Mechanisms

Possible Forward Paths

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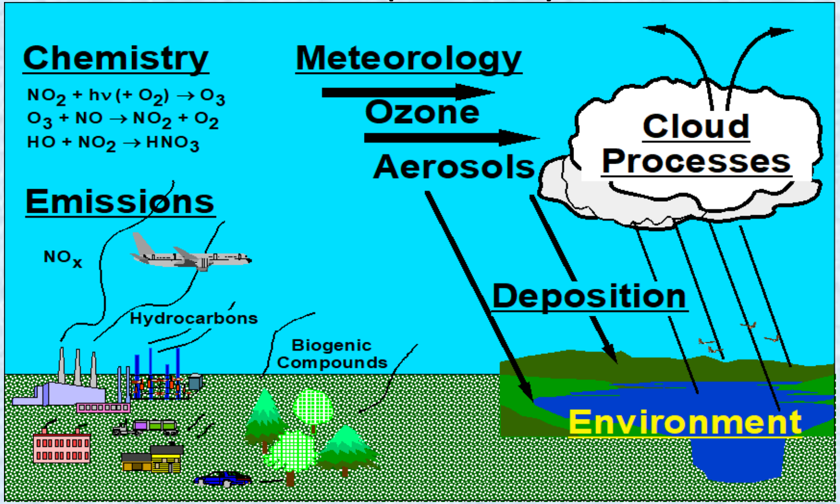
Eulerian Air Quality Models, Meteorology and Processes

The Atmospheric System



Air Quality Model Modules

Meteorological Observations

Air Quality Monitoring Data
- Chemical Initial Conditions
- Lateral and Top Boundary Conditions

Meteorological Forecast Model
Meteorological Parameters
Fields of Winds, Temperatures, Humidity and others

Air Quality Model or Subroutine

Air Quality Simulation Results
Time Resolved 3-Dimensional Fields of Air Pollutants and 2-Dimensional Deposition Patterns

Modules in Air Quality Model

Emissions
- Determines emissions of VOC, NO_x, SO_2, etc.

Gas-Phase Chemistry
- Integration of chemical rate equations for VOC, NO_x, SO_2 and O_3.

Aerosol Chemistry and Physics

Transport
- 3-D advection
- vertical diffusion

Dry Deposition
- Loss to surfaces by non-precipitation processes

Cloud Effects
- Aqueous chemistry
- wet scavenging
- vertical redistribution

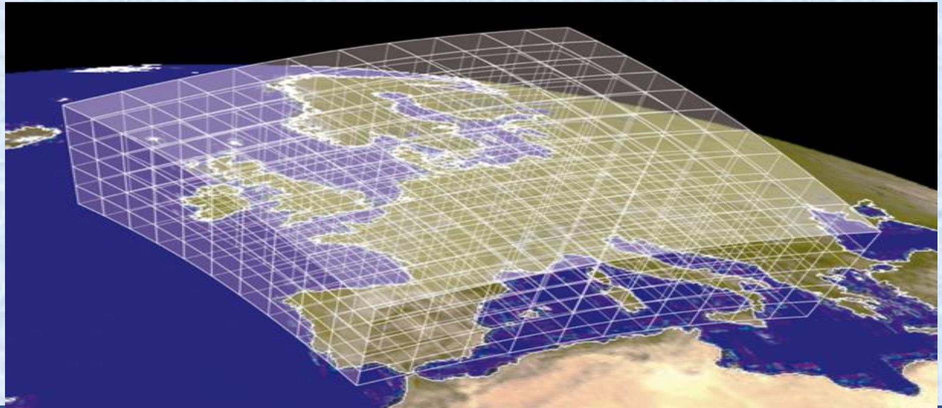
One Equation per Species per Grid Box

$$\frac{\partial c_i}{\partial t} = -\nabla_H \bullet V_H c_i + \left[\frac{\partial (c_i \eta)}{\partial z} - c_i \frac{\partial}{\partial z}\left(\frac{\partial h}{\partial z}\right)\right] - \nabla \bullet \rho K \nabla (c_i/\rho)$$

$$+ \left.\frac{\partial c_i}{\partial t}\right|_{Chemistry} + \left.\frac{\partial c_i}{\partial t}\right|_{Emissions} + \left.\frac{\partial c_i}{\partial t}\right|_{Deposition}$$

t	= time
c_i	= concentration of i^{th} species
V_H	= horizontal wind vector
h	= net vertical entrainment rate
z	= terrain following vertical coordinate
h	= layer interface height
r	= atmospheric density
K	= turbulent diffusion coefficient

