ANISORROPIA:
Development of the Adjoint of ISORROPIA
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CMAQ-Adjoint Development Team
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Direct Sensitivity Analysis: 
Forward Method

\[ \frac{\partial y}{\partial x} \]

\[ F'(x, \partial x) \]

\[ \partial x \text{ at } x_1 \]

\[ \partial y_1, \partial y_2, \partial y_3, \partial y_4, \partial y_5 \]
Direct Sensitivity Analysis:
Forward Method

\[ \frac{\partial (\text{concentrations})}{\partial (\text{emissions})} \]

\[ \partial (\text{emission parameters}) \]
\[ \partial (\text{NO}_x \text{ EGU Emissions}) \]

\[ F'(x, \partial x) \]

\[ \partial (\text{Nitrate Aerosol}) \]
\[ \partial (\text{Sulfate Aerosol}) \]
\[ \partial (\text{Ammonium Aerosol}) \]
\[ \partial (\text{Sodium Aerosol}) \]
\[ \partial (\text{Chloride Aerosol}) \]
Direct Sensitivity Analysis: 
Reverse Method

\[ F^T(x, \partial y) \]

\[ \frac{\partial y}{\partial x} \]

\[ \partial x \]

\[ \partial x_1 \rightarrow \partial y \] at \( y_1 \)

\[ \partial x_2 \rightarrow \partial y \]

\[ \partial x_3 \rightarrow \partial y \]

\[ \partial x_4 \rightarrow \partial y \]

\[ \partial x_5 \rightarrow \partial y \]
Direct Sensitivity Analysis: 
Reverse Method

\[ \frac{\partial (\text{concentrations})}{\partial (\text{emissions})} \]

\[ \partial (\text{emission parameters}) \]
\[ \partial (\text{SO}_x \text{ EGU Emissions}) \]
\[ \partial (\text{NH}_3 \text{ Area Emissions}) \]
\[ \partial (\text{NO}_x \text{ EGU Emissions}) \]
\[ \partial (\text{Seasalt Emissions}) \]
\[ \partial (\text{NO}_x \text{ Mobile Emissions}) \]

\[ F^T(x, \partial y) \]

\[ \partial (\text{modeled concentrations}) \]
\[ \partial (\text{Ammonium Aerosol}) \]
CMAQ-Adjoint Sensitivities

Inorganic Thermodynamic Equilibrium Contribution

ANISORROPIA

Mobile NO\textsubscript{x} Emissions

EGU NO\textsubscript{x} Emissions

Area NH\textsubscript{3} Emissions

EGU SO\textsubscript{x} Emissions

HNO\textsubscript{3} Concentrations

\frac{\partial \text{SO}_4^{2-}}{\partial ([\text{NO}_3^-] + [\text{HNO}_3])}

\text{SO}_4^{2-}

\frac{\partial \text{SO}_4^{2-}}{\partial ([\text{NH}_4^+] + \text{NH}_3)}

\text{NH}_3

\frac{\partial \text{SO}_4^{2-}}{\partial ([\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{H}_2\text{SO}_4])}

\text{SO}_4^{2-}

\text{H}_2\text{SO}_4

Ammonium Aerosol
Strategy for ANISORROPIA Development

**ISORROPIA**
(Nenes et al., 1998; Fountoukis et al., 2007)

- **Acidic Aerosol**
- **Neutralized Aerosol**
Strategy for ANISORROPIA Development

- **acidic aerosol**

  - ISORROPIA algorithm: explicit solution, iteration on activity coefficients
  - Direct application of automatic differentiation tool, TAPENADE

Hascoët and Pascual, 2004
Strategy for ANISORROPIA Development

**acidic aerosol**

- ISORROPIA algorithm: explicit solution, iteration on activity coefficients
- Direct application of automatic differentiation tool, TAPENADE

\[
\frac{\partial \text{(Partitioned Conc)}}{\partial \text{(Total Conc)}}
\]

Hascoët and Pascual, 2004

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Total Concentrations, RH, Temp

- Adjoint forcing
- Iterative root seeking algorithm
- Number of iterations
- Calculation of activity coefficients

Nitrate?
- Yes
  - Submodel for sulfate, ammonium, and nitrate
- No

Sulfate poor
- No

Sulfate rich
- Sulfate super rich
Strategy for ANISORROPOLIA Development

neutralized aerosol

- ISORROPOLIA algorithm: bisection method to minimize deviation of saturation ratio from 1

\[
\text{Saturation Ratio} = \frac{\left[ \text{NH}_4^{+}(aq) \right]}{K \left[ \text{NH}_3(g) \right] \left[ H^+(aq) \right]^\gamma}
\]

