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

Robert Harley
Dept. of Civil and Environmental Engineering
University of California, Berkeley

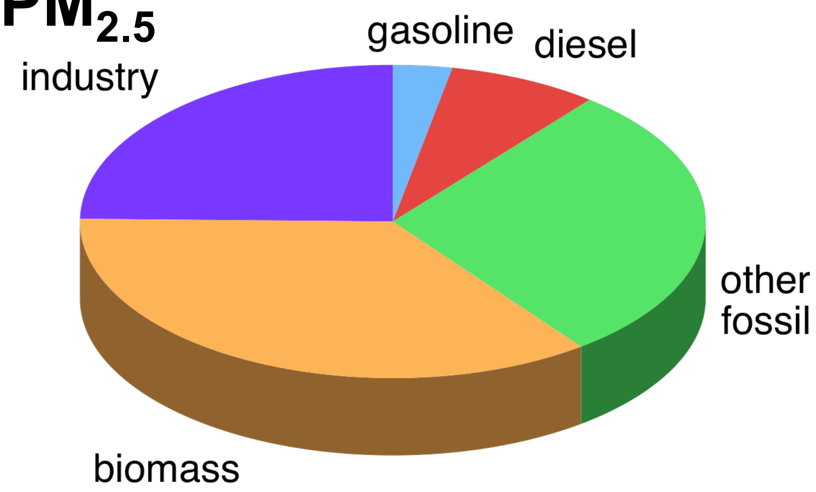
Air Quality Models

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

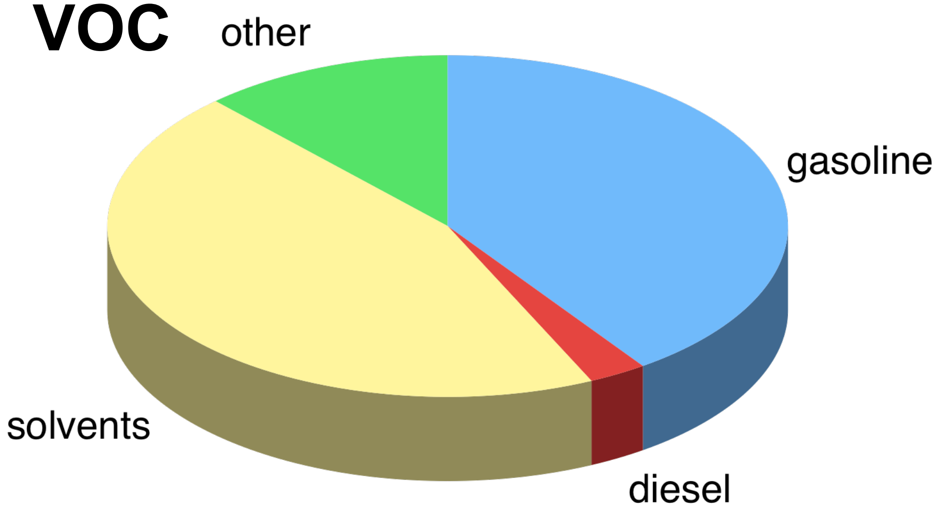
Air Pollutant Emissions

- U.S. EPA national estimates for 2002
- Natural & soil dust emissions not shown
- Also need CO, SO_2 & NH_3

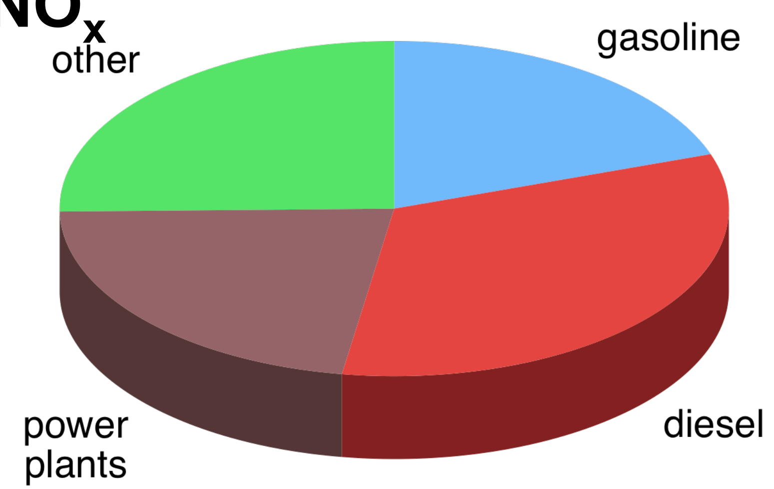
$PM_{2.5}$



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)

