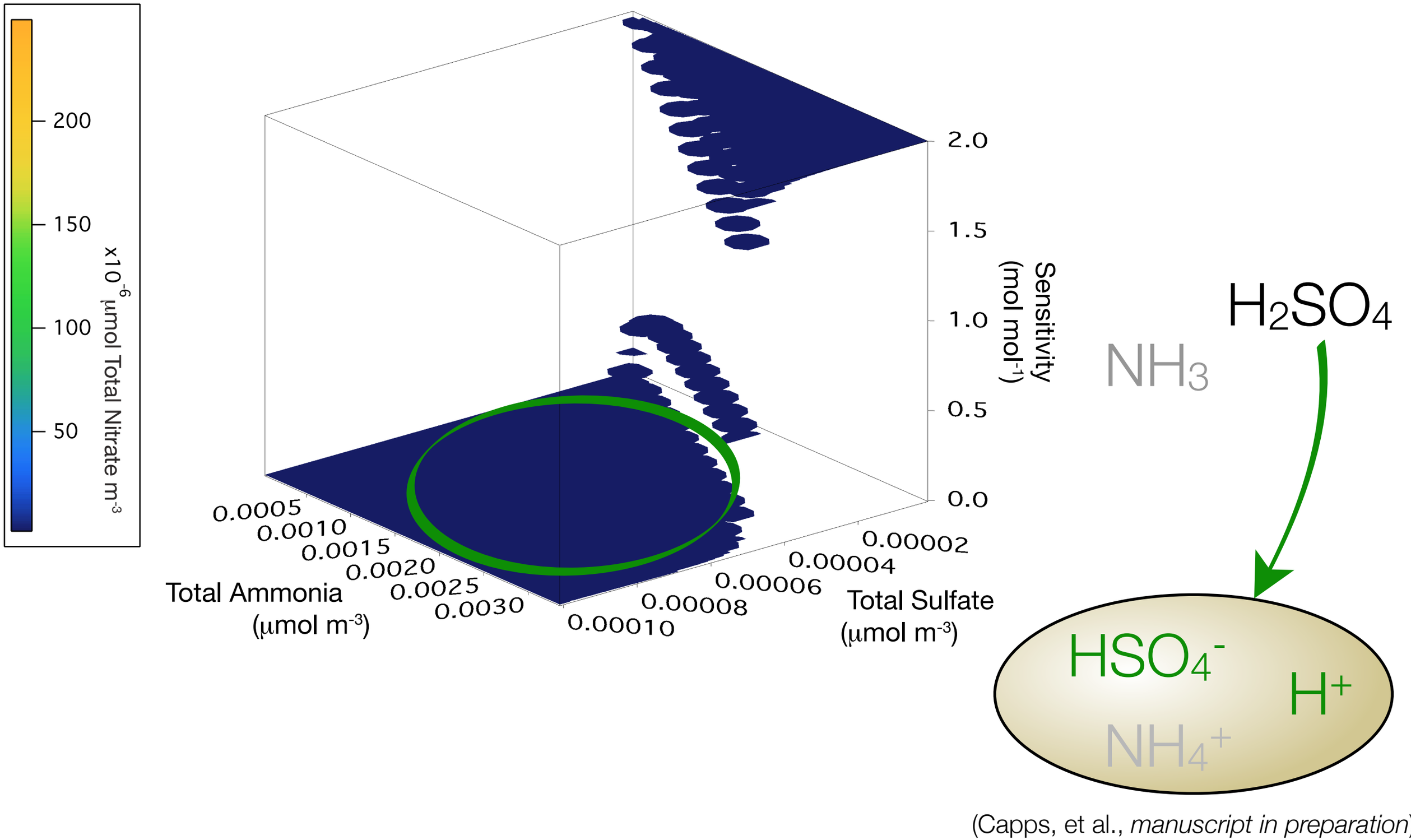

(Capps, et al., *manuscript in preparation*)

