

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



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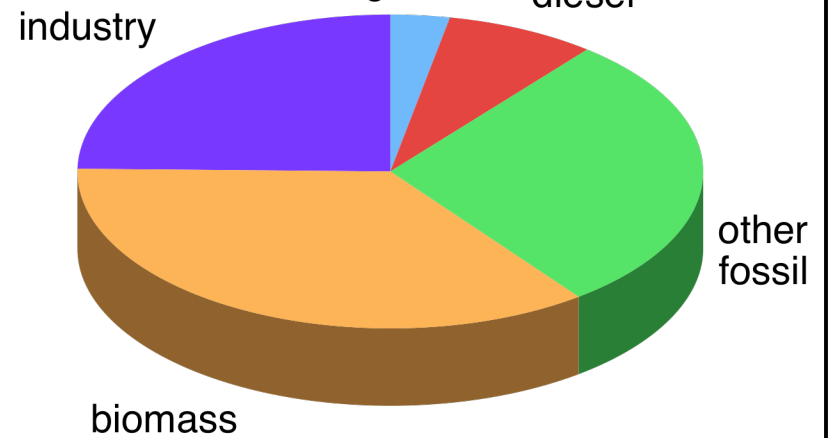
Air Quality Models

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

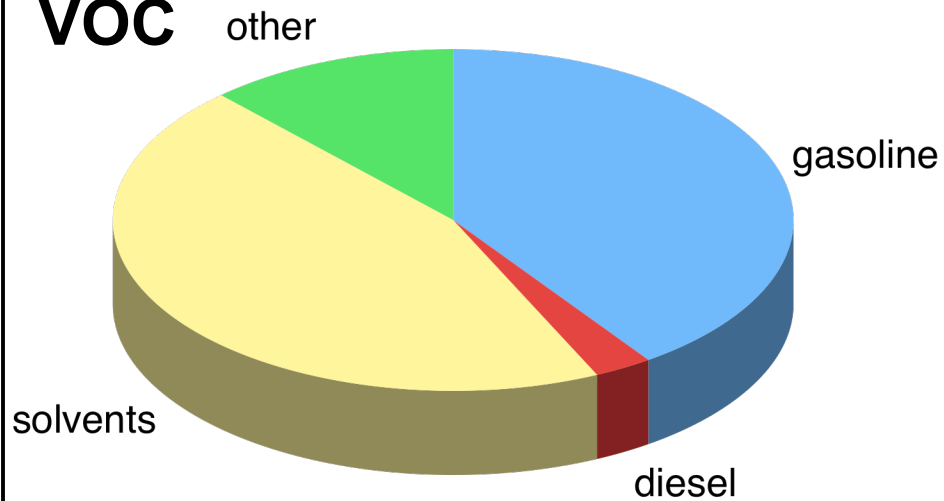
Air Pollutant Emissions

- U.S. EPA national estimates for 2002
- Natural & soil dust emissions not shown
- Also need CO, SO₂ & NH₃

