Particulate Matter Modeling: Including Nanoparticles

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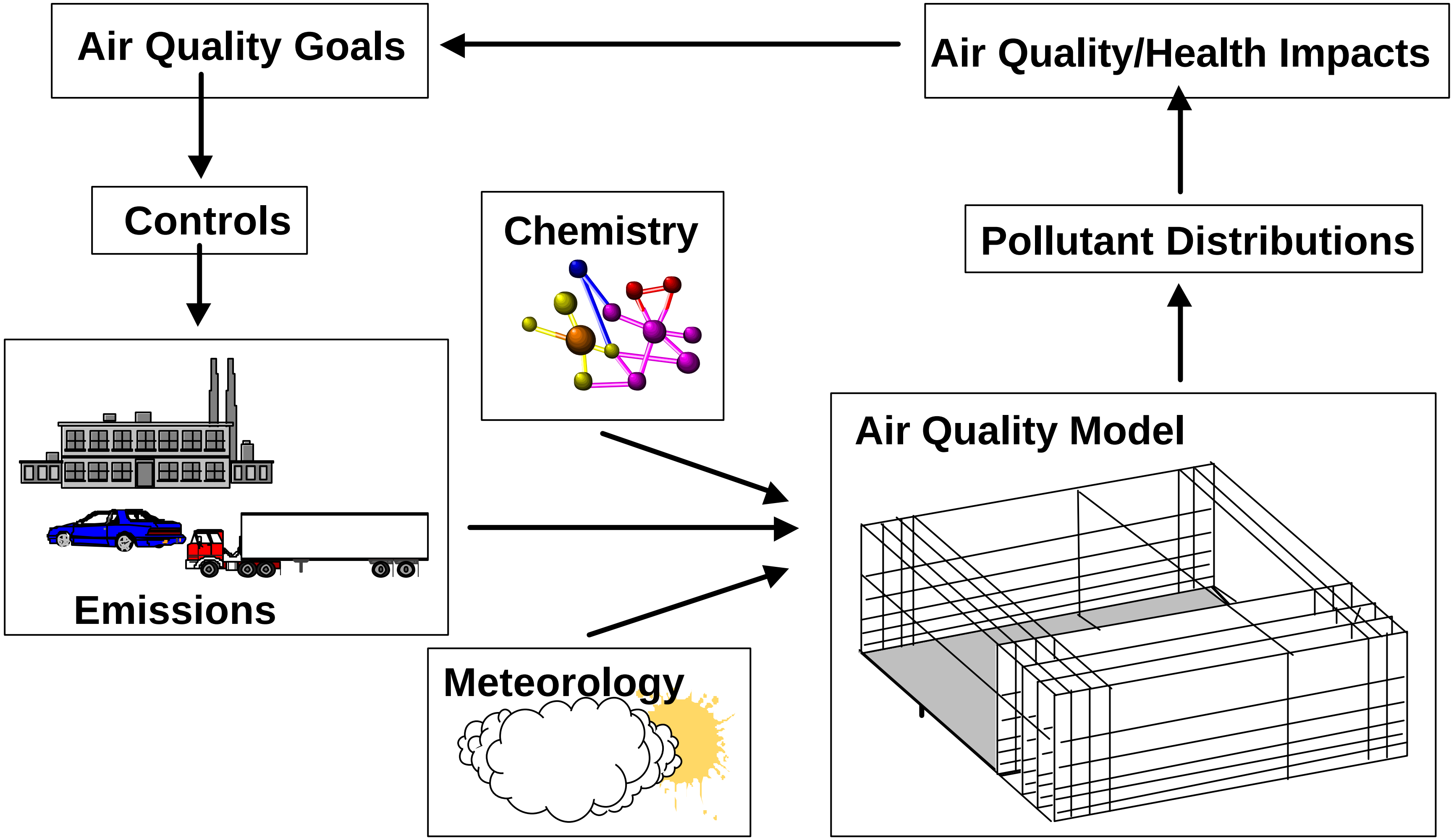
Issues

- Much of the suspected health and welfare effects from air pollution due to particulate matter
  - Health (the main concern)
    - Morbidity and mortality concerns
    - Asthma
    - etc.
  - Welfare
    - Visibility
    - Deposition
- Particulate matter modeling has significant challenges
  - Modeling techniques in development
  - input/output uncertainties impact model evaluation

Outline

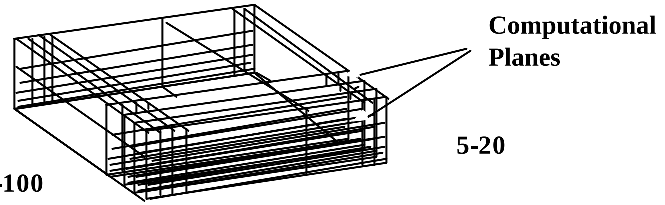
- Air quality modeling
  - Role
  - Scientific foundation
  - Model vs. process
- Particulate matter models
  - State of the science
  - Current research directions
- Conclusions

Role of Air Quality Modeling In Air Quality Management



Air Quality Model

- Representation of physical and chemical processes
  - Numerical integration routines
- Scientifically most sound method to link future emissions changes to air quality



Air Quality Model

$$\frac{\partial c_i}{\partial t} = -\nabla(\mathrm{u}c_i) + \nabla(\mathrm{K}\nabla c_i) + R_i + S_i$$

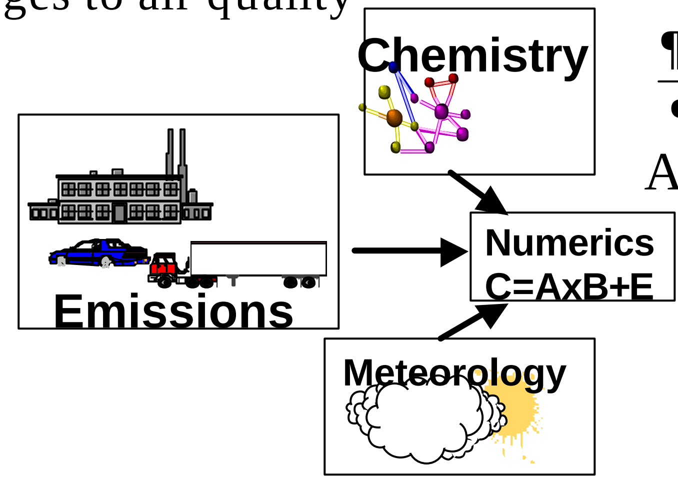
Atmospheric Diffusion Equation

Discretize

$$\frac{\partial c}{\partial t} + \mathrm{L}(\mathbf{x},t)c = f(\mathbf{x},t)$$

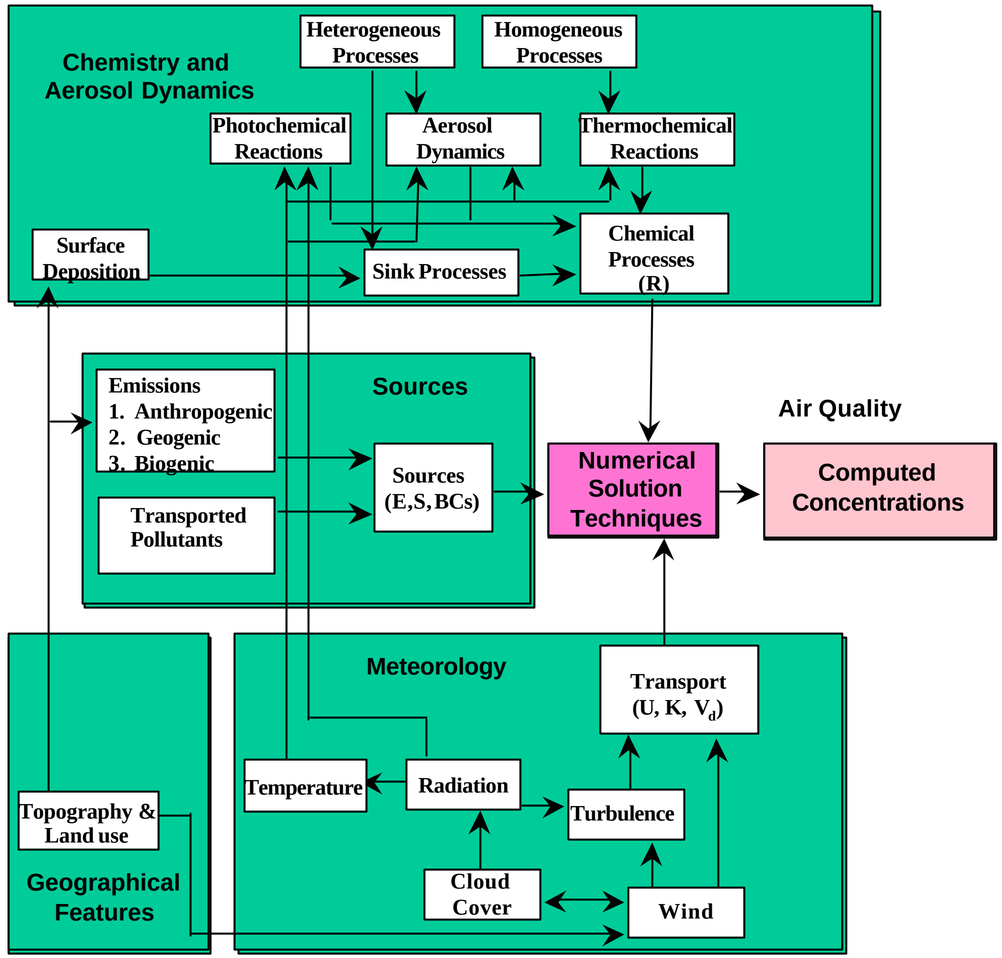
Operator splitting

$$c(t+2\Delta t) = L_x(\Delta t)\, L_y(\Delta t)\, L_{cz}(2\Delta t)\, L_y(\Delta t)\, L_x(\Delta t)\, c(t)$$

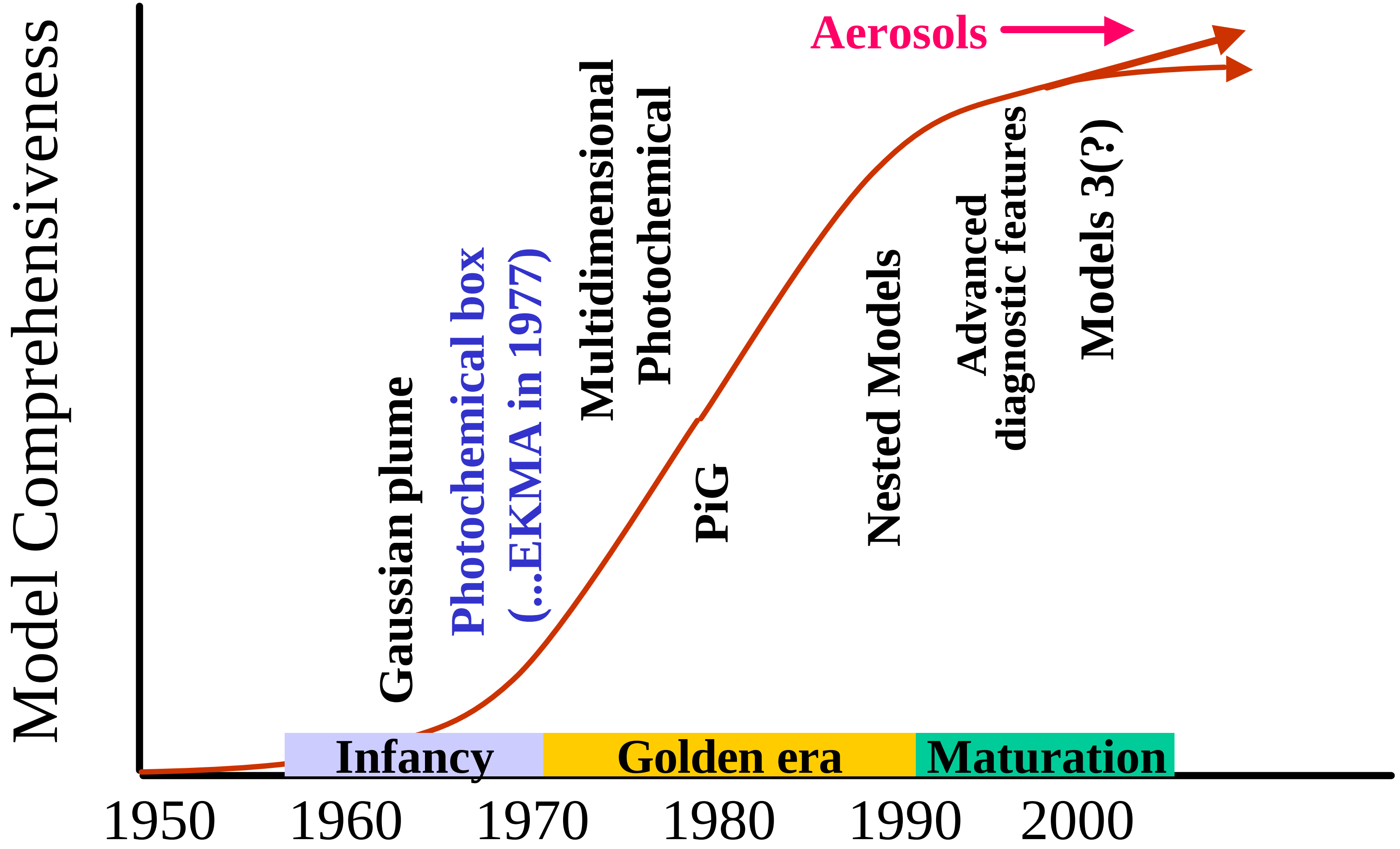


100 species x 5000 hor. grids x 10 layers= 5 million coupled, stiff non-linear differential equations