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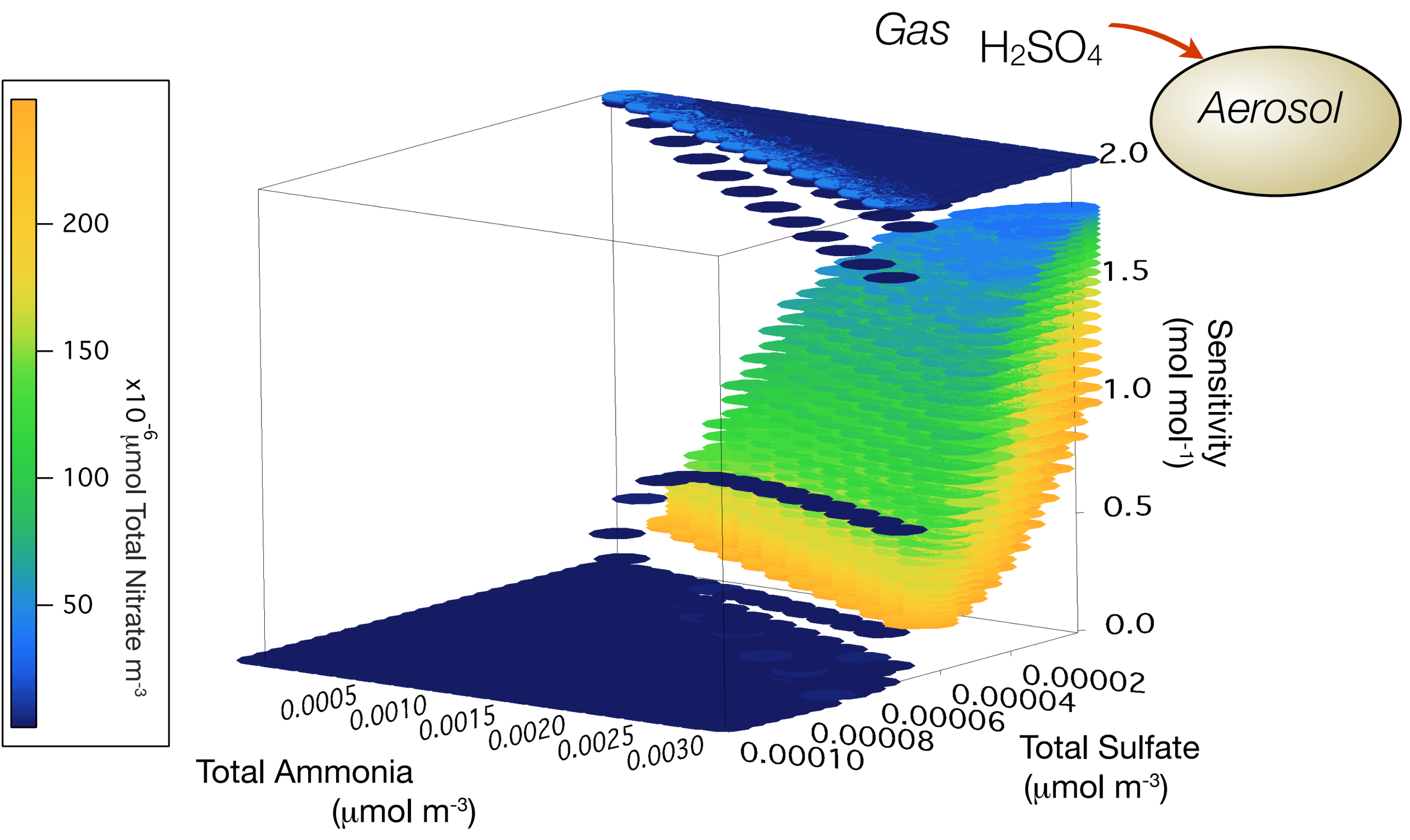

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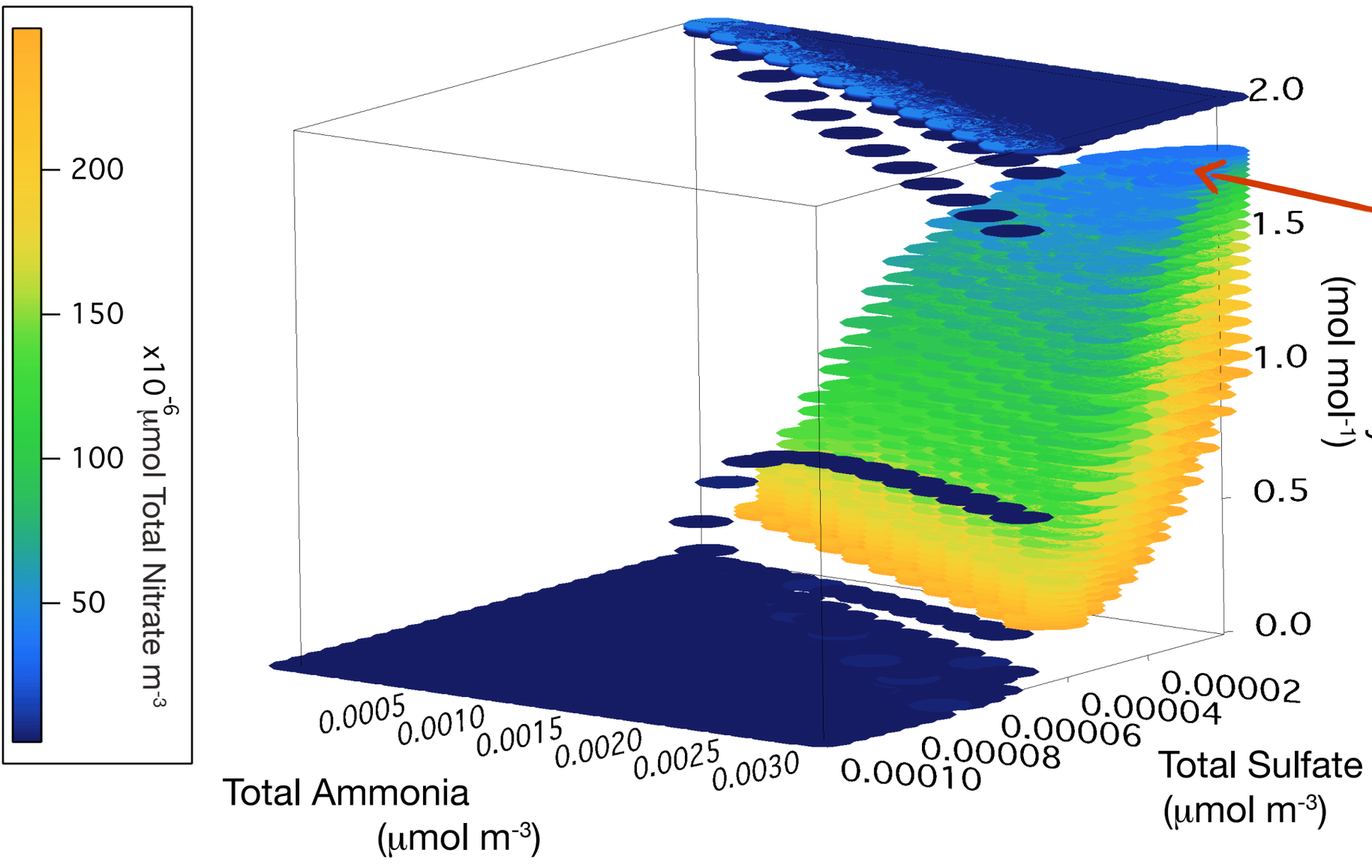