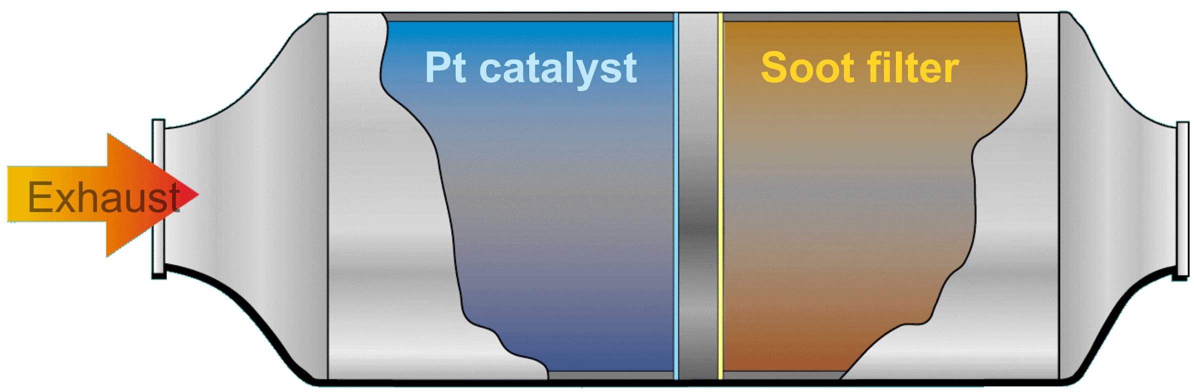
- Mechanisms differ in # of explicit VOC, lumping strategies, level of detail on products

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



~50% NO_2 fraction!

$2NO + O_2 \rightarrow 2NO_2$

$C + 2NO_2 \rightarrow CO_2 + 2NO$

$C + O_2 \rightarrow CO_2$

Particulate Matter Emissions

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

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

Meteorology

- Temperature
  - Dissociation of PAN and NH_4NO_3
- Water vapor
  - $O(^1D) + H_2O \rightarrow 2\ OH$
- 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)

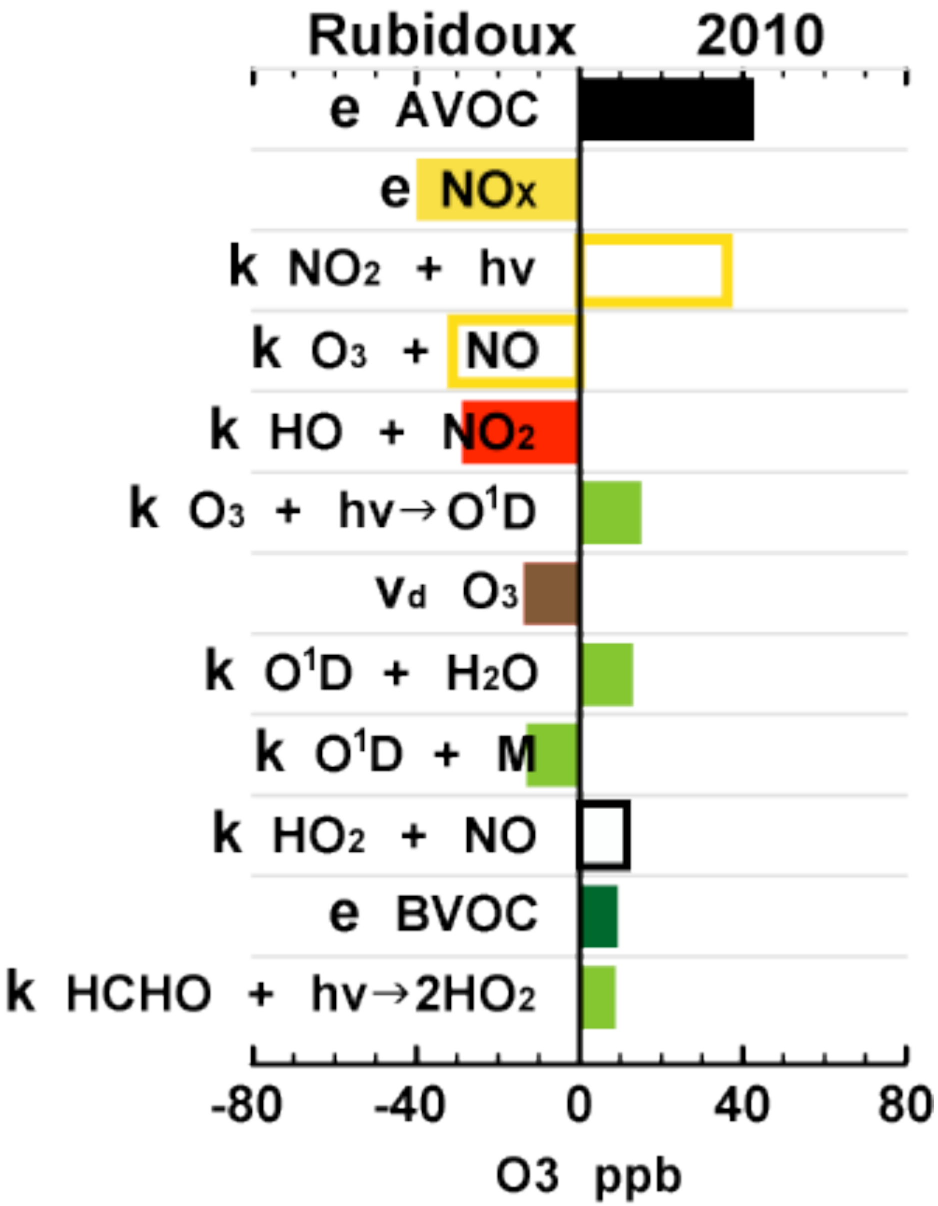
- AQ model predictions should match observations within specified tolerances
- Official inventory cannot be adjusted
- Motivates model tuning:
  - » Discard cases that “don’t work”
  - » Select met fields that give best AQ results
  - » Adjust boundary conditions, NO_x speciation etc. to compensate for 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:

