Chemical Mechanisms and 3-D Models for Ozone and Particulate Matter

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Air Quality Models

- Input Data
  - Emissions
  - Meteorology
  - Other (IC, BC, surface properties)
- Chemical Mechanism
- Computational Aspects
- Performance Evaluation
- Sensitivity & Uncertainty Analysis
Air Pollutant Emissions

- U.S. EPA national estimates for 2002
- Natural & soil dust emissions not shown
- Also need CO, SO$_2$ & NH$_3$

### PM$_{2.5}$

- Industry
- Gasoline
- Diesel
- Other fossil
- Biomass

### VOC

- Solvents
- Gasoline
- Diesel
- Other

### NO$_x$

- Power plants
- Gasoline
- Diesel
- Other
Volatile Organic Emissions

- Thousands of VOC, so typically “lump”:
- Alkanes (3-5 groups)
- Alkenes (2 groups plus…)
  - Ethene (explicit)
  - Isoprene and terpenes (biogenic)
- Aromatics (2 groups)
- Product species (oxygenated)

- Mechanisms differ in # of explicit VOC, lumping strategies, level of detail on products
Nitrogen Oxide Emissions

Most of the NO\textsubscript{x} is emitted as nitric oxide (NO).

Current emission speciation (all sources):
88% NO, 10% NO\textsubscript{2}, 2% HONO

Diesel Exhaust Particle Filters

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]
\[ \text{C} + 2\text{NO}_2 \rightarrow \text{CO}_2 + 2\text{NO} \]
\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

\~50% NO\textsubscript{2} fraction!
## Particulate Matter Emissions

<table>
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<tr>
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<th>0.1-1 µm</th>
<th>1-2.5 µm</th>
<th>2.5-10 µm</th>
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<td>EC</td>
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<td>Gives wt%</td>
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<td>Of total PM</td>
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<td>Sea salt</td>
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<td>Emissions</td>
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Eldering & Cass (*JGR* 1996) use 15 size bins 0.01-10 µm
Meteorology

- Temperature
  » Dissociation of PAN and NH₄NO₃
- Water vapor
  » O(^1D) + H₂O → 2 OH
- Clouds, fog & solar radiation
  » Photolysis rates; aqueous phase chemistry
- Wind velocity
- Turbulent diffusivity

- Air pollution can affect meteorology via aerosols and clouds
Performance Evaluation (1)

• AQ model predictions should match observations within specified tolerances

• Official inventory cannot be adjusted

• Motivates model tuning:
  » Discard cases that “don’t work”
  » Select met fields that give best AQ results
  » Adjust boundary conditions, NO\textsubscript{x} speciation etc. to compensate for inventory bias
Performance Evaluation (2)

• Mechanisms should be evaluated separately from their use in 3-D models

• Challenges:
  » Sometimes evaluation not possible because available data already used to develop mechanism
  » Recommend more evaluation of products other than $O_3$ (e.g., HCHO, HNO$_3$, SOA)
Sensitivity Analysis Example

Top ranked 12 (out of 900) Riverside $O_3$ sensitivities to model input data and parameters ($k$, IC, BC, $e$, $v_d$)

Semi-normalized results:
ppb $O_3$ per 100% change in listed parameter

Adjoint method (Martien and Harley, *ES&T* 2006)
Uncertainty Analysis

- Error propagation formula:
  \[
  \sigma_{O_3} = \frac{\partial[O_3]}{\partial k_j} \sigma_{k_j} = s_{O_3,k_j} \sigma_{k_j}
  \]

- Uncertainty contribution for \( k_j \):
  \[
  \text{UC(\%)} = 100 \cdot \frac{\left(s_{O_3,k_j} \sigma_{k_j}\right)^2}{\sum_j \left(s_{O_3,k_j} \sigma_{k_j}\right)^2}
  \]

- Largest uncertainty contributions from **influential** and **uncertain** parameters
Top Mechanism Uncertainties
(Riverside O$_3$ Example; high NO$_x$ conditions)

This is for the SAPRC99 mechanism
Conclusions

- Emissions uncertainties are as large or larger than gas-phase mechanism uncertainties

- $k$(OH+NO$_2$) and NO$_2$ photolysis rate are major mechanism sources of O$_3$ uncertainty

- Extend sensitivity and uncertainty analysis to other pollutants & locations