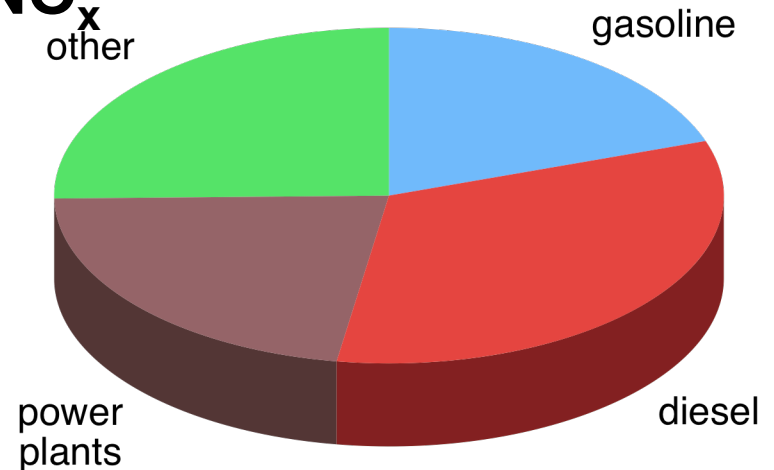
PM_{2.5}



VOC



NO_x



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

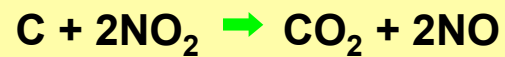
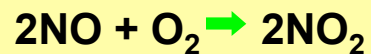
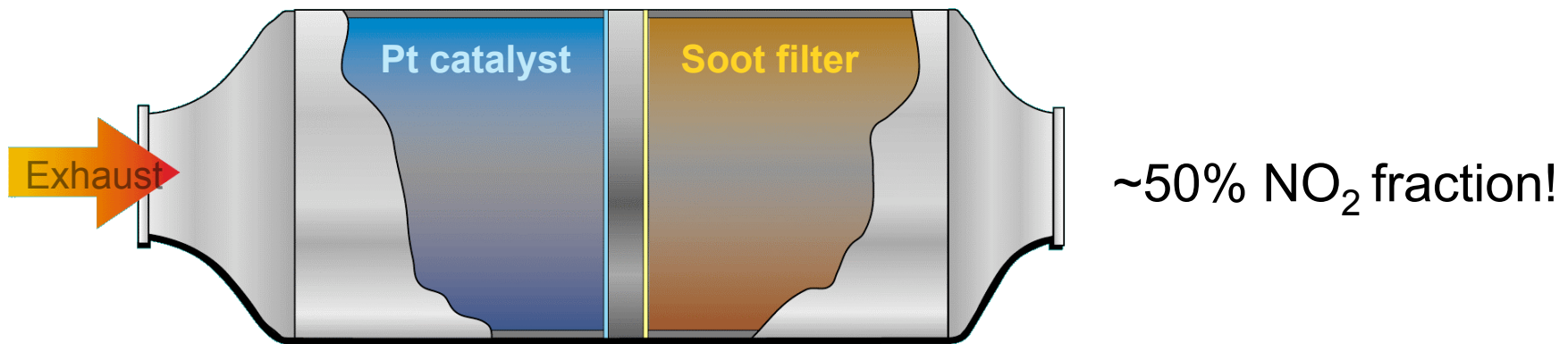
Nitrogen Oxide Emissions

Most of the NO_x is emitted as nitric oxide (NO)

Current emission speciation (all sources):

88% NO, 10% NO_2 , 2% HONO

Diesel Exhaust Particle Filters



Particulate Matter Emissions

	0.1-1 μm	1-2.5 μm	2.5-10 μm
EC			
OC		<i>Each entry</i>	
Crustal		<i>gives wt%</i>	
Metals		<i>of total PM</i>	
Sea salt		<i>emissions</i>	

Eldering & Cass (*JGR* 1996) use 15 size bins 0.01-10 μm

Meteorology

- Temperature
 - » Dissociation of PAN and NH_4NO_3
- Water vapor
 - » $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH}$
- Clouds, fog & solar radiation
 - » Photolysis rates; aqueous phase chemistry
- Wind velocity
- Turbulent diffusivity