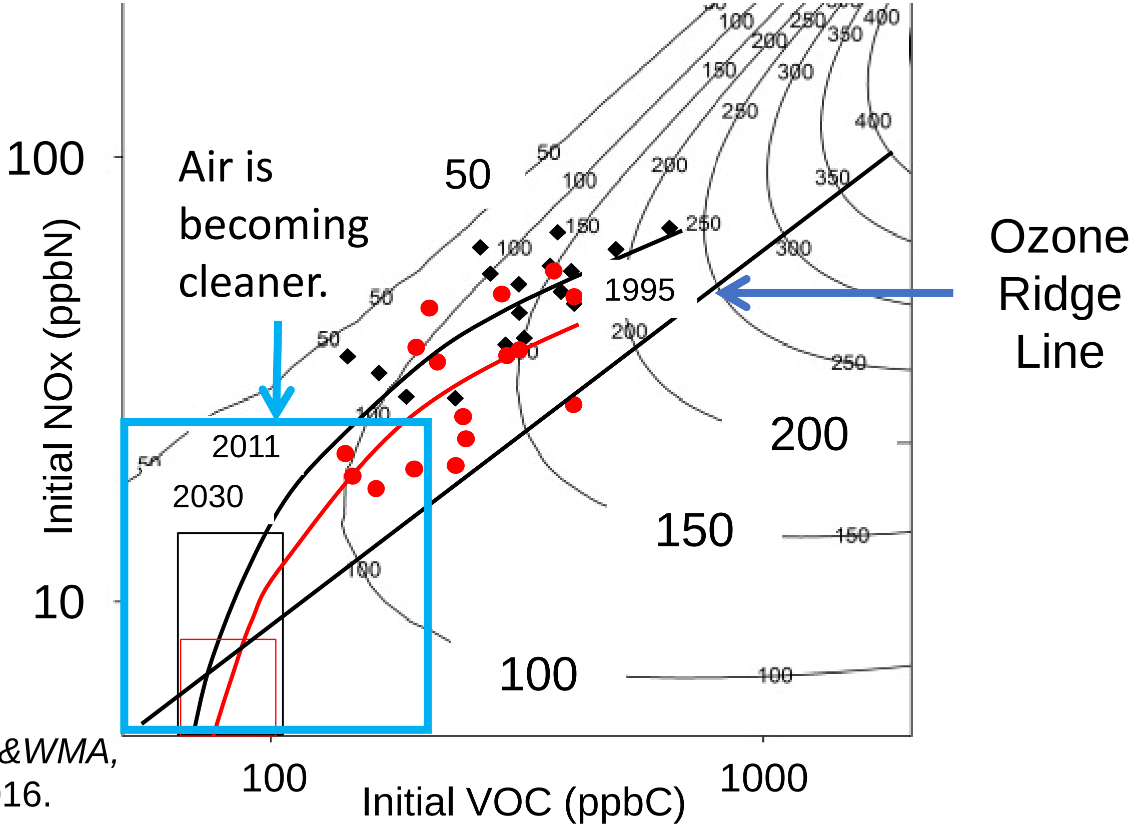
A Very Large Number of Grid Boxes



Maintaining a Balance in the Treatment of Processes In Eulerian Air Quality Models – Meteorology vs. Chemistry

- **Meteorology vs. Chemistry**
    - Finer grid resolution, more microscale physics vs. more detailed chemistry?
    - Improved Meteorology with better PBL parameterization?
    - Development of Mesoscale to Microscale coupling and even to Synoptic scales?
    - Better Aerosol Radiation Interaction?
- **Multi-phase Chemistry**
    - Coupling gas-phase and aerosol chemistry more closely?
- **Emissions**
    - Finally, more accurate emissions are necessary.