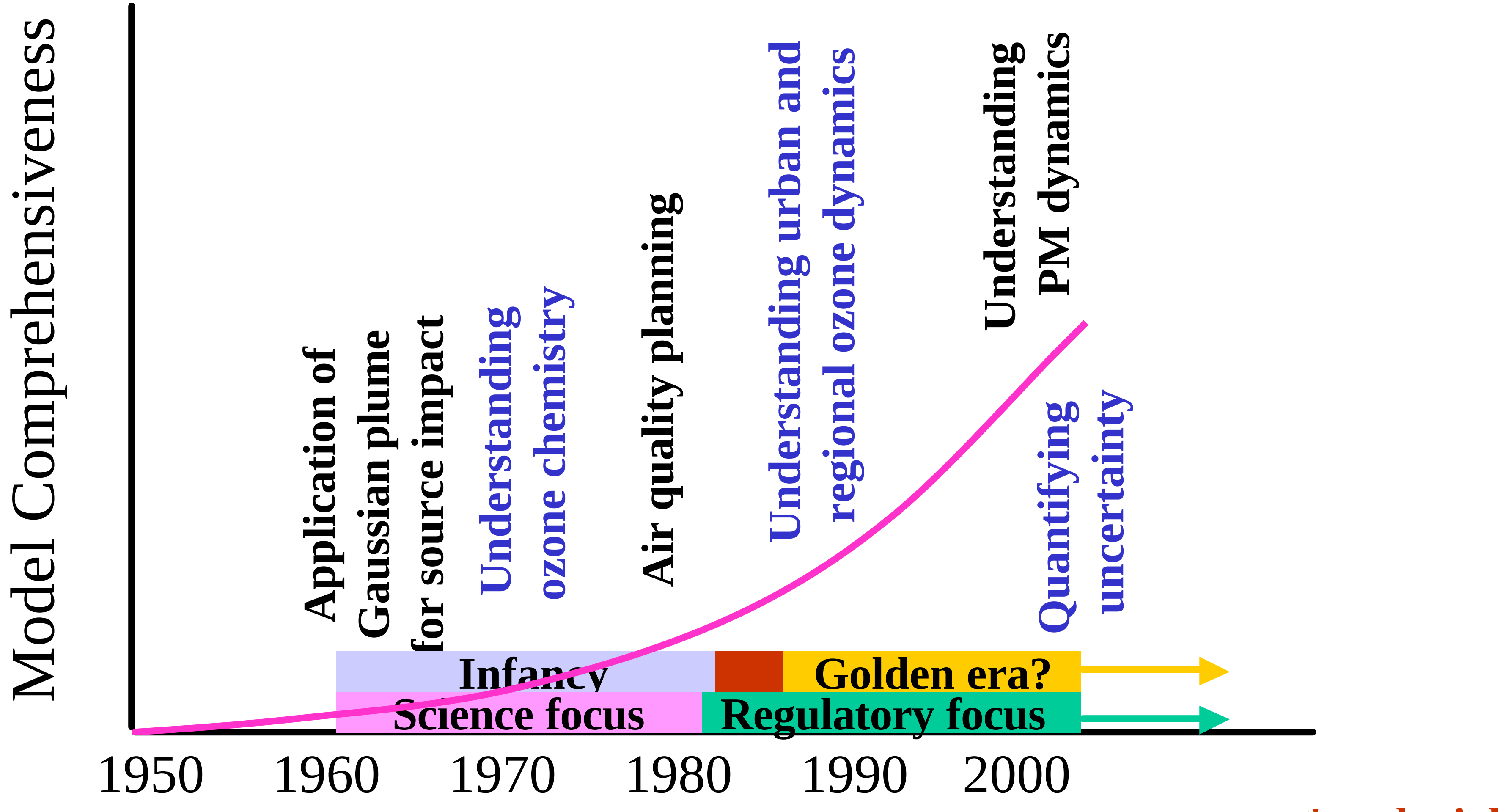
Air Quality Model



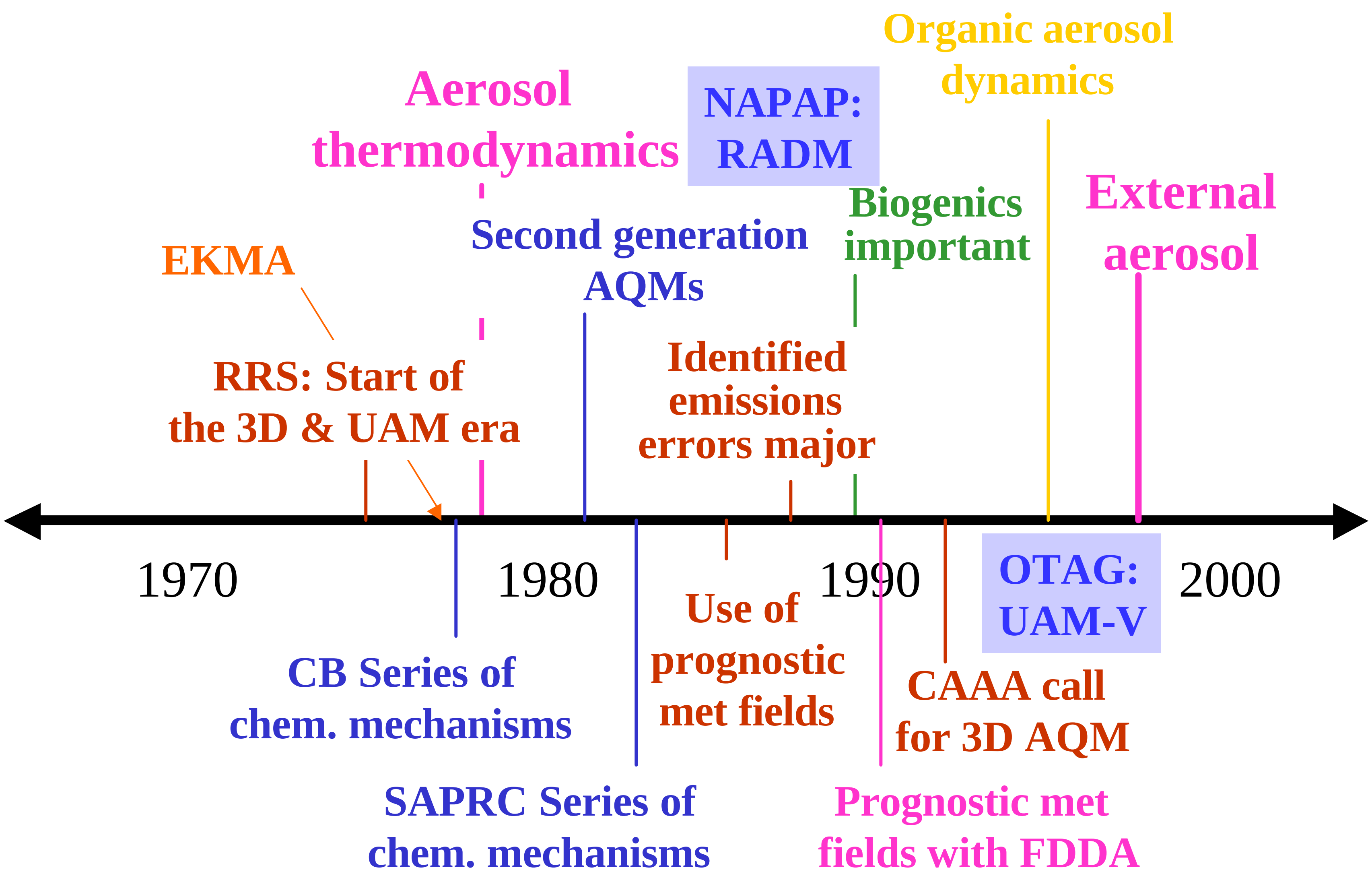
Evolution in Air Quality Model Development



Evolution in Air Quality Model Application



Important Milestones



How Good Are They?

- All evidence suggests that they describe the processes most affecting the evolution of ozone and (if equipped) particulate matter (o.k., many components of PM) after pollutant emission
- Current limitations
  - Input errors
    - Emissions
    - Meteorology
  - Monitoring data
    - Sparse, ground level
      - Don't effectively use upper-air data
  - Model components / formulation / design

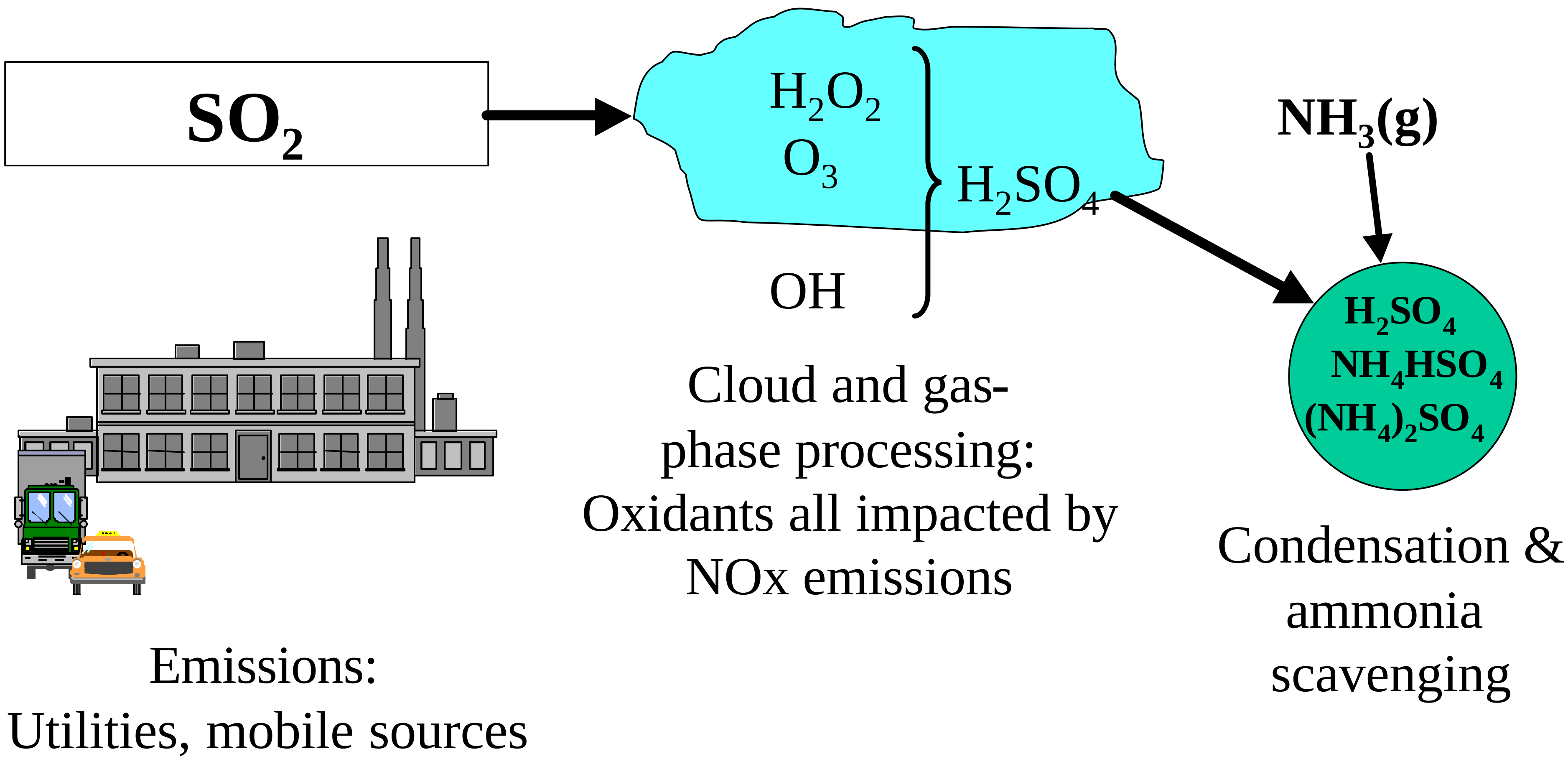
Particulate Matter Dynamics

- Particulates are exceptionally complex
  - Complete description must include size and chemical composition
    - Continuous size distribution
    - Chemical composition varies continuously with size
    - Phase conversion important
  - PM function concentration function is more complex:
    - $C(x,t,d_p)$: space, time and particle diameter
      - Composition may not be uniform for a given size: $C(x,t,d_p, s_i)$: s_i is source i
  - Makes ozone modeling look really easy