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

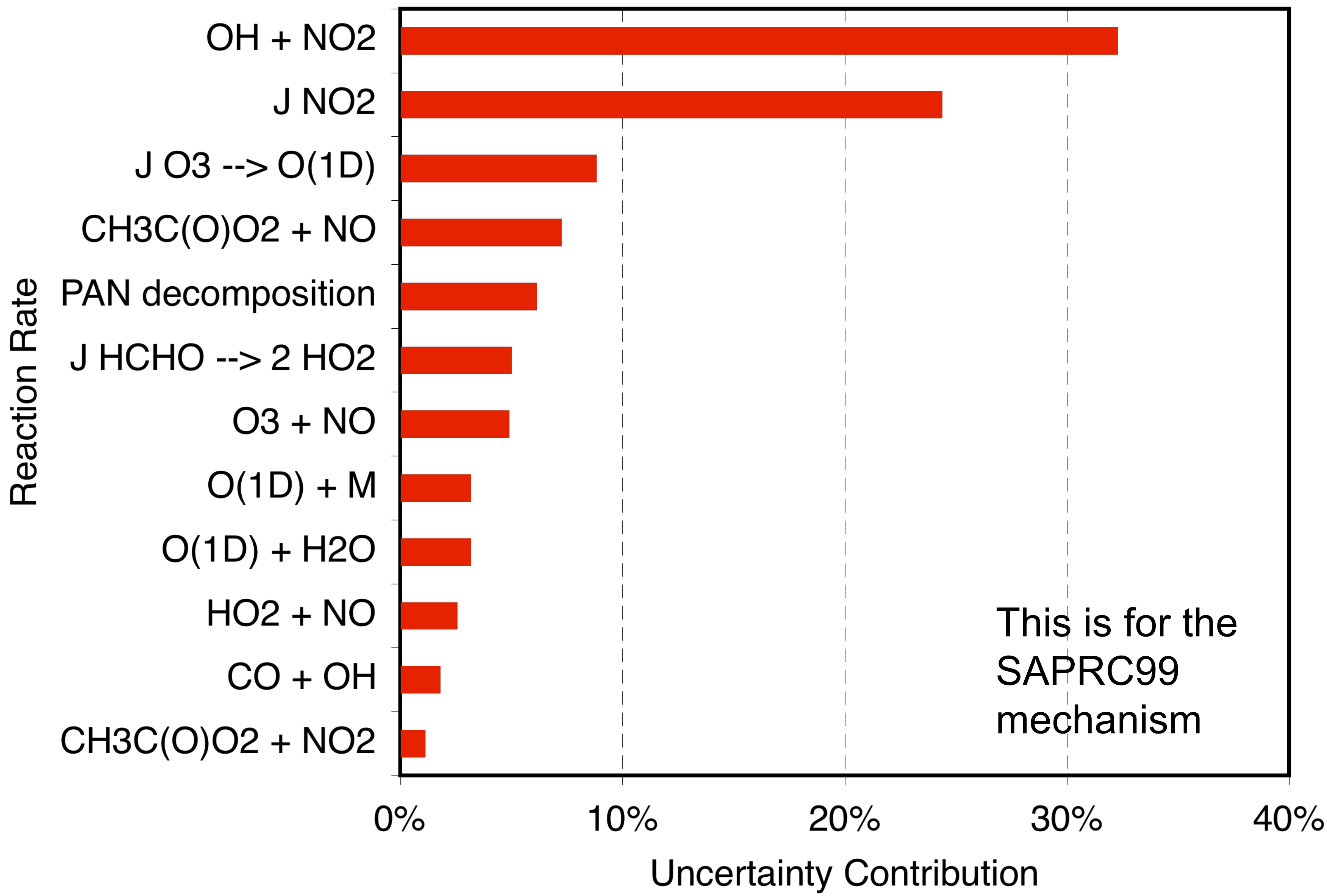
- Uncertainty contribution for k_j:

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

- Largest uncertainty contributions from <u>influential</u> and <u>uncertain</u> parameters

Top Mechanism Uncertainties

(Riverside O_3 Example; high NO_x conditions)



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