Daily Average Ozone
Azusa – Avg. VOC and NO_x, Years 1995-2011
Black diamonds = weekdays; Red circles = weekends



Do we need more chemical knowledge for cleaner and lower NO_x regimes?

Fujita, et al., *JA&WMA, 66,* 201-214, 2016.

The Current Paradigm

Kinetic Database, Measurements, SARS etc.

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An Explicit Mechanism

$NO_2 + h\nu \rightarrow NO + O(^3P)$	j_1
$O_3 + h\nu \rightarrow O_2 + O(^1D)$	j_2
$O(^3P) + O_2 + M \rightarrow O_3 + M$	k_1
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	k_2
$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	k_3
$O_3 + NO \rightarrow NO_2 + O_2$	k_4
$O(^1D) + H_2O \rightarrow 2\ HO$	k_5
...	
$HO + VOC \rightarrow Products$	k_i
... Millions of Reactions	

→

Differential Equations

$$\frac{d[X]_i}{dt} = \left\{ \sum P_{X_i} - \sum L_{X_i}[X]_i \right\}$$

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Differential Equation Solver

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Simulations

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Condensation

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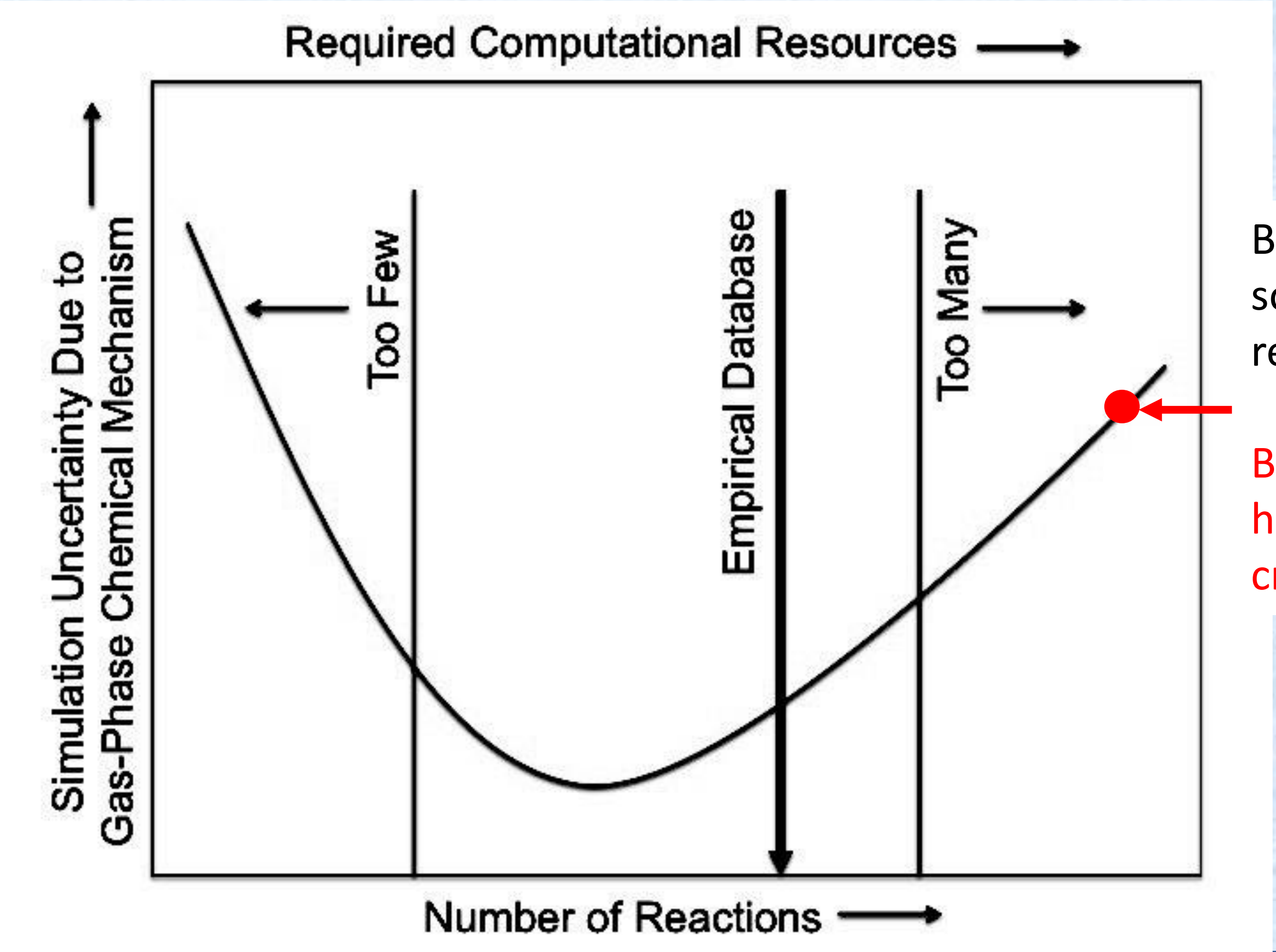
Applications