- Air pollution can affect meteorology via aerosols and clouds

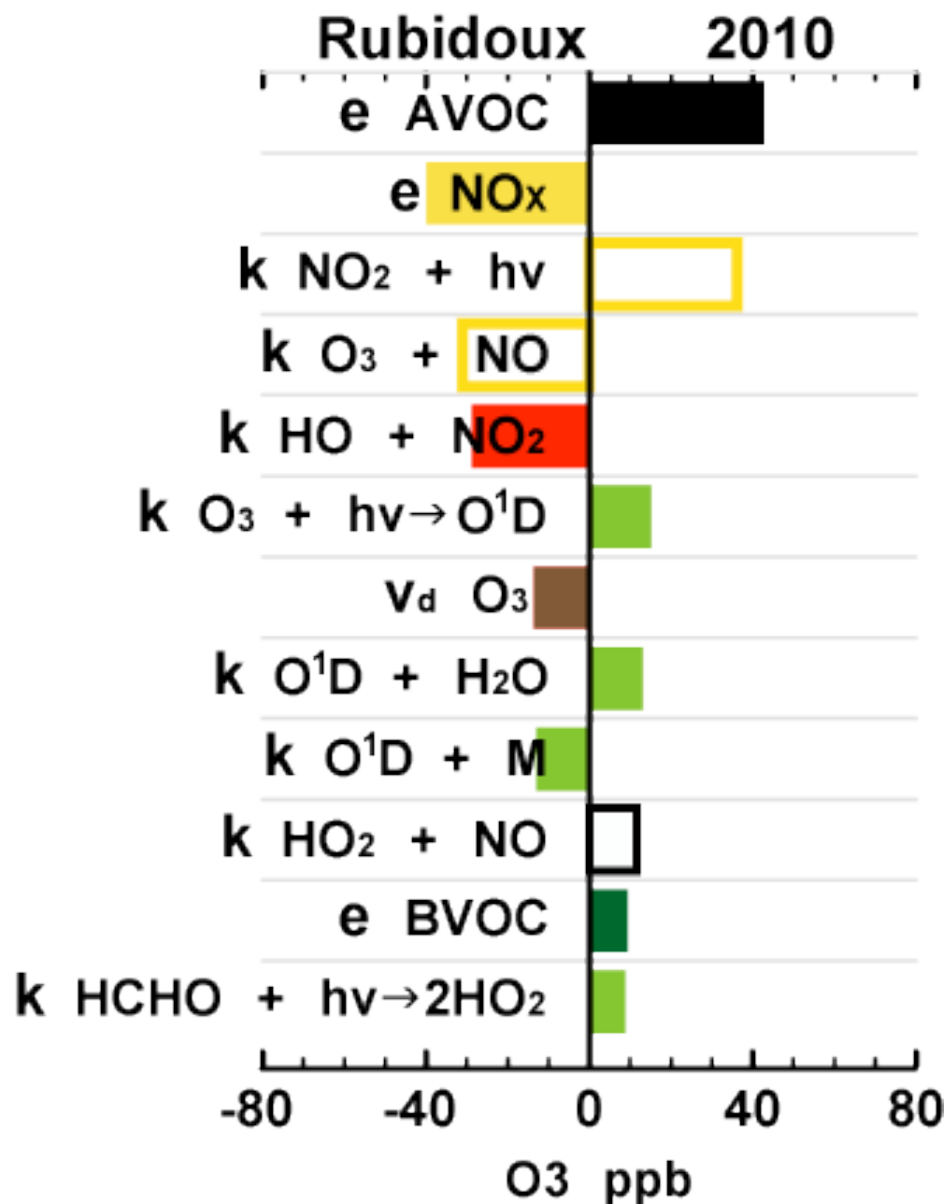
Performance Evaluation (1)

- 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_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 O₃ (e.g., HCHO, HNO₃, SOA)

Sensitivity Analysis Example



Top ranked 12 (out of 900) Riverside O₃ sensitivities to model input data and parameters (k , IC, BC, e , v_d)

Semi-normalized results:
ppb O₃ per 100% change
in listed parameter

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

Uncertainty Analysis

- Error propagation formula:

$$\sigma_{O_3} = \frac{\partial[O_3]}{\partial k_j} \sigma_{k_j} = S_{O_3, k_j} \sigma_{k_j}$$