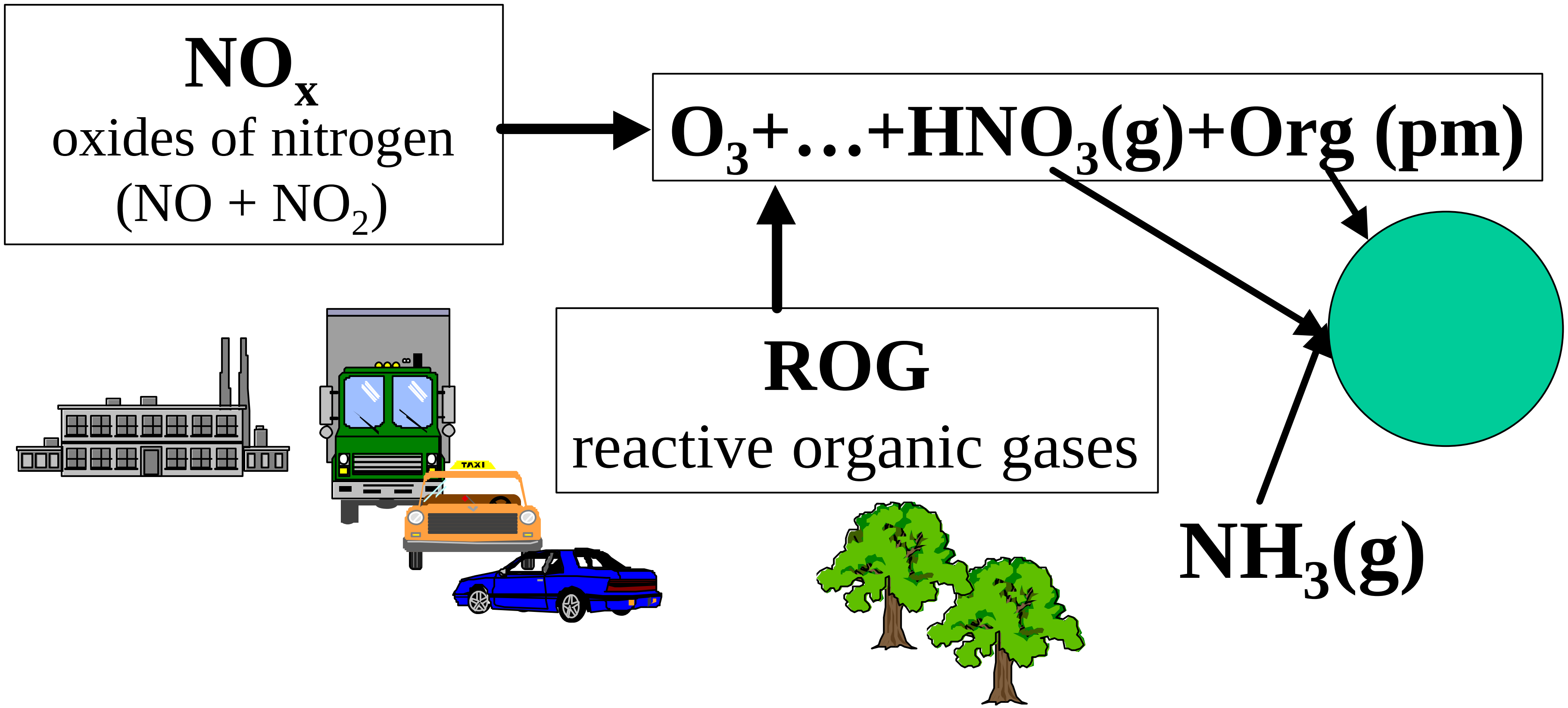
Sources of Particulate Matter

- PM has both primary and secondary components
  - Primary
    - Organic & elemental carbon (OC/EC), crustals, metals, water
    - Mobile sources, industry, utilities, dust
  - Secondary
    - Sulfate, nitrate, ammonium and organic carbon
    - Utilities, mobile sources, industry, biogenic, fertilizer, emissions control equipment

Particulate Sulfate Formation



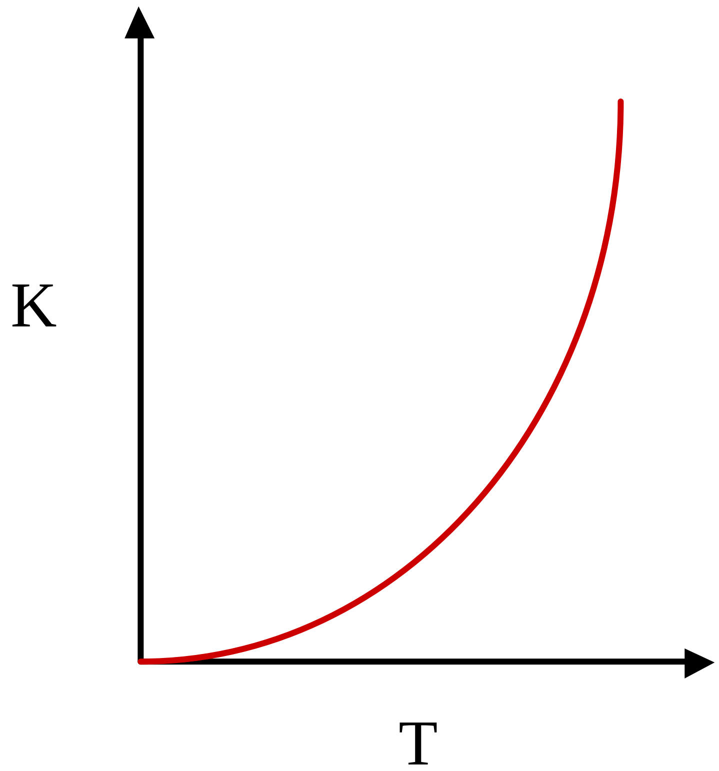
Particulate Nitrate & OC Formation



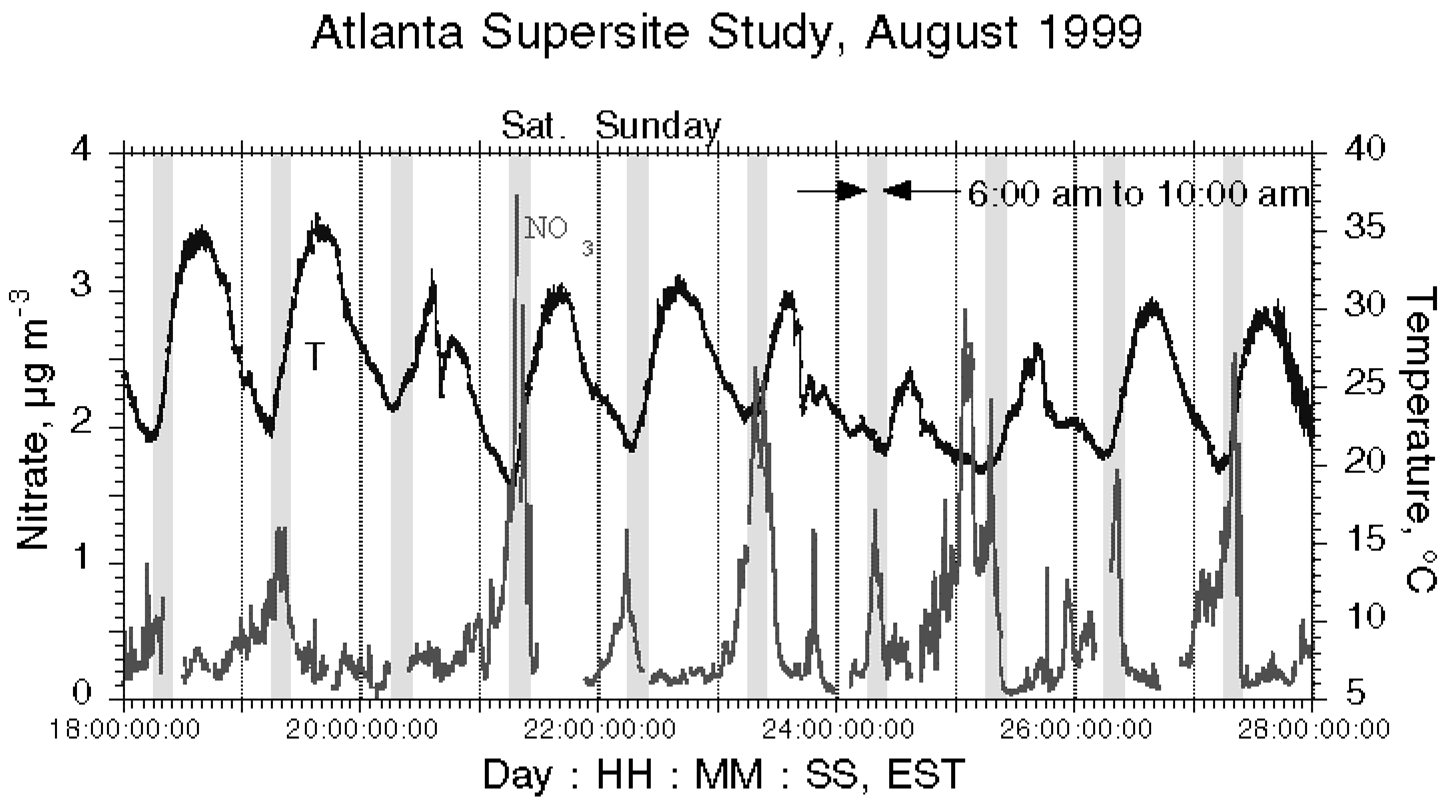
PM Nitrate Formation

- Gaseous nitric acid formed from NOx emissions
- Ammonia derived directly from emissions
- Combine via equilibrium reaction
  - Sensitive to temperature