Evaluations

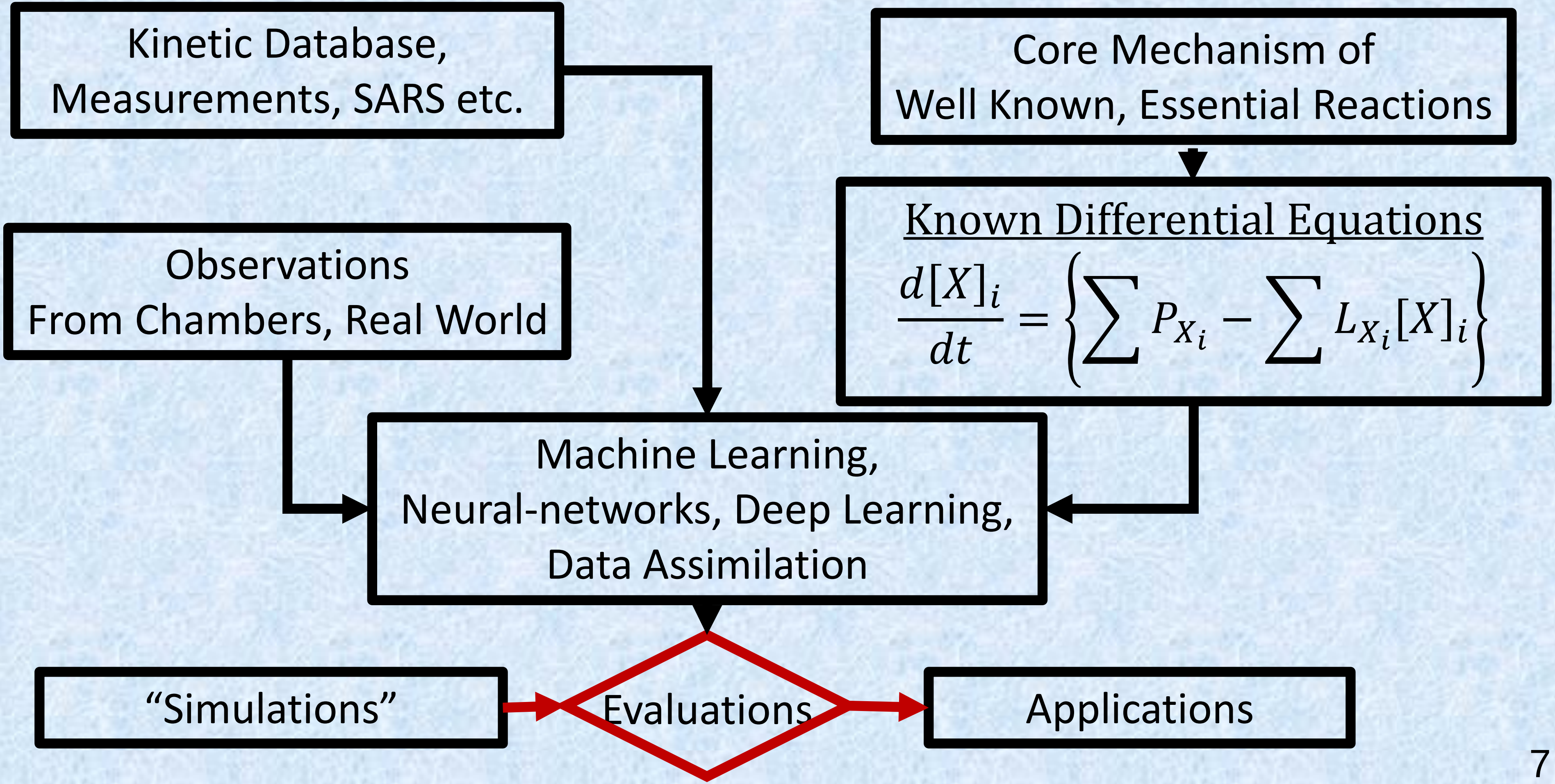
Is Bigger Always Better?