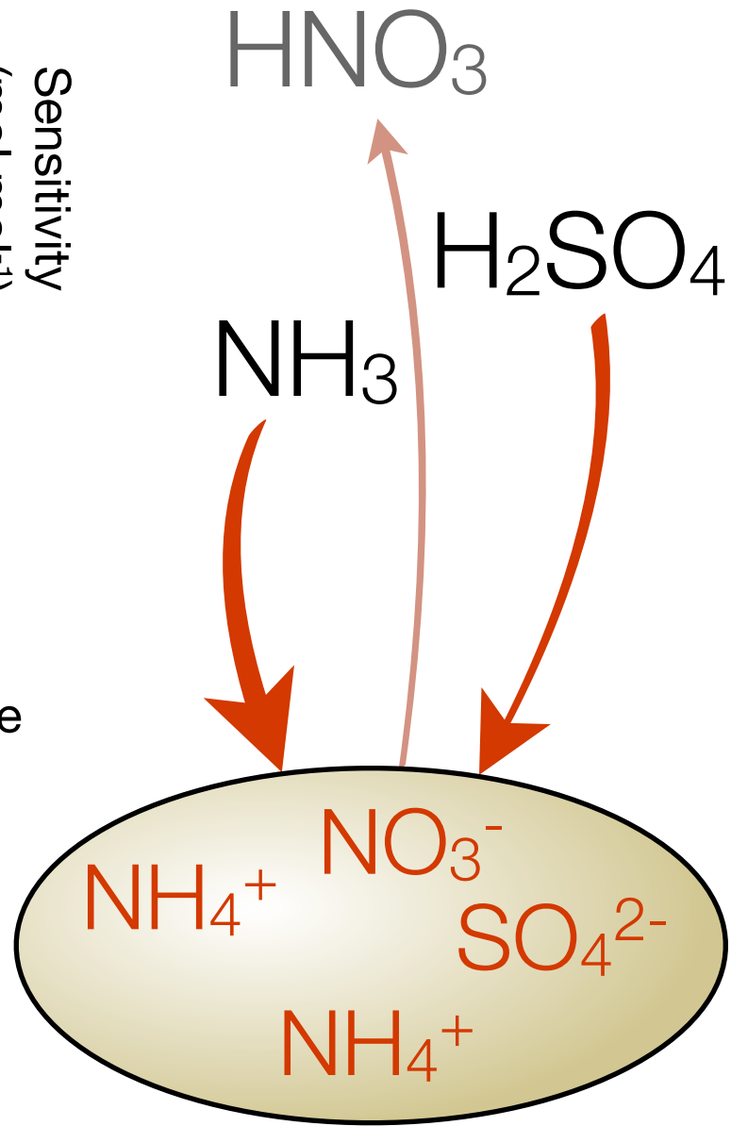

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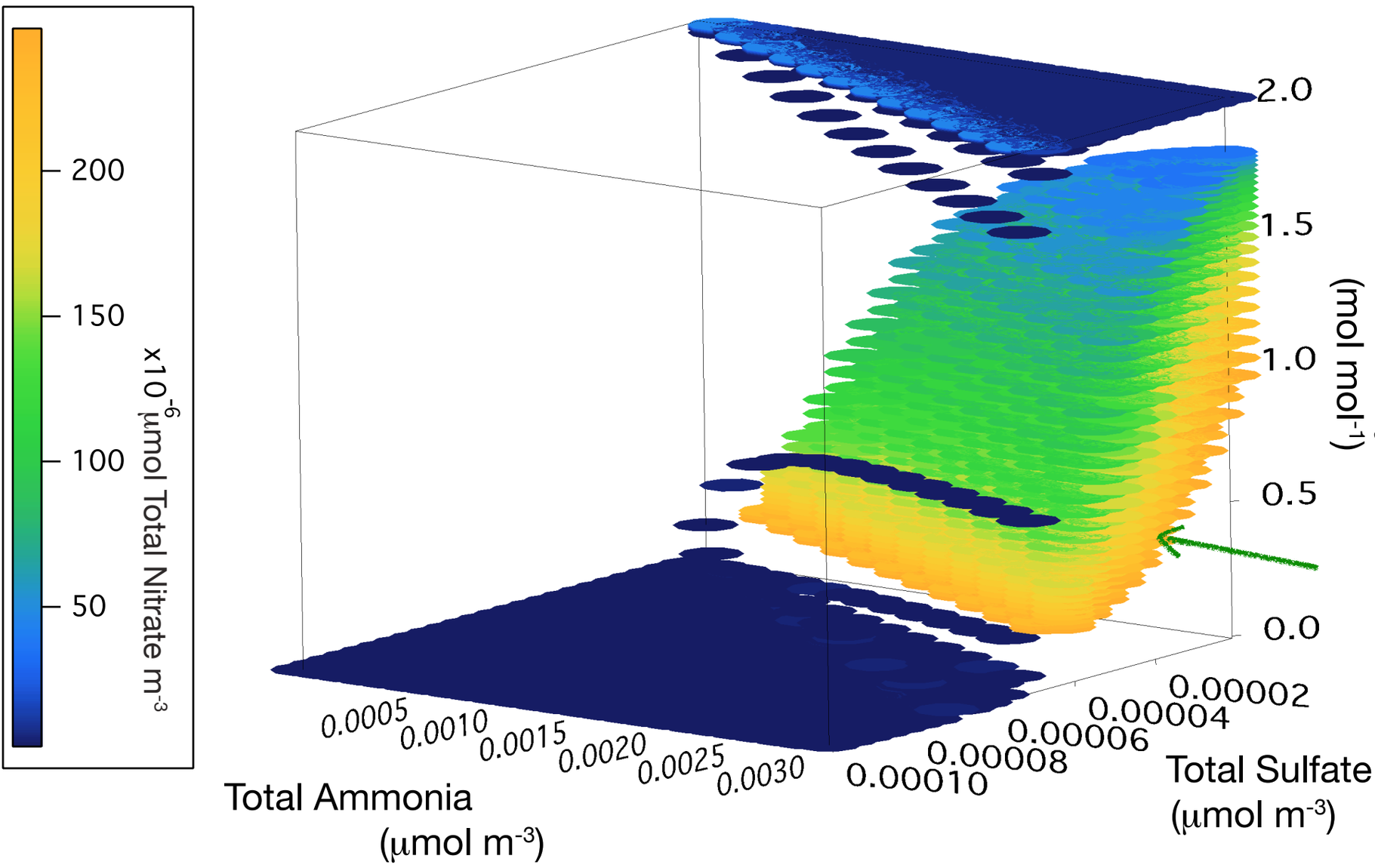
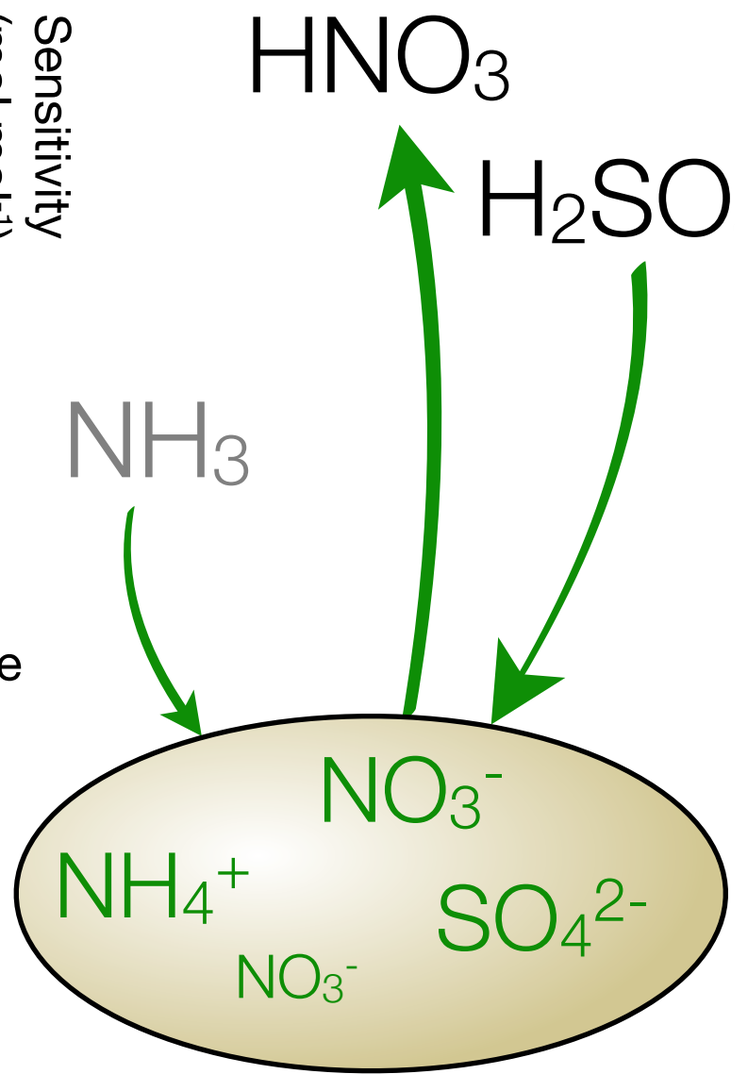




nitrate acts as buffer

Regional sensitivity exploration: Characterization from ANARChE in Atlanta

Selection of excellent **inorganic aerosol composition** and **gas precursor** measurements