$K=[HNO3(g)][NH3(g)]$



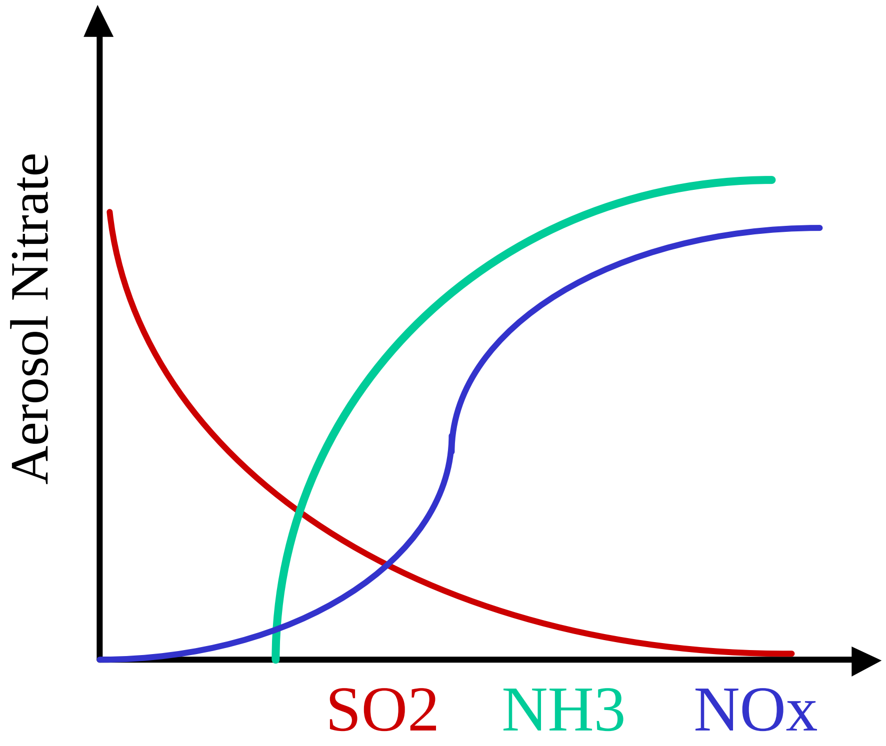
Diurnal Nitrate Pattern



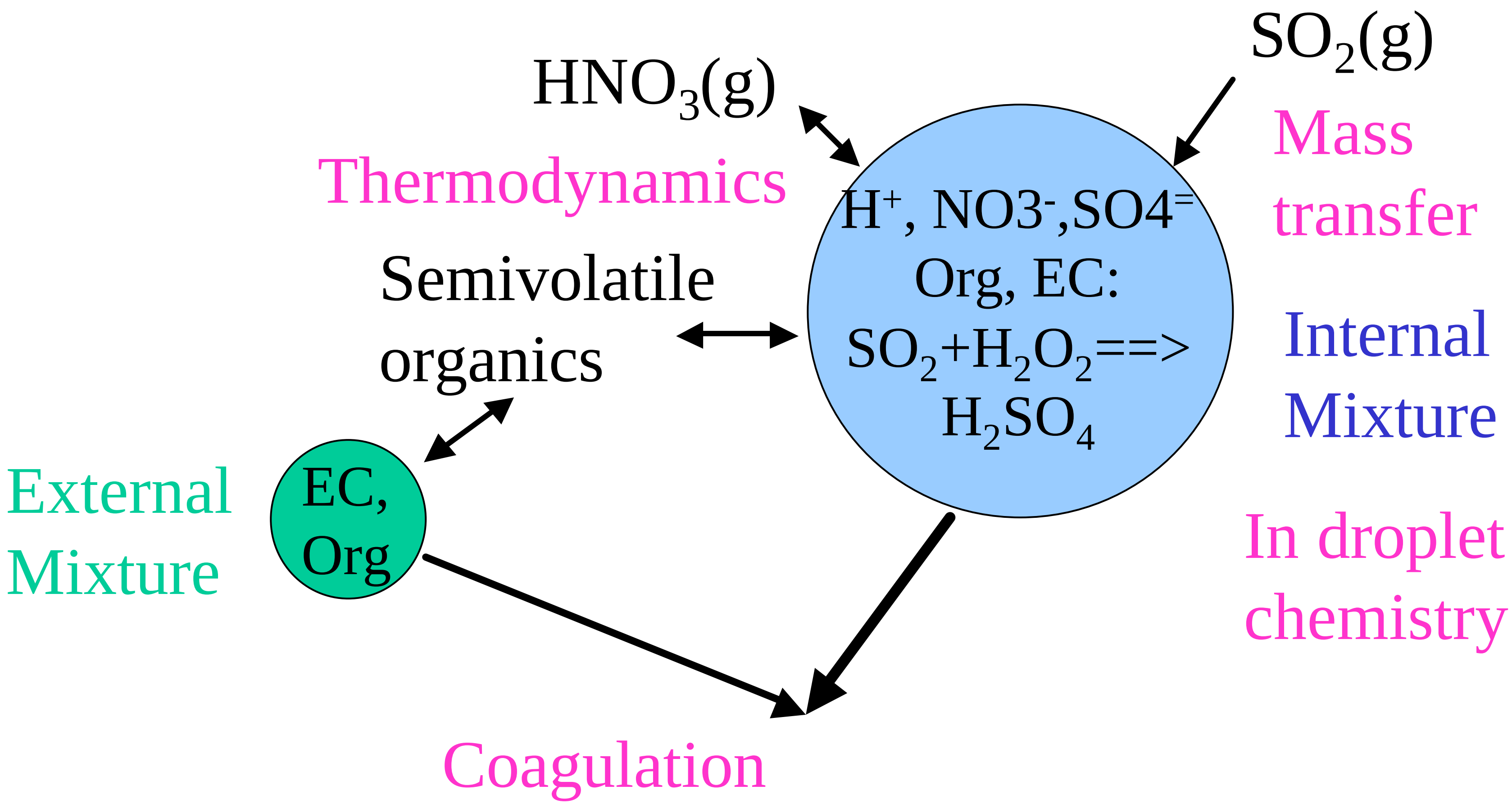
Source: R. Weber

PM Nitrate Formation

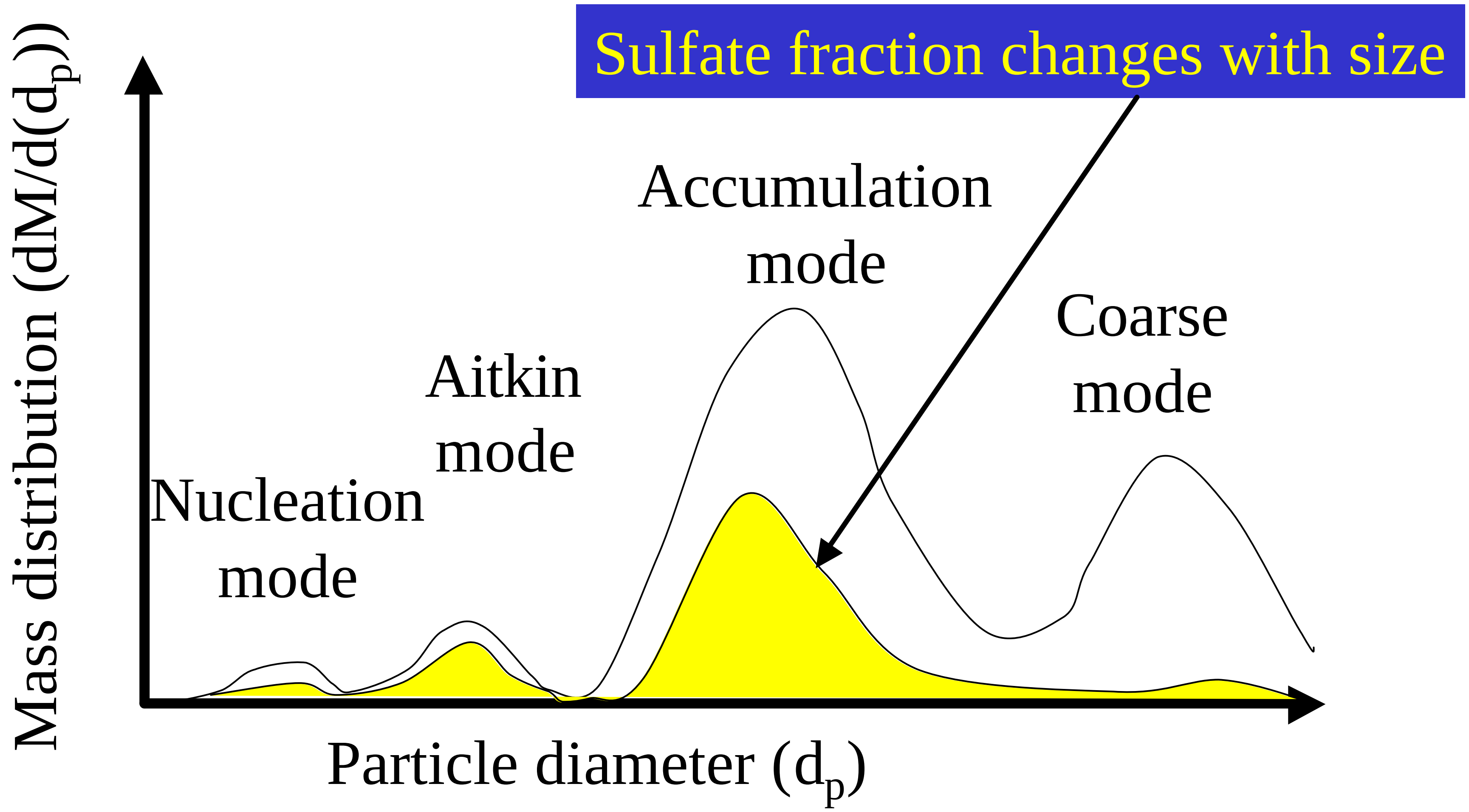
- Nitric acid reacts with (free) ammonia
  - As ammonia emissions increase, nitrate will increase until gas phase nitric acid depleted
  - Sulfate reduces free ammonia/increases acidity, reducing nitrate formation
- Reducing NOx will decrease HNO3 formation, but may not decrease PM nitrate much



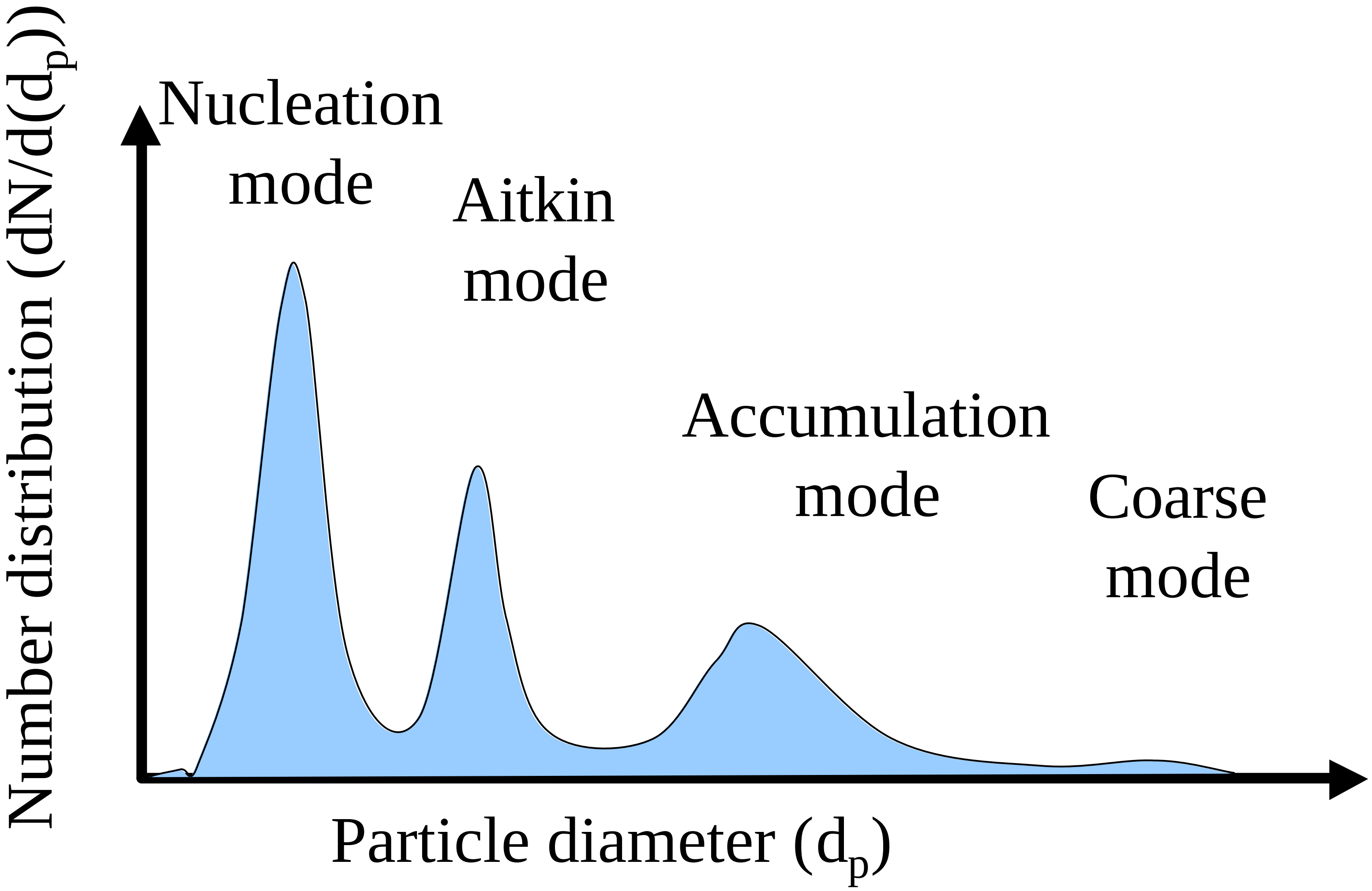
Particulate Matter Dynamics



Particle size distribution



Particle number distribution



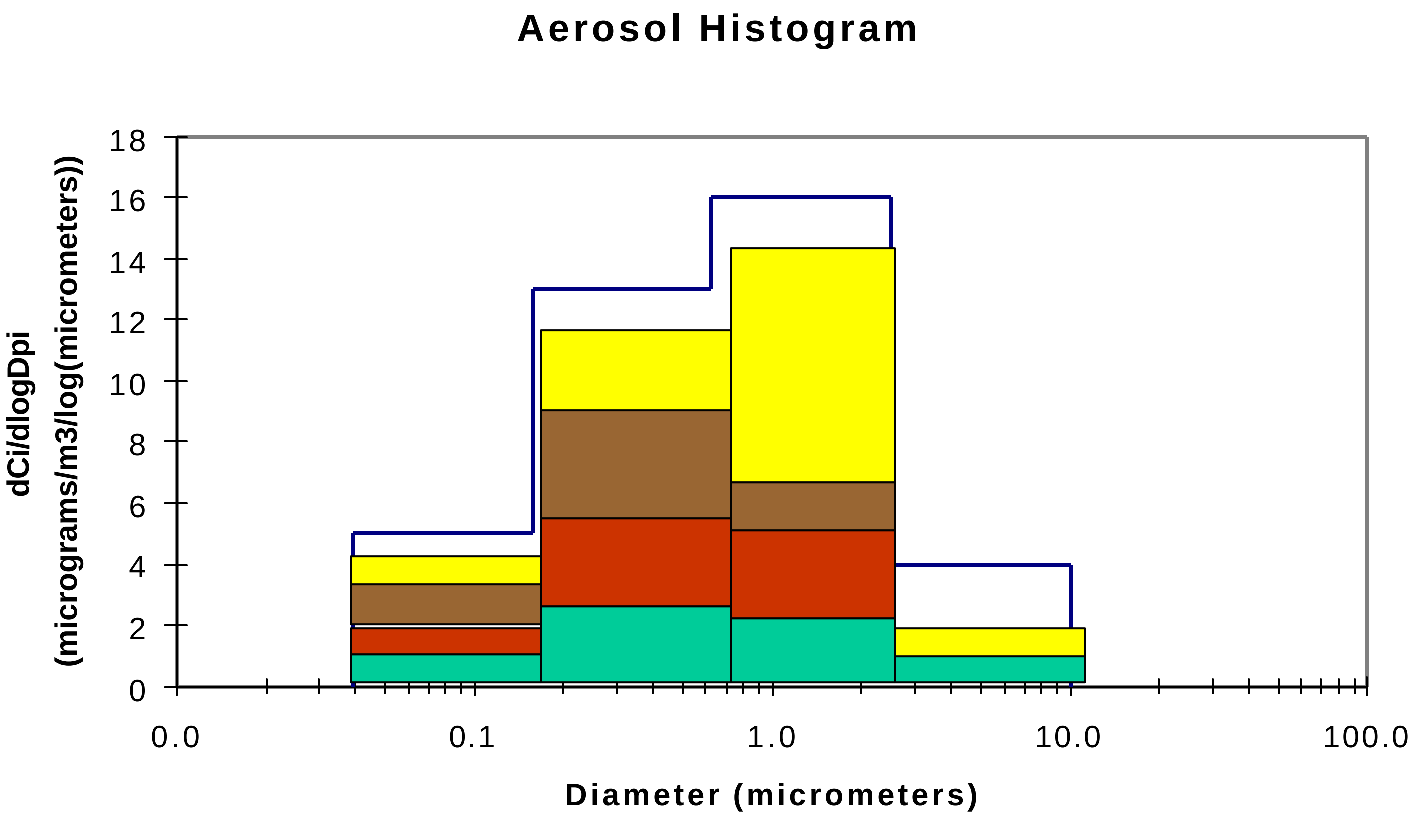
Particulate Matter Modeling Approaches

- Size distribution
  - None
  - Sectional
  - Modal
- Gas-to-particle conversion
  - Inorganic
  - Organic
- Aerosol particle description
  - Internal mixture
  - External mixture