HNO$_3$, H$_2$SO$_4$, and NH$_3$ present
Strategy for ANISORROPIA Development

- ISORROPIA algorithm: bisection method to minimize deviation of saturation ratio from 1

\[
\text{Saturation Ratio} = \frac{\left[ \text{NH}_3^{+} \right]_{aq}}{K \left[ \text{NH}_3(g) \right] \left[ \text{H}^+ \right]_{aq} \gamma}
\]

- Derivative cannot be traced across bisection steps

neutralized aerosol
Strategy for ANISORROPIA Development

- **neutralized aerosol**
  - Stable determination of root by bisection
  - Apply single iteration of Newton-Raphson at root
    - \[ x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \]
  - TAPENADE-produced forward sensitivity code
  - Adjoint only of post-convergence N-R step

Bartholomew-Biggs, 1996
Activity Coefficient Sensitivities

Differentiated code properly captures the sensitivity of activity coefficients involved in the calculation.
• For neutralized aerosol, accumulation of sensitivities through the activity coefficient calculations can be significant.

  • Lower relative humidities
  • Sensitivities to total ammonia
Adjoint-produced sensitivities (mol/mol)

Finite difference sensitivities (mol/mol) (Capps et al., manuscript in preparation)
Sensitivity Space: Ammonium and Sulfate

Sensitivity of Ammonium to Sulfate

Total Sulfate ($\mu$mol m$^{-3}$)

Total Ammonia ($\mu$mol m$^{-3}$)

H$_2$SO$_4$

NH$_3$

Aerosol
Sensitivity Space: Ammonium and Sulfate

Sensitivity of Ammonium to Sulfate

Sensitivity Space:

$\text{NH}_3$

$\text{H}_2\text{SO}_4$

$\text{SO}_4^{2-}$

$\text{NH}_4^+$
Sensitivity Space: Ammonium and Sulfate

Total Ammonia ($\mu$mol m$^{-3}$)

Total Sulfate ($\mu$mol m$^{-3}$)

Sensitivity of Ammonium to Sulfate

NH$_3$

H$_2$SO$_4$

NH$_4^+$

SO$_4^{2-}$

NH$_4^+$
Sensitivity Space: Ammonium, Sulfate, and Nitrate

- H$_2$SO$_4$
- NH$_3$
- NH$_4^+$
- NO$_3^-$
- SO$_4^{2-}$

Total Sulfate (µmol m$^{-3}$)

Total Ammonia (µmol m$^{-3}$)

Total Nitrate (µmol m$^{-3}$)

Sensitivity of Ammonium to Sulfate

Sensitivity Space: Ammonium, Sulfate, and Nitrate
Sensitivity Space: Ammonium, Sulfate, and Nitrate

Sensitivity of Ammonium to Sulfate

Sensitivity Space: Ammonium, Sulfate, and Nitrate

HNO₃

H₂SO₄

NH₃

NH₄⁺, NO₃⁻, SO₄²⁻
Sensitivity Space: Ammonium, Sulfate, and Nitrate

- Total Sulfate ($\mu$mol m$^{-3}$)
- Total Ammonia ($\mu$mol m$^{-3}$)
- Total Nitrate ($\mu$mol m$^{-3}$)

Sensitivity of Ammonium to Sulfate

35% Relative Humidity

Sensitivity Space: Ammonium, Sulfate, and Nitrate

- $\text{HNO}_3$
- $\text{H}_2\text{SO}_4$
- $\text{NH}_3$
- $\text{NH}_4^+$
- $\text{NO}_3^-$
- $\text{SO}_4^{2-}$
Sensitivity Space: 
Ammonium, Sulfate, Nitrate, Chloride, and Sodium

Excludes activity coefficient 
sensitivities in neutralized aerosol

0.1 µmol m\(^{-3}\) Total Chloride, 85% Relative Humidity
Sensitivity Space:
Ammonium, Sulfate, Nitrate, Chloride, and Sodium

- Limited by 2:1 ammonium to sulfate ratio
- Buffering effect of nitrate

0.1 µmol m⁻³ Total Chloride, 85% Relative Humidity
Sensitivity Space: Ammonium, Sulfate, Nitrate, Chloride, and Sodium

- Sodium extends range of non-zero ammonium sensitivity
- Buffering effect of nitrate

\[ \text{H}_2\text{SO}_4 \rightarrow \text{NH}_3 \rightarrow \text{HNO}_3 \]

\[ \text{NO}_3^- \rightarrow \text{SO}_4^{2-} \]

\[ \text{NH}_4^+ \rightarrow \text{Na}^+ \rightarrow \text{Cl}^- \]
Future Work

• Attributing speciated aerosol concentration to sources requires implementation within the full CMAQ-Adjoint - see ShunLiu Zhao’s talk at 4:40 pm

• Further refining routines with Na⁺-Cl⁻

• Extending to K⁺-Mg²⁺-Ca²⁺

image credit: Google Earth; adapted from Daven Henze’s representation of sensitivity methods