Atlanta, GA
July-August 2002

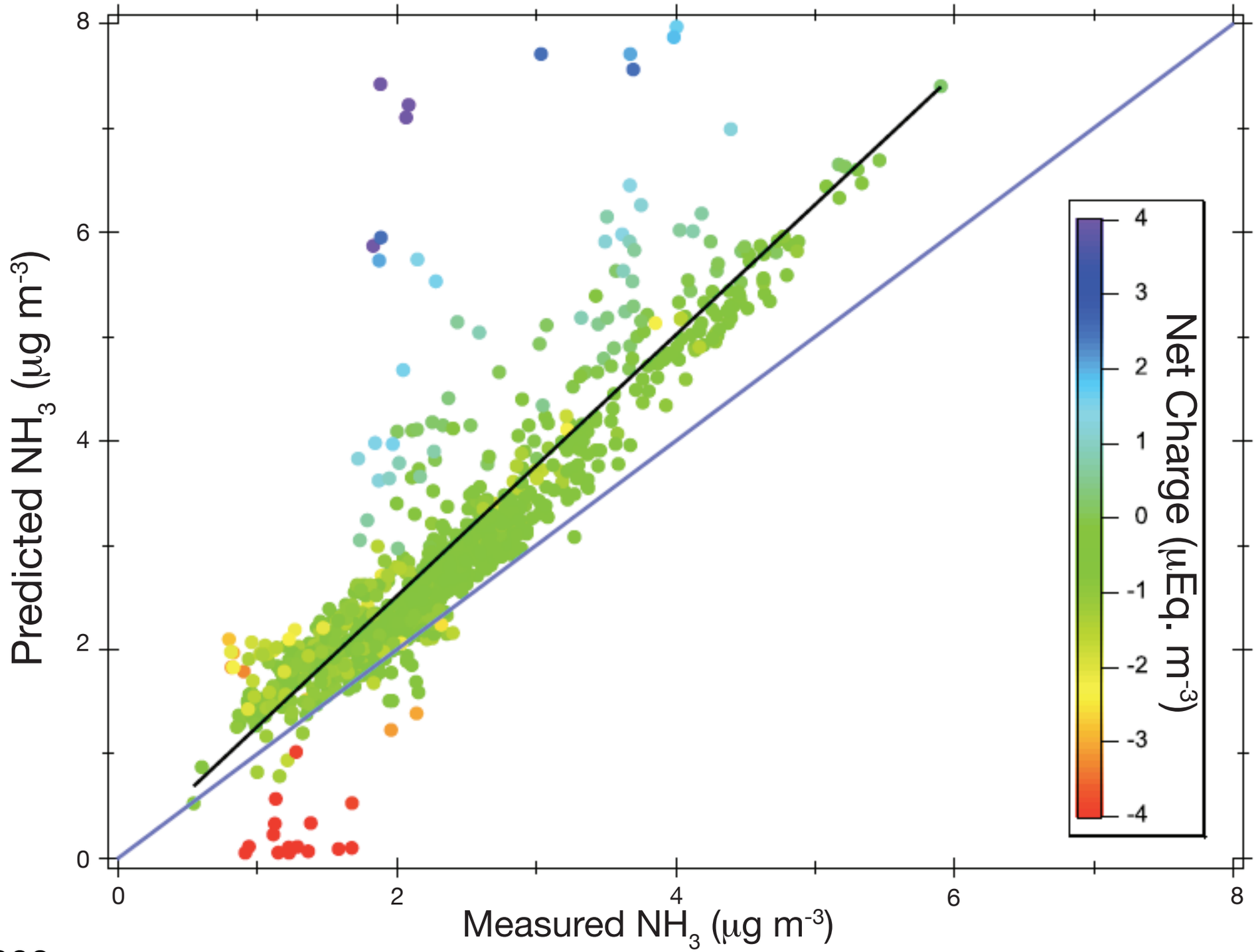
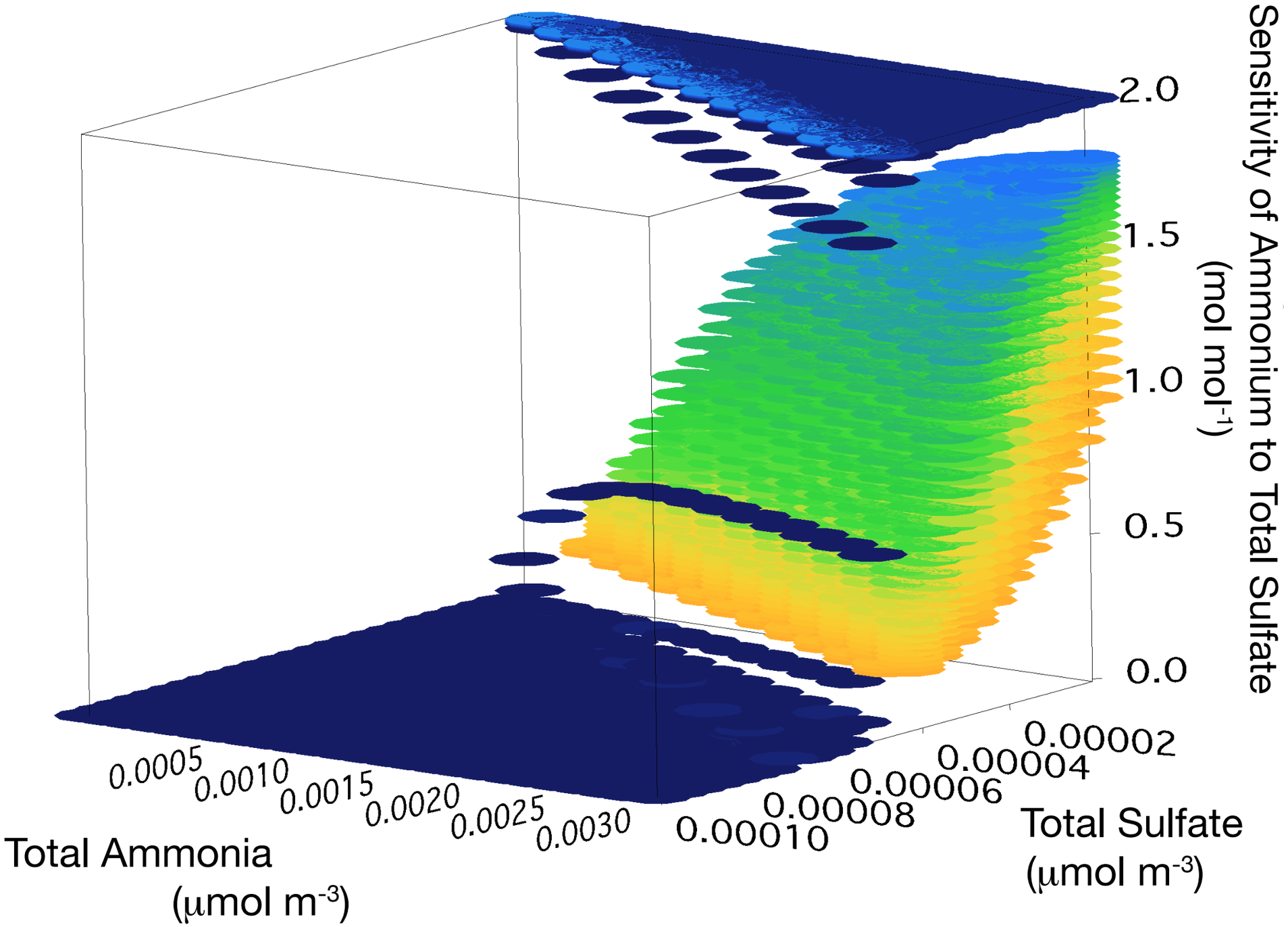