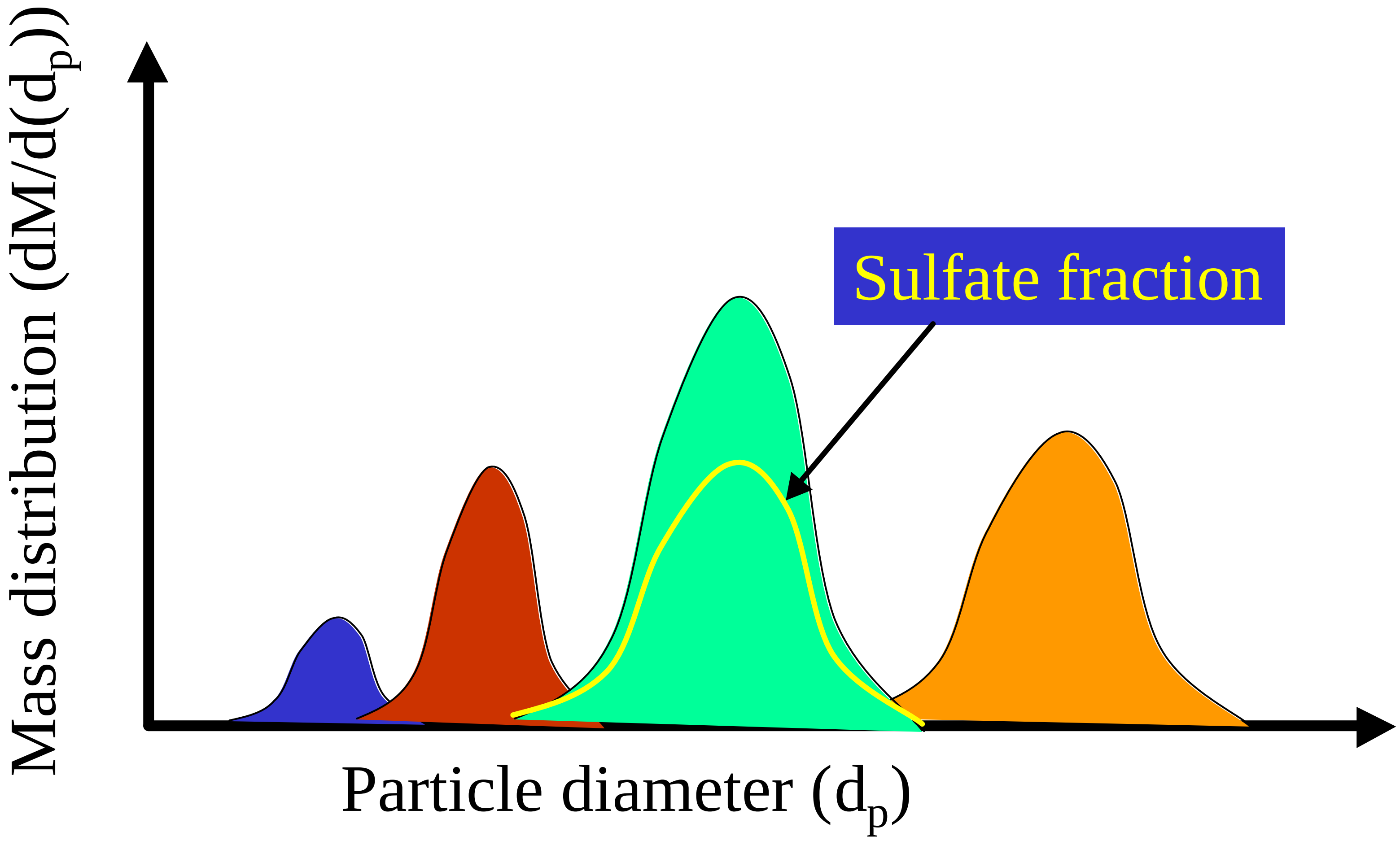
Size Distribution

- No description
  - All PM is together: no information on size or composition as a function of size
- Sectional
  - Size distribution made up of a user defined number of bins
    - Can have many bins (>20) or few (4)
    - Describes compositional changes as a function of size
- Modal
  - Size distribution made up of 2-4 "modes" corresponding to modes in size distribution
  - Mode shaped like log-normal profiles

Sectional Approach



Modal Approach



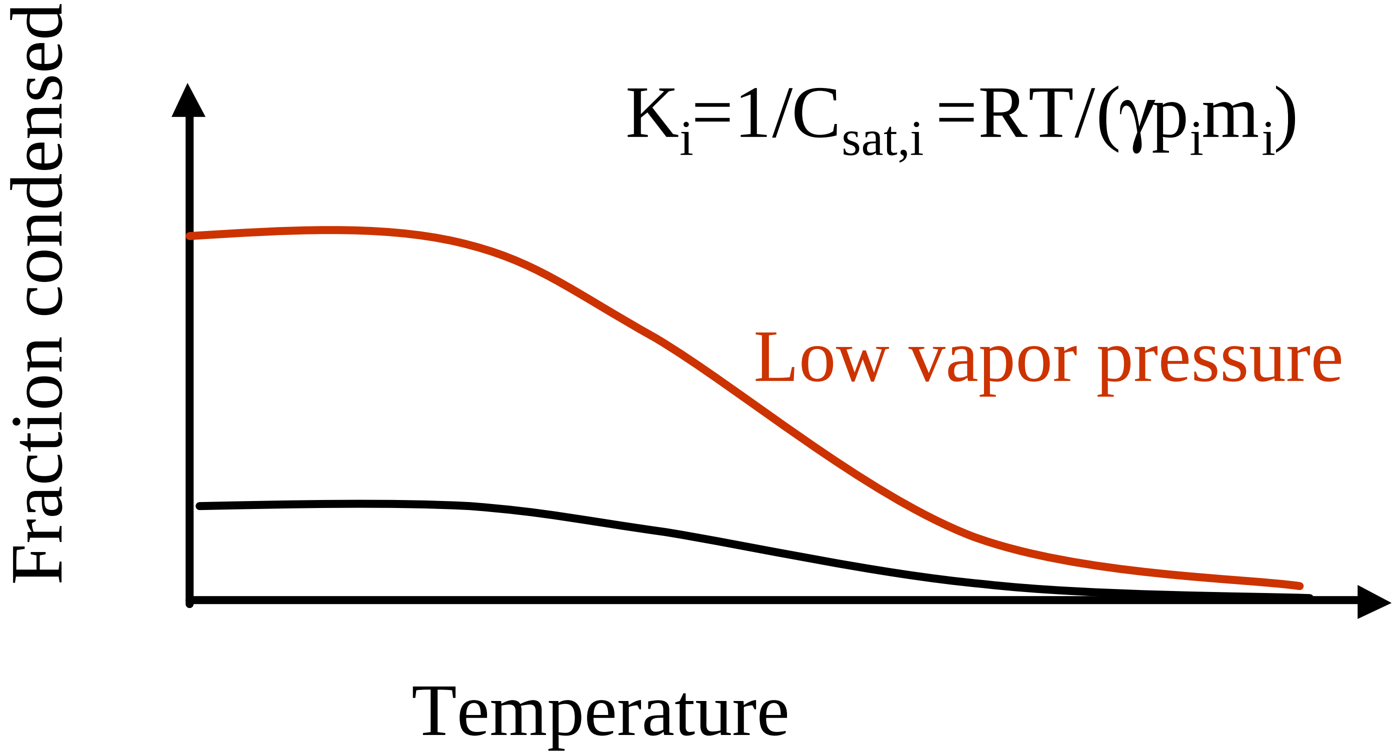
Gas-to-Particle Conversion

- Gas phase species can condense upon, and volatilize from, particulate matter
  - Inorganics
    - Thermodynamic equilibrium usually assumed
      - ISORROPIA
      - AIM
  - Organics
    - Semivolatiles and low-vapor pressure organics
    - One and two-step approach
      - One step: gas phase chemistry leads to condensable species which goes to particulate phase
      - Two step: gas phase chemistry leads to semivolatile product that partitions between gas and condense phases