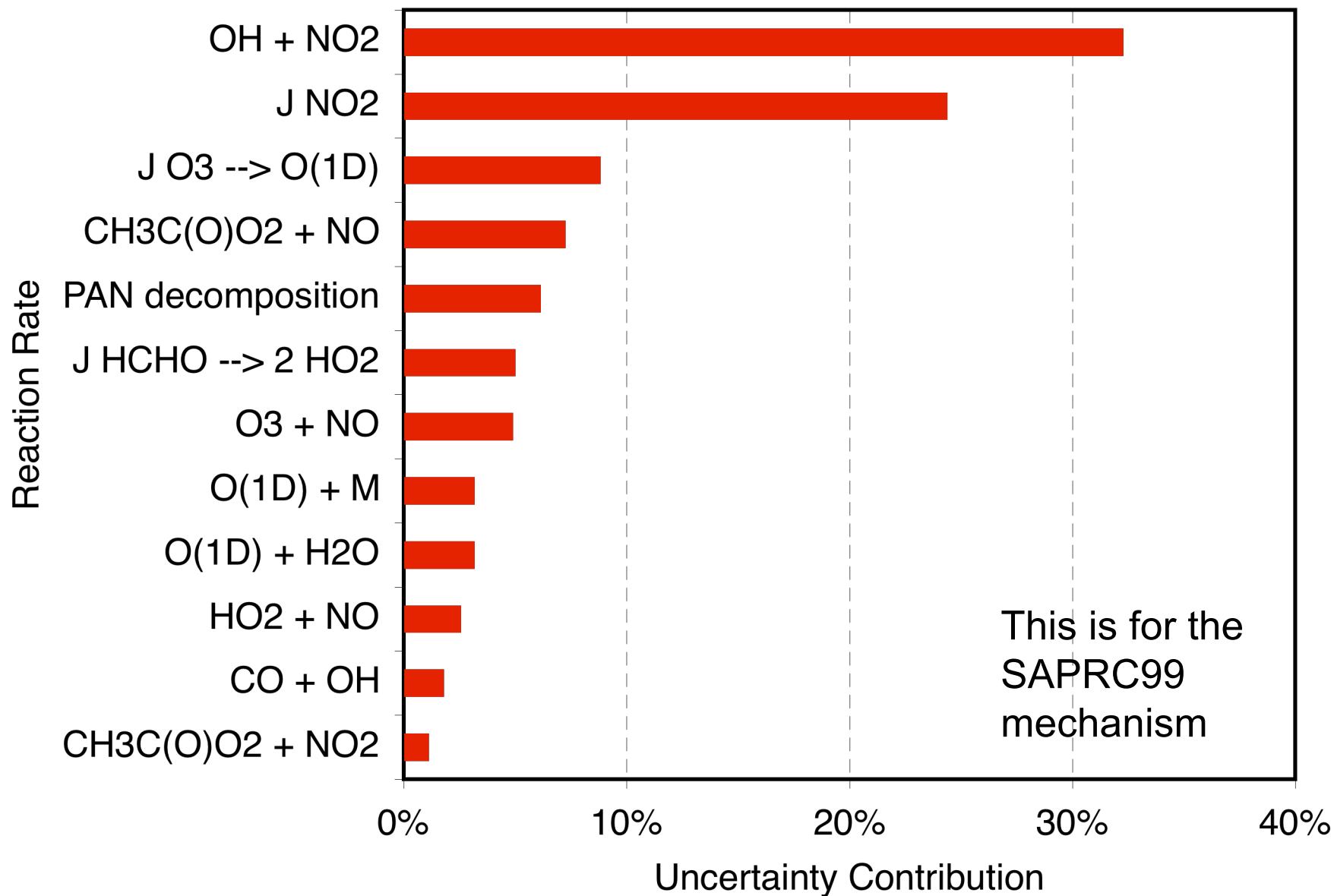
- Uncertainty contribution for k_j :

$$\text{UC}(\%) = 100 \cdot \frac{\left(S_{O_3, k_j} \sigma_{k_j} \right)^2}{\sum_j \left(S_{O_3, k_j} \sigma_{k_j} \right)^2}$$

- Largest uncertainty contributions from influential and uncertain parameters

Top Mechanism Uncertainties

(Riverside O₃ Example; high NO_x conditions)



Conclusions

- Emissions uncertainties are as large or larger than gas-phase mechanism uncertainties
- $k(\text{OH}+\text{NO}_2)$ and NO_2 photolysis rate are major mechanism sources of O_3 uncertainty
- Extend sensitivity and uncertainty analysis to other pollutants & locations