Figure from Nowak et al., 2002

Sensitivity exploration for Atlanta:
Ammonium ion to total sulfate adjoint-derived sensitivity



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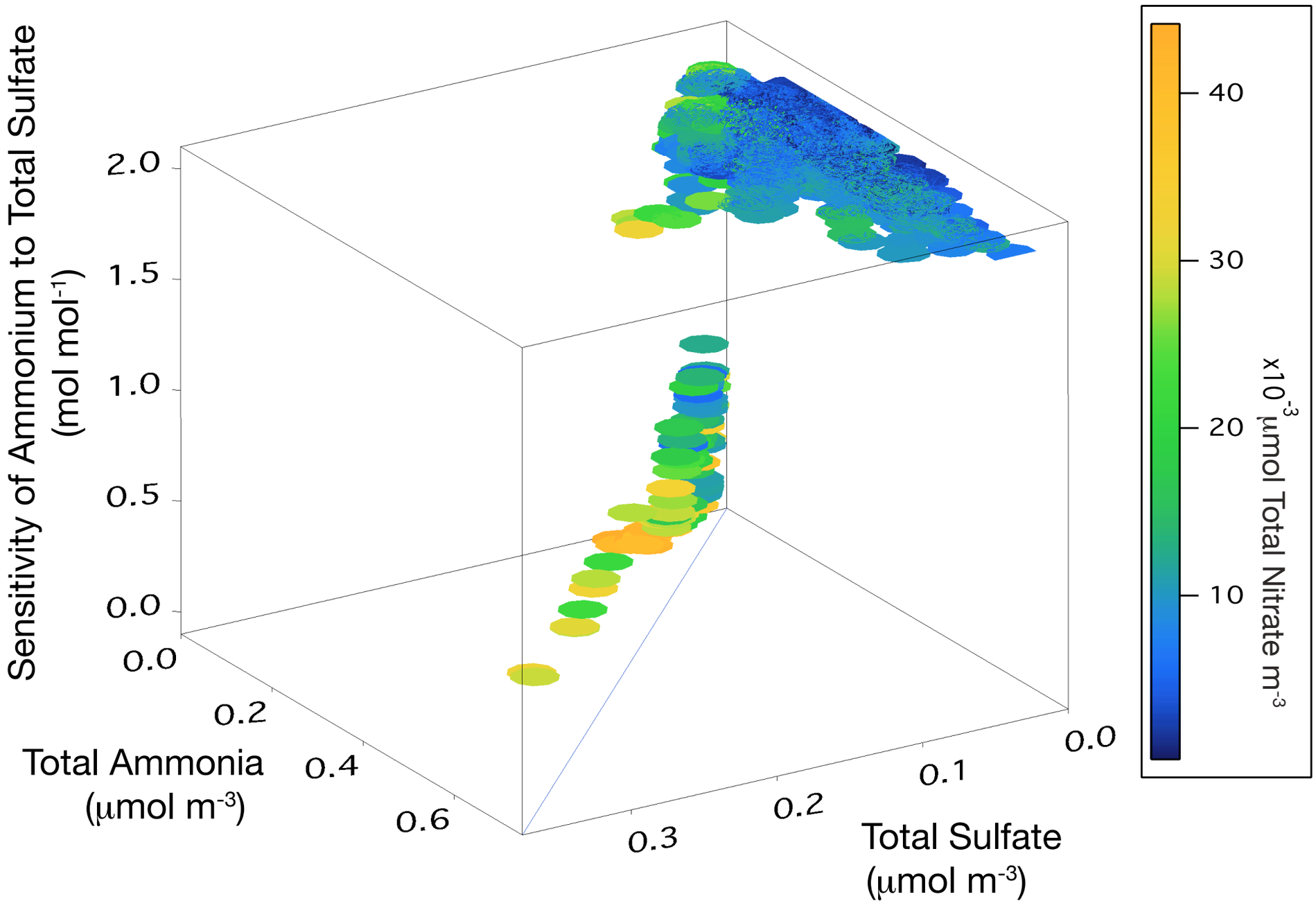