Bigger is better for some science research studies.

But does starting here really add credibility for policy?

Are There Alternatives to the Standard Paradigm?



A Diverse and Balanced Community

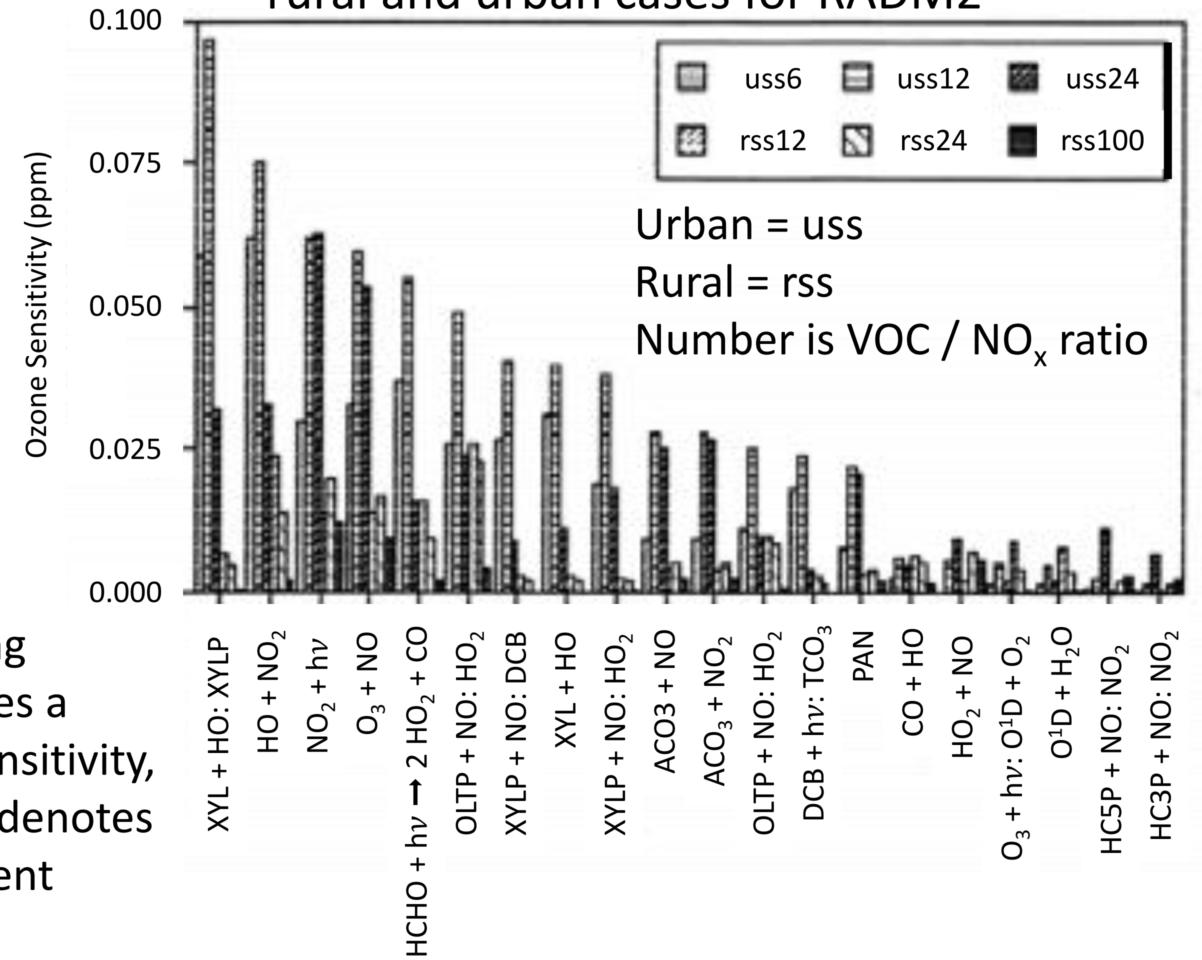
- Maintain a diverse community of scientists. Diverse in terms of sex, race, culture and scientific discipline (e.g. more applied mathematicians are desperately needed).