Organic Partitioning Coefficient

$$\text{Yield}=M_0[\alpha K_i/(1+K_iM_0)]$$

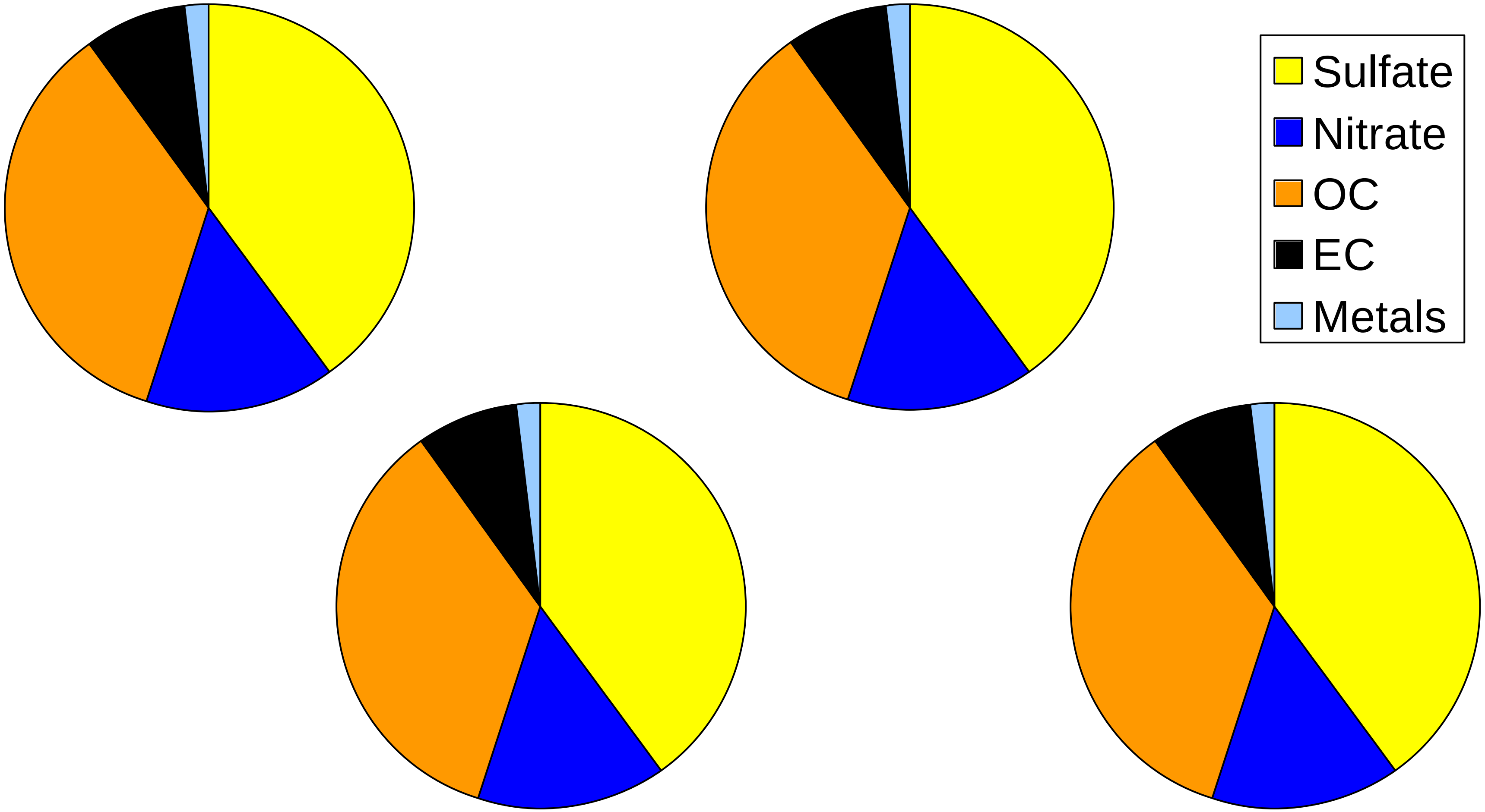
$$K_i=1/C_{sat,i}=RT/(\gamma p_i m_i)$$



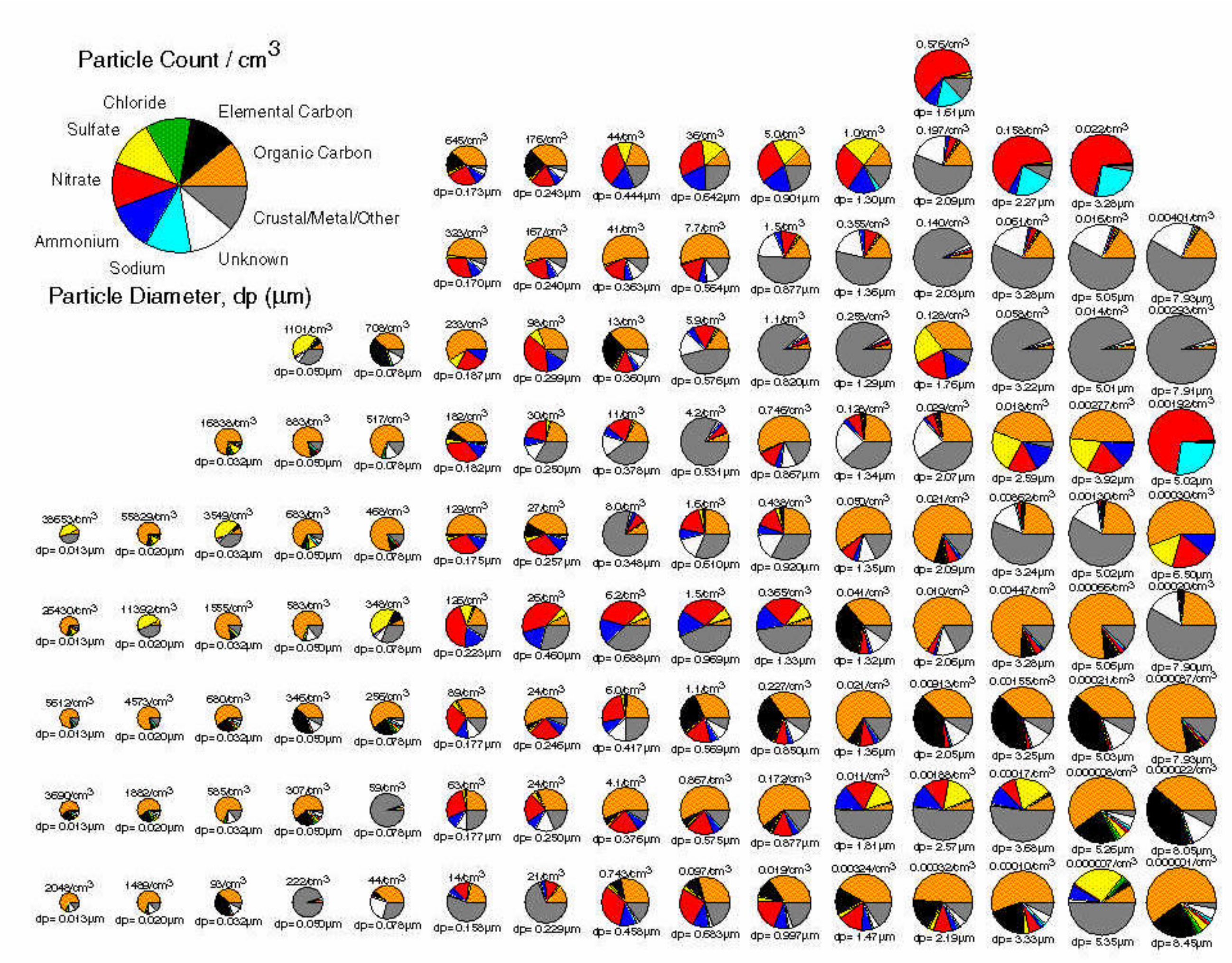
Internal vs.External Mixtures

- Particle composition can be very inhomogenous even in the same size distribution
  - Traditional approaches assume homogenous mixture in each size range / bin: $C(x,t,d_p)$:
    - "Internal mixture"
    - See prior slides
  - Theory and evidence suggests that particle composition varies within a size range
    - Source-based differences: $C(x,t,d_p, s_i)$

Internal Mixture



External Aerosol Modeling

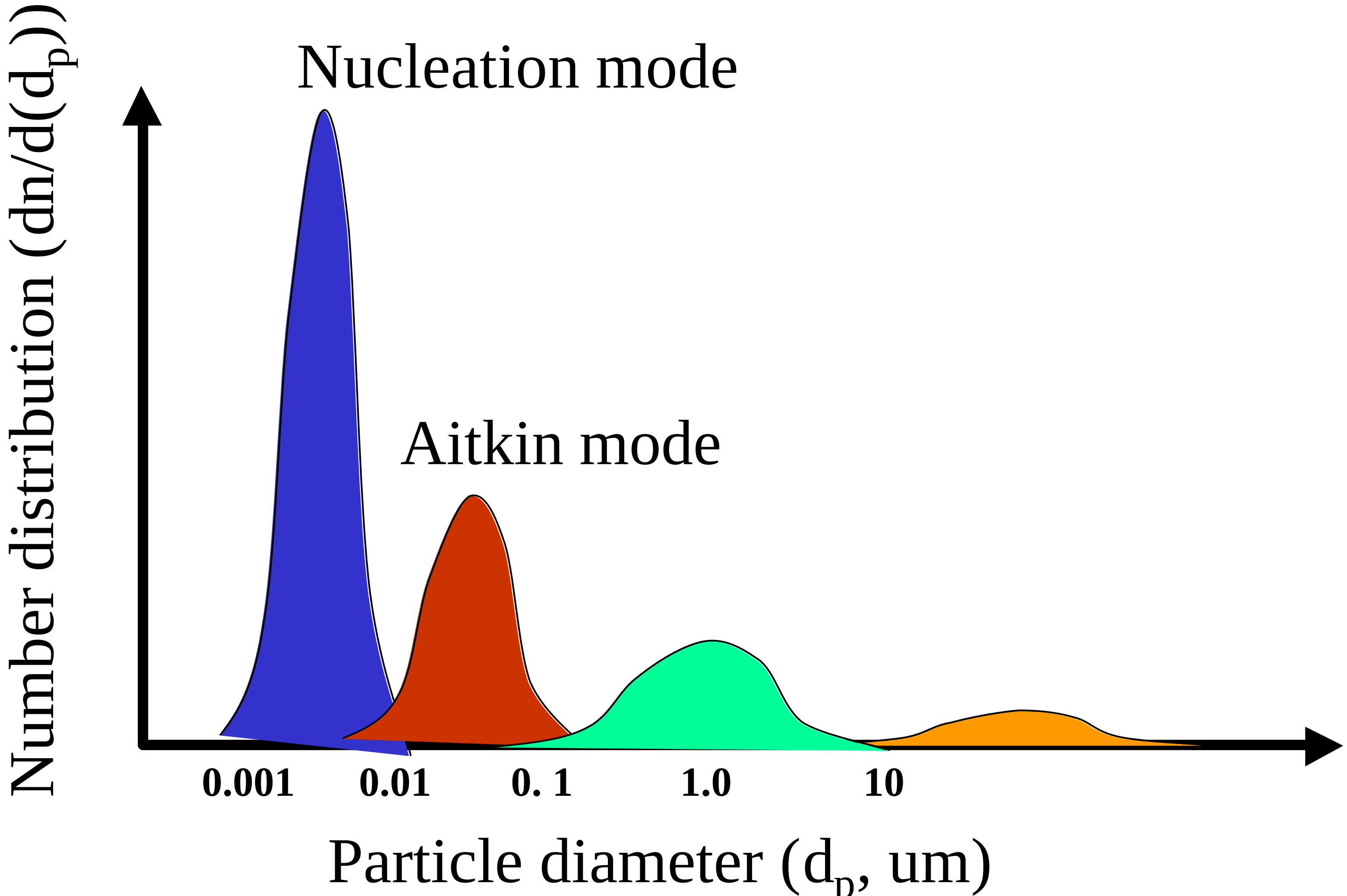


From Kleeman, Cass and Eldering, 1997

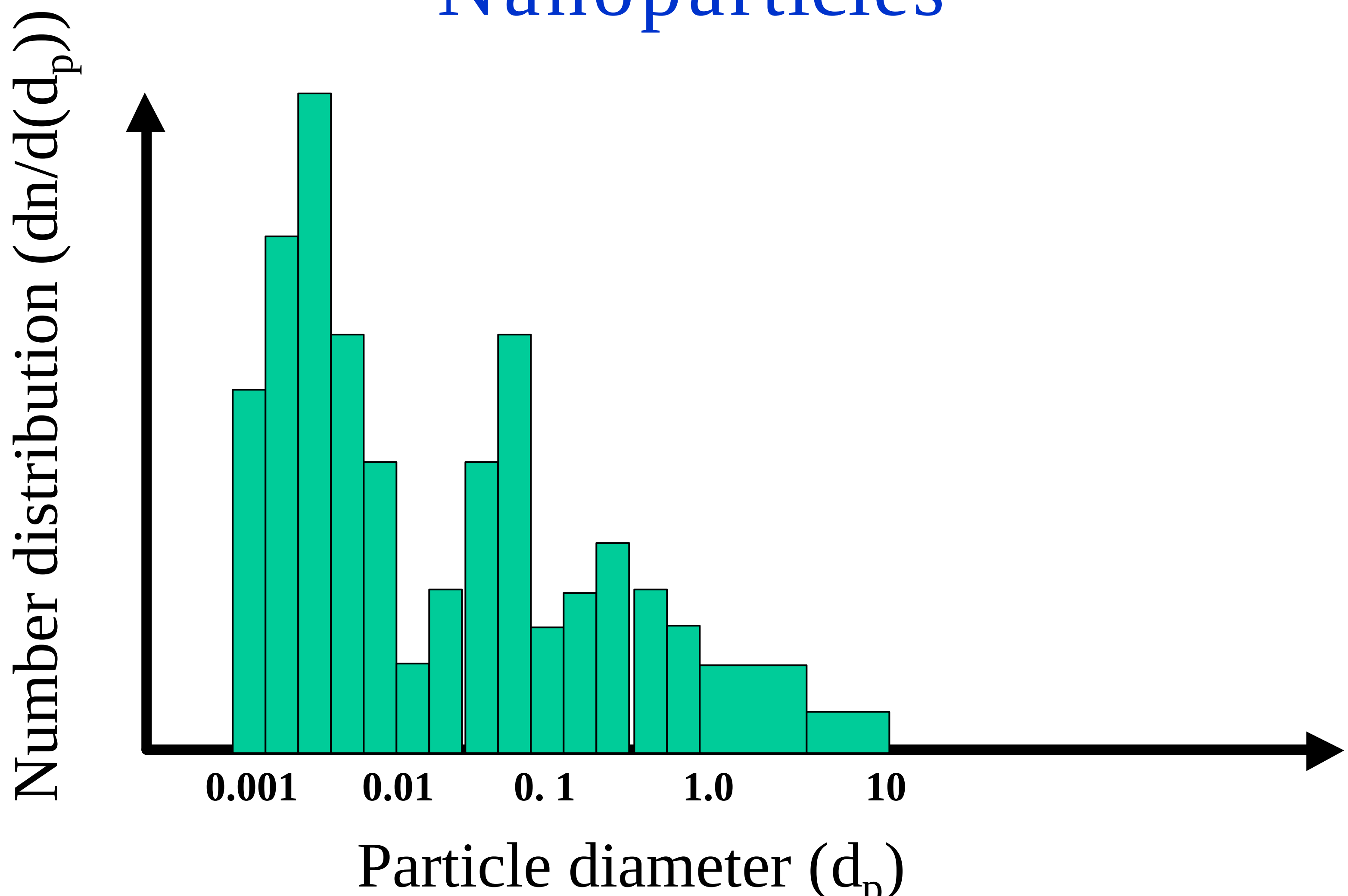
Nanoparticle Modeling

- Nanoparticles represent an important fraction, in terms of total number but not total mass, of PM, and are unique
  - Very short lifetimes
  - Directly emitted or, possibly, due to nucleation in short term events
- Models have not dealt so much with nanoparticles because of their short lifetimes and small fraction of the mass
- Three approaches for modeling:
  - Sectional
    - Can add multiple sections in the nano-modes
  - Modal
    - Adding a new nucleation mode in addition to Aitkin mode
  - External, source oriented approach

Modal Approach to Nanoparticles



Sectional Approach for Nanoparticles



Strengths and Weaknesses

- Modal
  - Strengths
    - Computationally efficient
  - Weaknesses
    - Lack of detailed information (all nano-particles similar)
- Sectional
  - Strength: Tremendous capacity for detail, very flexible
  - Weakness: Computationally time consuming
- External mixture
  - Strengths: Tremendous detail, particles tied directly to sources
  - Weakness: Computationally expensive
- All
  - **Nucleation theory is highly uncertain**
    - Not a major factor if particles are primary in origin