- Excess ammonia keeps aerosol **highly sensitive** to sulfate

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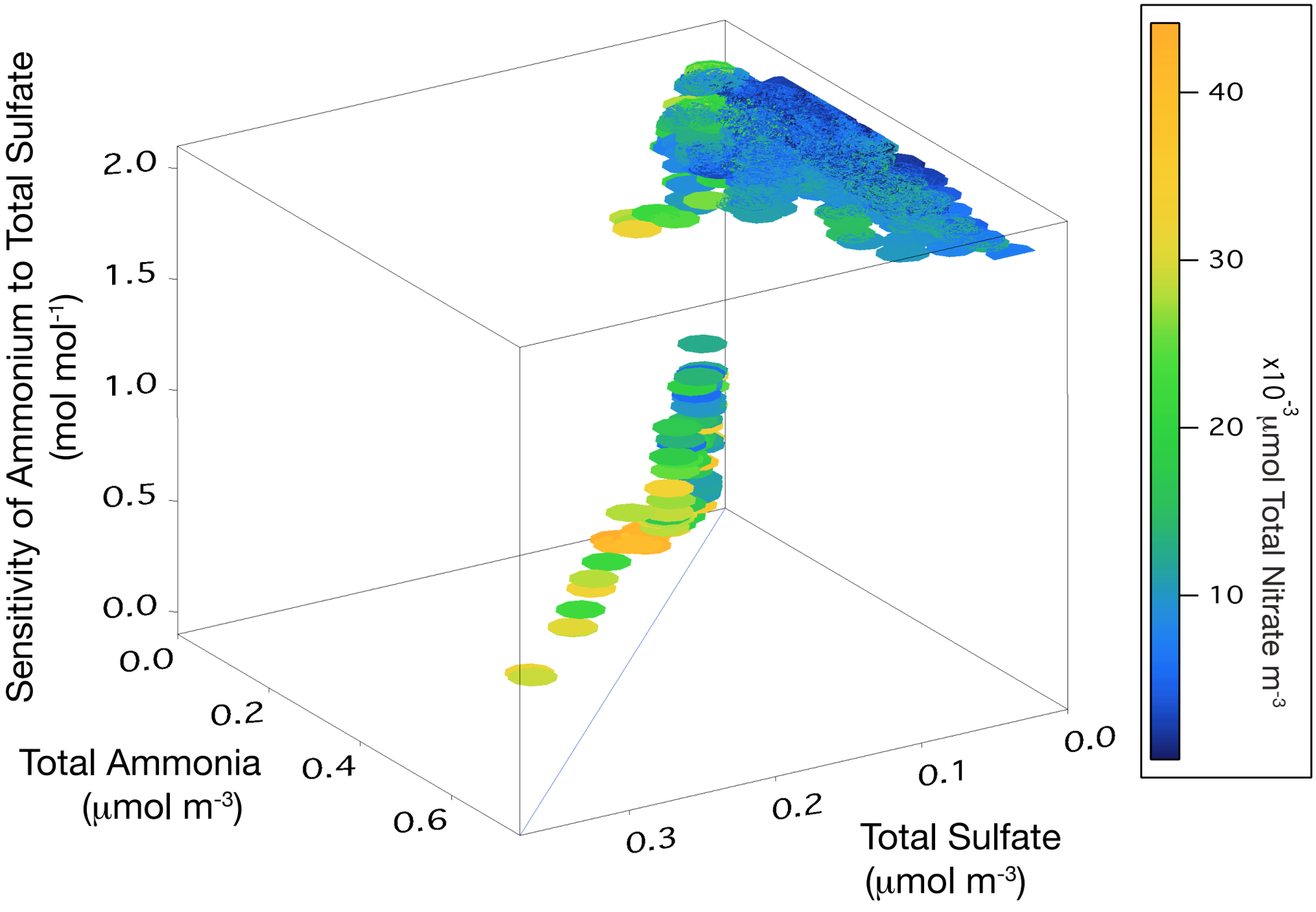

- Excess ammonia keeps aerosol **highly sensitive** to sulfate
- High nitrate concentrations with low ammonia levels can **reduce ammonium sensitivity**

On-going work & Applicability

- **Completion of the adjoint of ISORROPIA**
  - Treatment of Na and Cl
  - Including crustal species of ISORROPIA II
- **Integration into CMAQ-ADJ**
- **Augmented capability for regional model data assimilation**
  - Inclusion of inorganic aerosol and aerosol precursors
- **Efficient source-apportionment for selected receptors**
  - Potentially beneficial for epidemiological studies
  - Useful for regulatory applications

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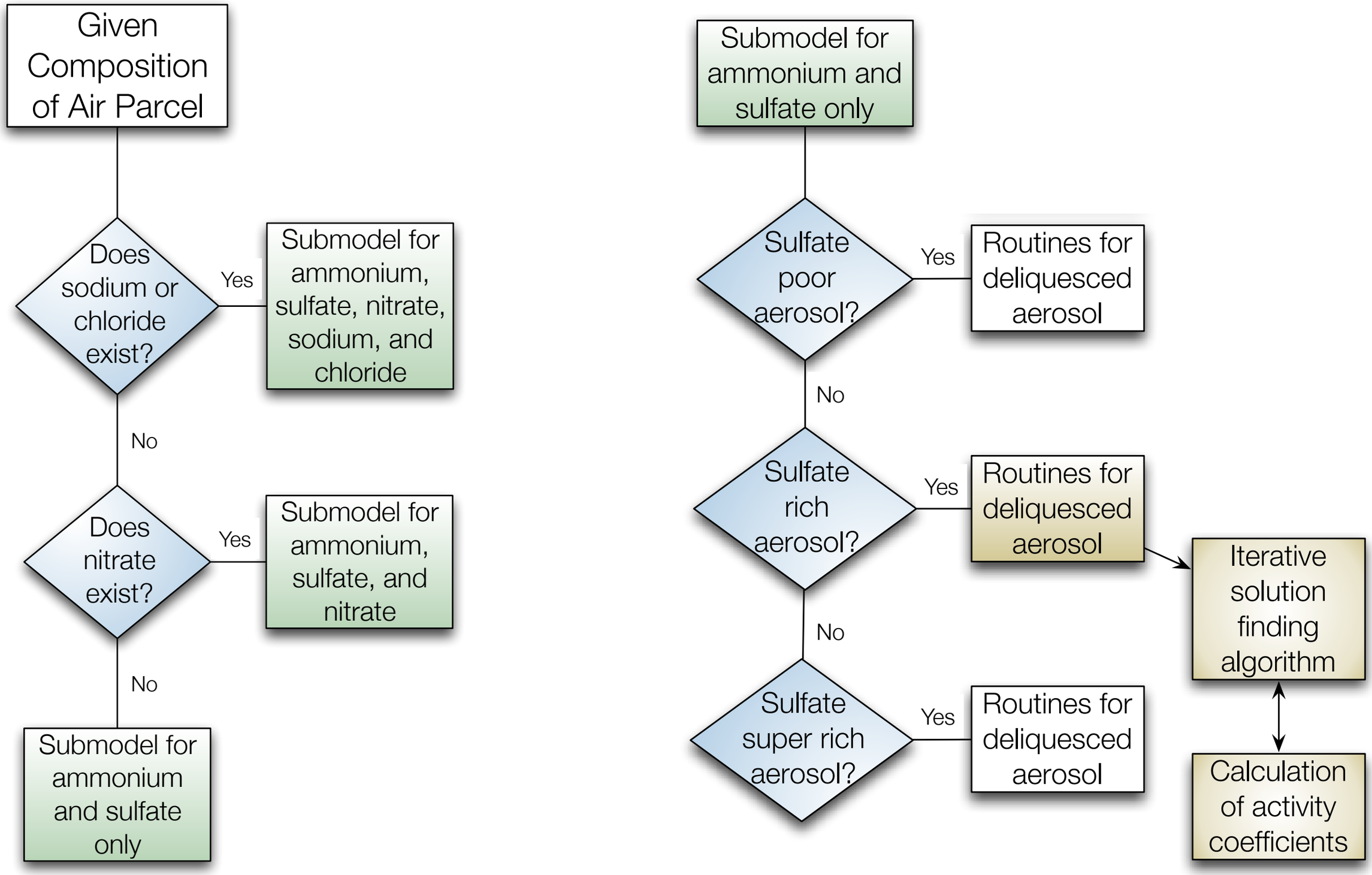
- *ANARChE Data*: Greg Huey, Rodney Weber, Amy Sullivan, Di Tian
- *Funding Sources*
  - NSF Graduate Research Fellowship
  - Eastman Chemical Summer Graduate Fellowship
  - Conoco-Phillips, Model Development Support
  - Georgia Tech Institute Fellowship