- A diverse community should provide new approaches and provide an important check on mainstream trends. – Reduce groupthink.

- Greater mixing between atmospheric chemists, air quality modelers and policy makers would encourage greater balance in all three areas.

Comparison of time-averaged sensitivity coefficients for ozone across rural and urban cases for RADM2

Not a very exotic list



Product following reactants denotes a product yield sensitivity, otherwise label denotes the rate coefficient sensitivity.

Gao, D., W.R. Stockwell and J.B. Milford, First Order Sensitivity and Uncertainty Analysis for a Regional Scale Gas-Phase Chemical Mechanism, J. *Geophys. Res., 100*, 23153-23166, 1995.

Funding

- New thinking is needed for funding the needed research necessary to build the laboratory chemical kinetics database.
- Many studies have shown that ozone concentrations are particularly sensitive to reactions that are relatively well known.
- Greater analysis and utilization of field observations and chamber experiments needs to be funded. Increase funding for data analysis.
- Improve instrumentation for HO and RO_2 measurements.
- Reducing the uncertainty in the rate coefficients of these reactions from, say 10%, to 5%, would significantly improve confidence in air quality model simulations.
- Fund research on closer coupling between gas-phase and aerosol-phase chemistry in models.
- Funding agencies may need to reexamine their priorities.

Take Home Message on Alternatives to Current Protocols:

- Does a detailed explicit mechanism, in the traditional sense consisting of reactions with their reactants, products (with yields) and rate coefficients, need to be created to have a credible chemical module to simulate O_3, PM and other atmospheric constituents of regulatory interest?
- Investigate alternatives to current mechanism development paradigms
  - Cheminformatics (information science, data mining and machine learning).
  - A first test could be to create a chemical module that makes calculations for higher molecular weight compounds based on SAR data directly rather than by first estimating explicitly the reactants, products, product yields and rate coefficients of unmeasured reactions.
- More data is needed
  - Laboratory data for cleaner and low NO_x conditions.
  - Greater analysis and utilization of field observations and chamber experiments.

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Extra Slides

Uncertainty is Associated with Every Reaction in a Mechanism

A + B → Yield_C C + Yield_D D with Rate Coefficient k

This reaction has three uncertain quantities: $\boldsymbol{\sigma}_{\text{YieldC}}$; $\boldsymbol{\sigma}_{\text{YieldD}}$; and $\boldsymbol{\sigma}_{\text{k}}$

Propagation of Errors Formula:

$$\boldsymbol{\sigma}_q = \left(\sum_{1}^{z} \left\{ \frac{\partial F}{\partial M_i} \sigma_i \right\}^2 \right)^{1/2}$$

It is not practical to use the propagation of errors formula to estimate the uncertainty in kinetics differential equations but using it as a guide, the terms such as $\left([A][B]\ \sigma_{k_1}\right)^2$ contribute to $\sigma_{\frac{d[A]}{dt}}$.