Particulate Matter Sensitivity Analysis and Source Attribution

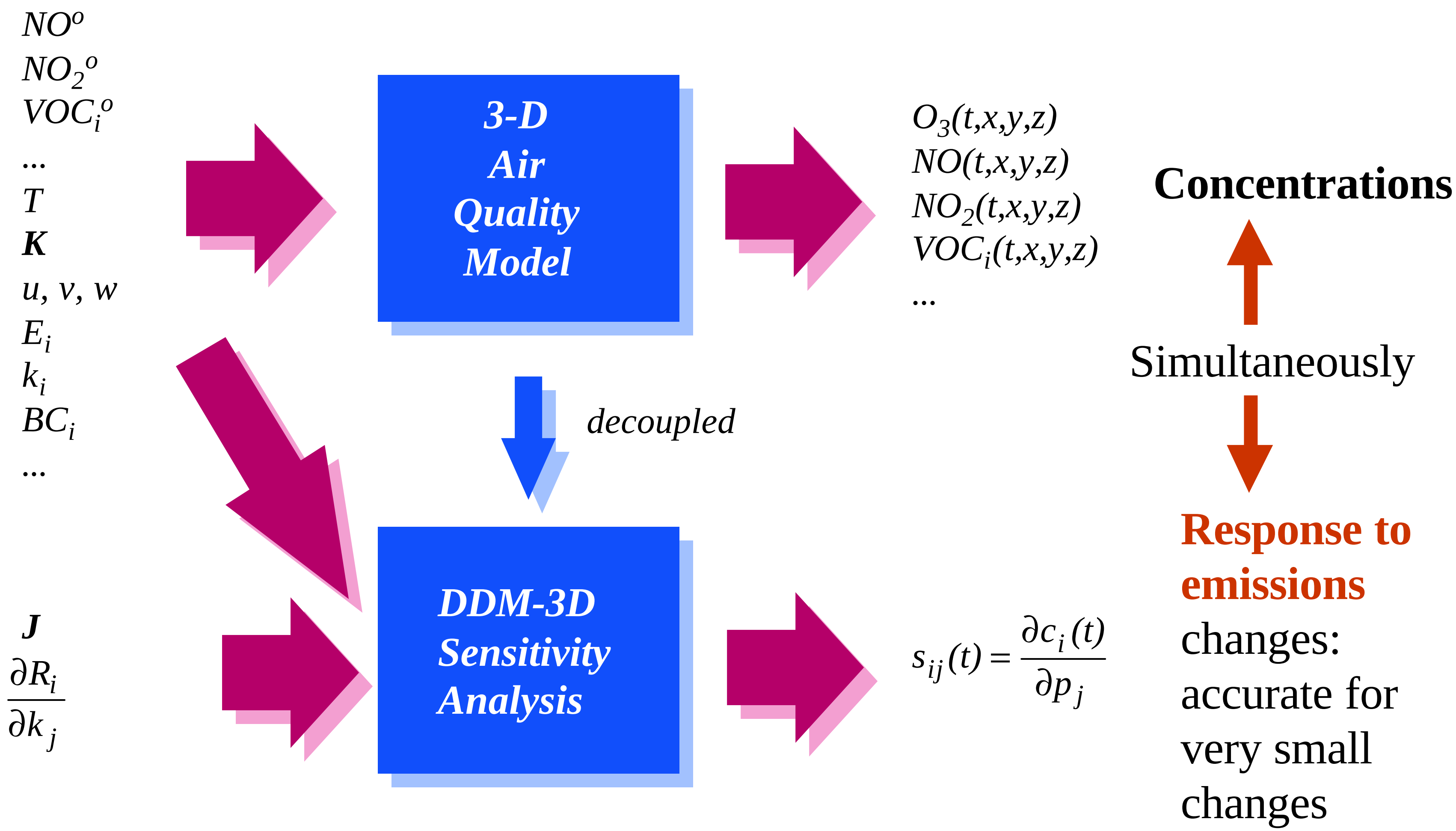
- AQM's major function is to link source emissions to air quality: Source attribution
  - Individual vs. regional/category analysis
    - Assessing impact of individual sources difficult
      - Small perturbation to noisy process
      - Small difference between two large numbers
        - » e.g.: 10 Ton/day source in a 1000 ton/day area

(10 ton/day/1000 ton/day)*0.1(% change in O3/%change in NOx)*120 ppb=0.12 ppb

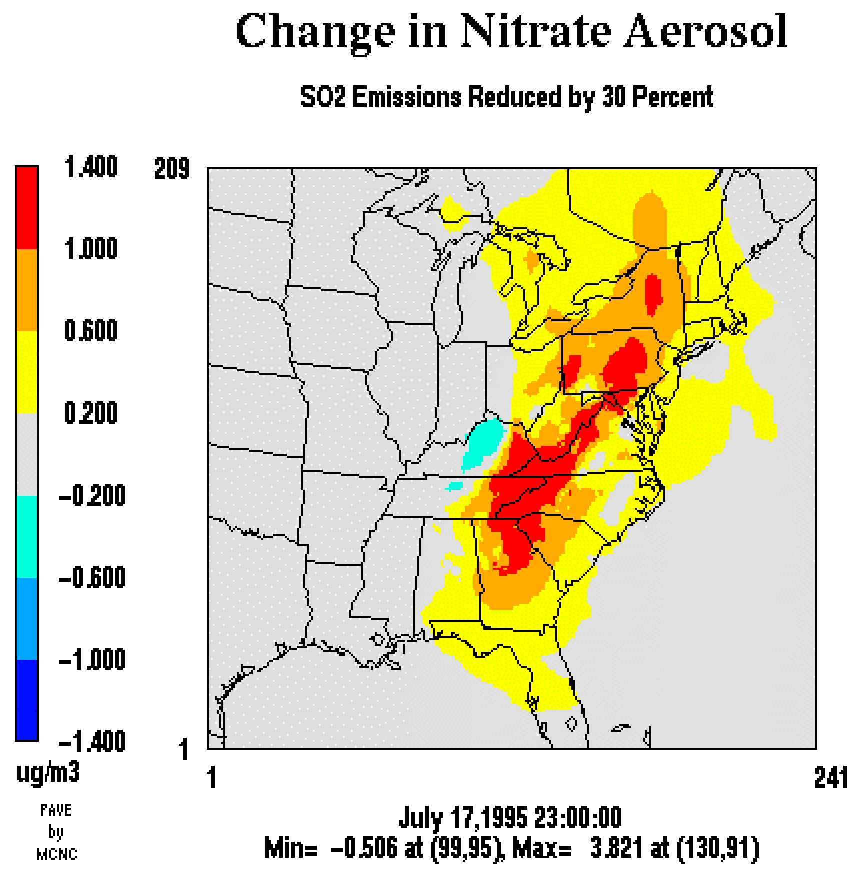
Can a model "see" this accurately?

    - Assessing categories/regions/complete strategies more appropriate for typical approach if reductions are reasonable
      - Unrealistic changes to minimize noise raises additional issues
    - New approach: direct sensitivity analysis

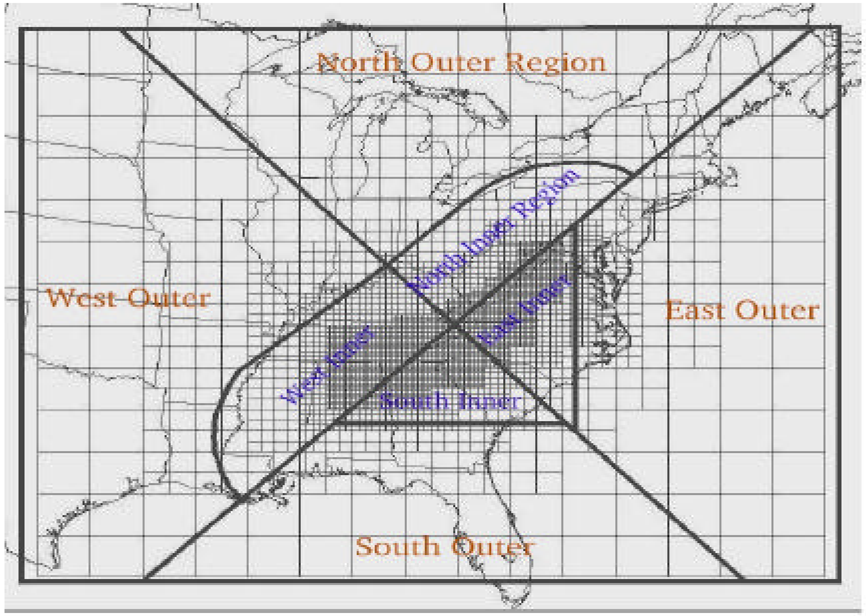
Source Attribution using Direct Sensitivity Analysis



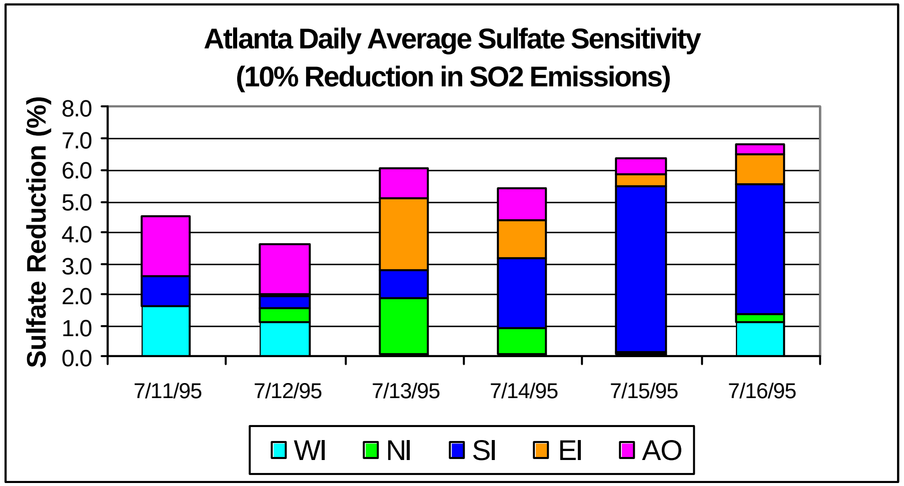
Response of Fine Nitrate to SO2 reductions



Source Attribution: Sulfate by Source Region



Direct Sensitivity Analysis



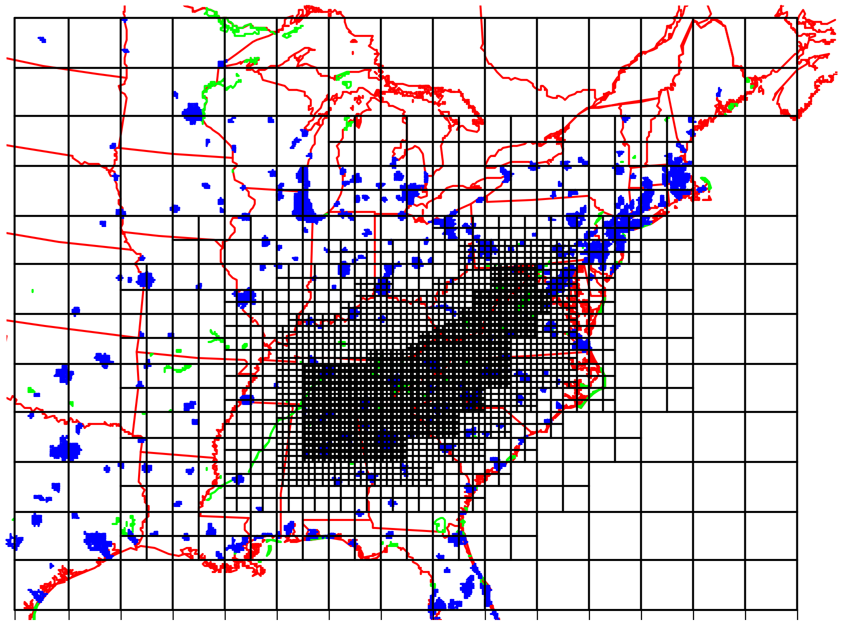
Particulate Matter Modeling and Chemical Mechanisms

- Current generation of gas-phase mechanisms (e.g., SAPRC99+, RACM) in pretty good shape for ozone
  - Flexible
  - Evolutionary
  - Appear to adequately describe gas phase kinetics for ozone, etc
  - **Limited information for determining organic composition of PM**
    - Important information for identifying sources and impacts lost
- Aqueous phase mechanisms
  - Likely adequate for inorganics and ozone
  - Questions about organic oxidation

PM Modeling State of the Science: Where are We?