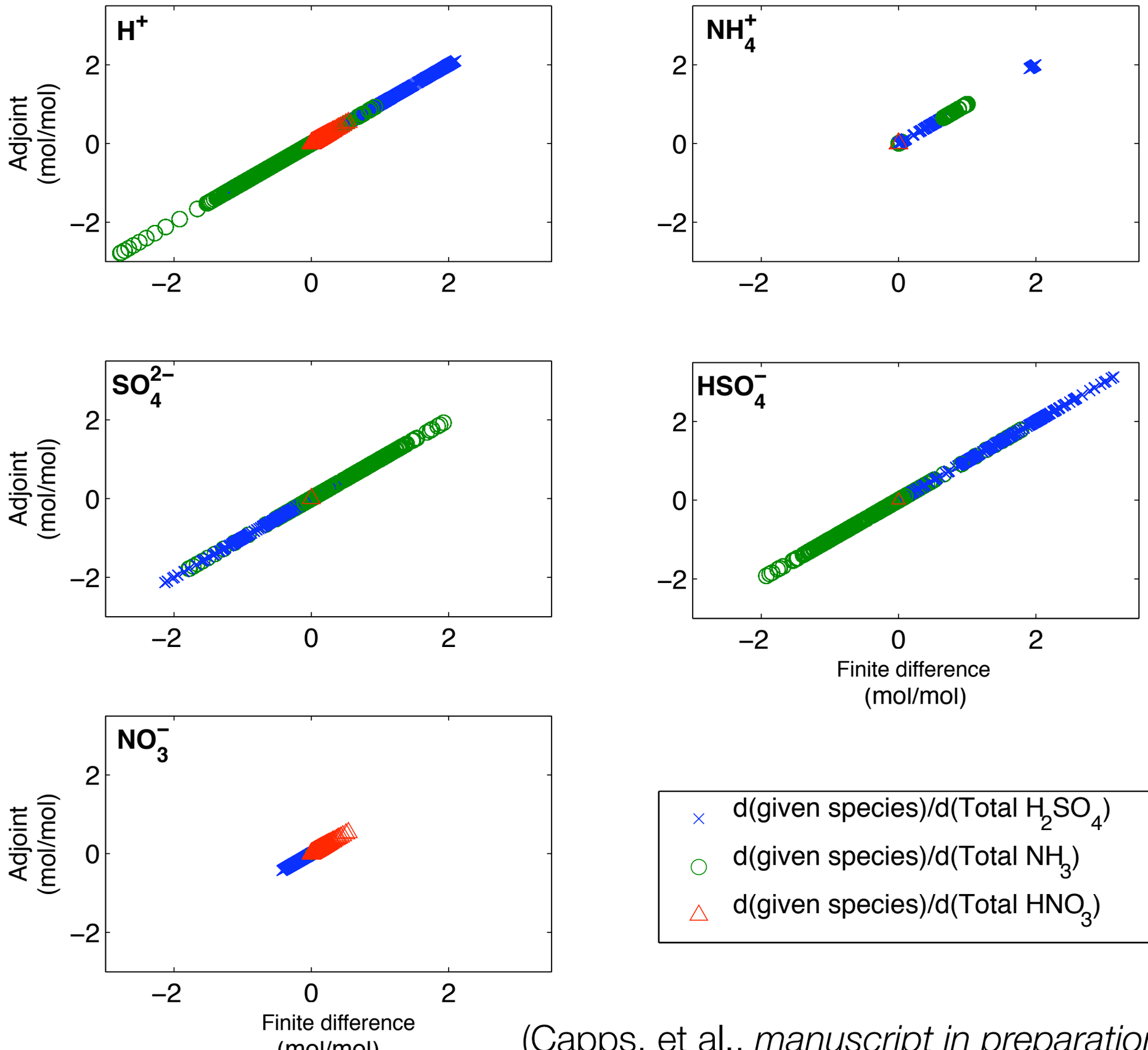
Supplemental Slides

Solution algorithm of ISORROPIA



Verification of adjoint performance

- RH ranges from 5% to 95%
- Comprehensive treatment of sulfate-ammonium systems
- Sulfate rich ammonium-sulfate-nitrate systems



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