- Ozone models are "mature"
- PM Models still evolving
- "One atmosphere"/"3rd generation" urban-to-regional models are at the forefront
  - Combined gas/aerosol/deposition & nested/multiscale
  - Some built in diagnostic features
    - Sensitivity analysis

Regional Multiscale Model



Attributes of Advanced Models: Internal Mixture Models

- Usual attributes of advanced internal mixture models
  - Advanced chemical mechanism
  - Sectional or modal approach
  - Thermodynamic inorganic
  - One-step organic formation
    - Two step on the way, but large uncertainties
  - Advanced diagnostic features
  - Examples: URM, CMAQ, CIT-AERO, UAM-AERO
    - URM extensively evaluated over eastern US as part of SAMI
    - CMAQ is to become the community model

Attributes of Advanced Models: External Mixture Models

- Features
  - Limited applications to date
  - Very time and resource consuming
  - AIM thermodynamics/growth
  - Trajectory and grid-based versions of CIT model
    - See Cass, Kleeman and co-workers
  - Expect wider application in next 10 years

Example Model Application: SAMI

- Southern Appalachians Mountains Initiative (SAMI)
  - Stakeholder process to develop regional strategy to deal with:
    - Ozone (Sum06), PM, haze, acid deposition
    - Single model applied to suite of 5, 10 day episodes
      - Episodes chosen to represent typical year

SAMI Modeling

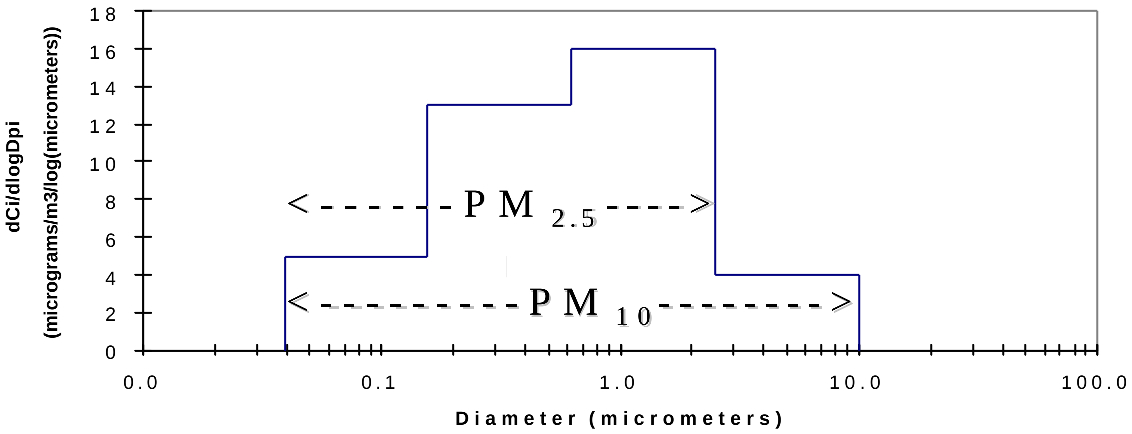
- Air Quality: URM-1ATM (Urban-to-Regional Multiscale One Atmosphere) Model
  - Horizontal cells of varying dimensions (12 - 192 km)
  - 7 vertical layers extending from surface to 12.8 km
- Meteorology: RAMS (Regional Atmospheric Modeling System)
  - temperature, air density, wind speed and direction, total solar radiation, ultraviolet radiation, mixing height, turbulent momentum diffusivity, precipitation, cloud parameters
- Emissions: EMS-95 (Emission Modeling System)
  - Gas: NO_x, VOCs, CO, NH_3, SO_2
  - Aerosols: OC, EC, Ca, Mg, K, NO_3, SO_4, “other” PM

Urban-to-Regional Multiscale One Atmosphere (URM-1ATM) Model

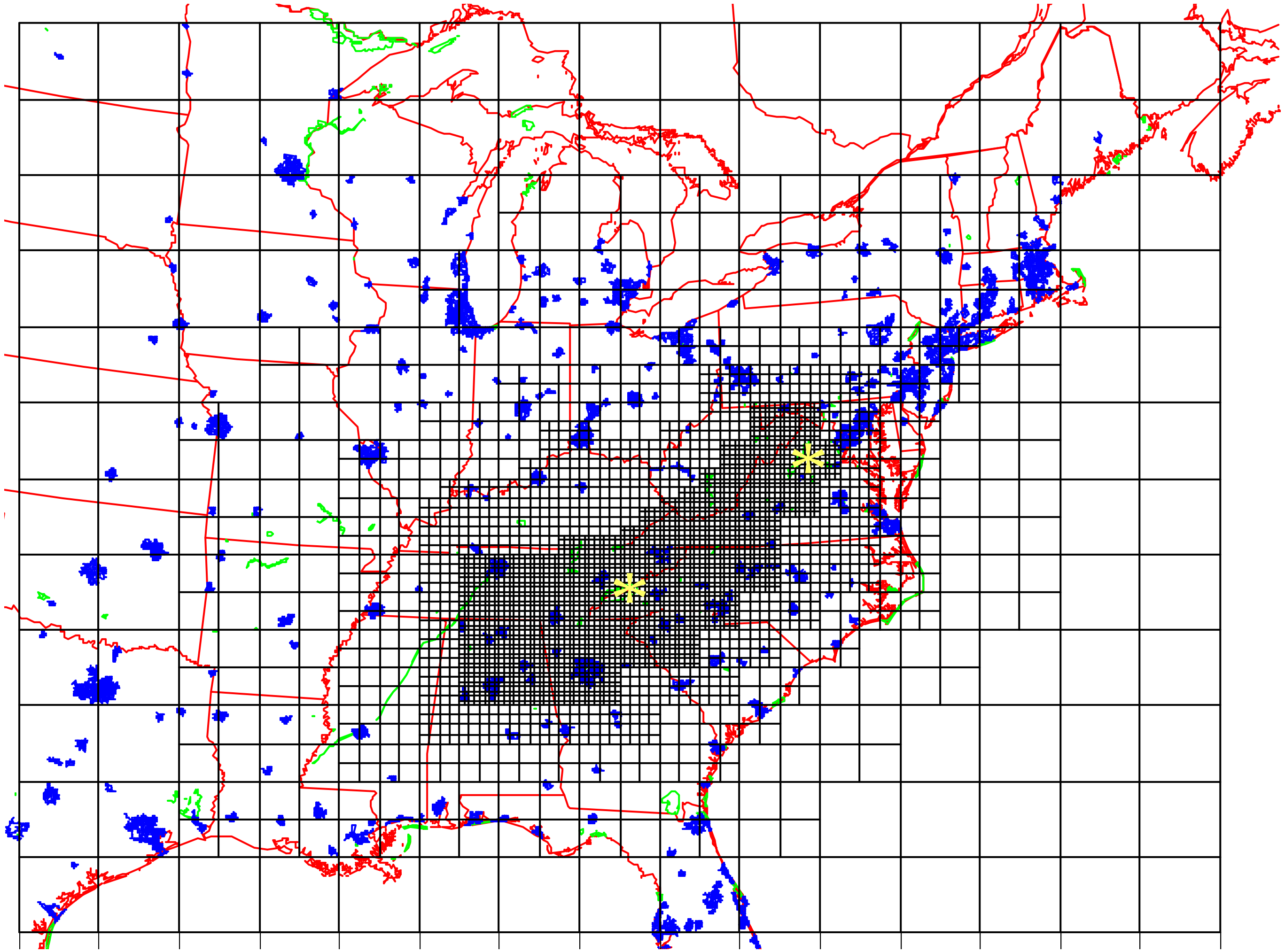
- Three-dimensional Eulerian photochemical model
  - Finite element, multiscale transport scheme (Odman & Russell, 1991)
  - Gas-phase chemistry
    - SAPRC-93 mechanism (Carter, 1994)
  - Aqueous-phase heterogeneous sulfate chemistry
  - Aerosol dynamics
    - Sectional approach (Gelbard and Seinfeld, 1980)
    - ISORROPIA thermodynamic equilibrium (Nenes, *et al.*, 1998)
    - Organic aerosol yields (Pandis, *et al.*, 1992)
  - Acid deposition
    - Wet: Reactive Scavenging Module (Berkowitz, *et al.*, 1989)
    - Dry: three-resistance approach
- "One atmosphere" modeling approach

Aerosol Module

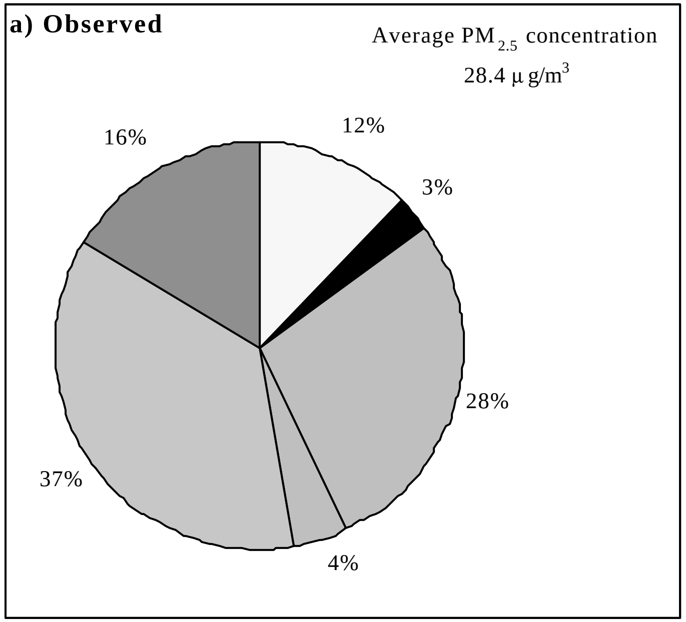
- Inorganic aerosols - ISORROPIA
  - sulfate, nitrate, ammonium, chloride, sodium, hydrogen ion
  - condensation / evaporation (thermodynamic equilibrium)
- Organic aerosols
  - experimental and estimated aerosol yields from VOC oxidation
- Inert Species
  - EC, Mg, Ca, K, other PM
- Sectional Size Distribution

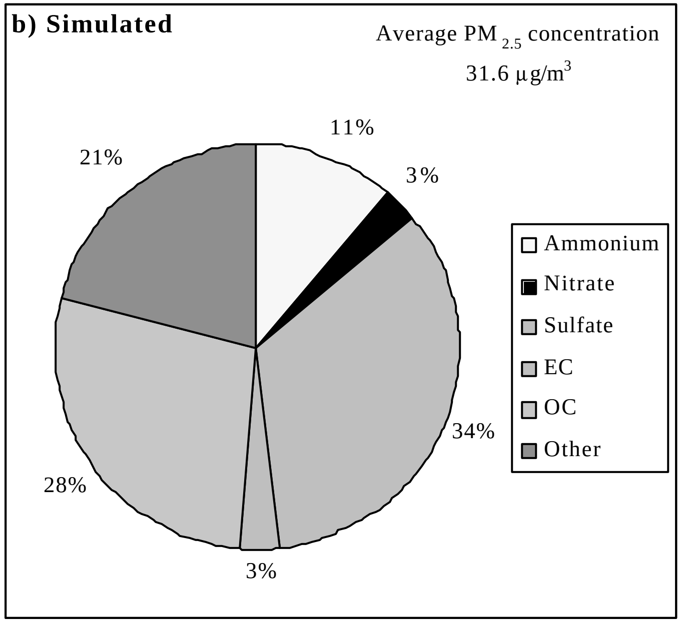


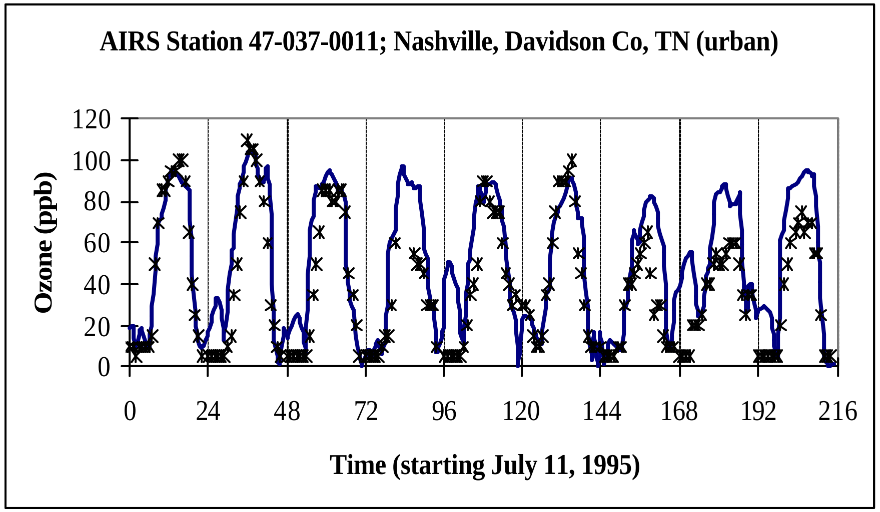
SAMI Modeling Domain and Grid

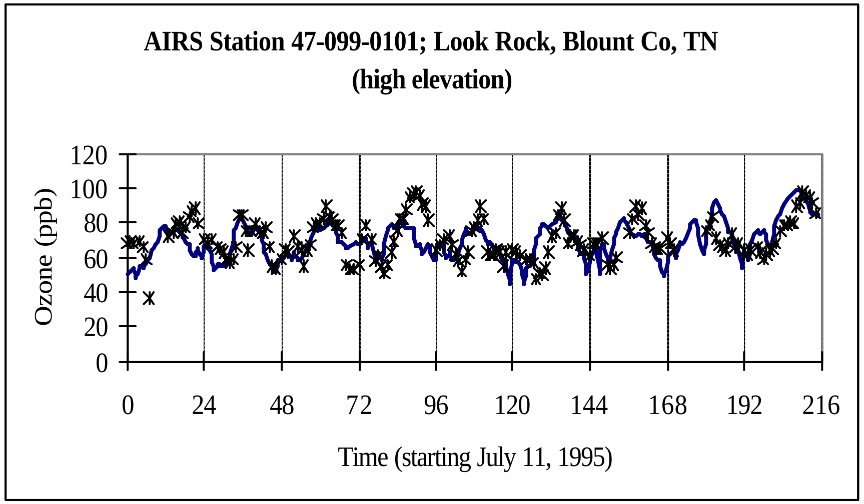


Performance

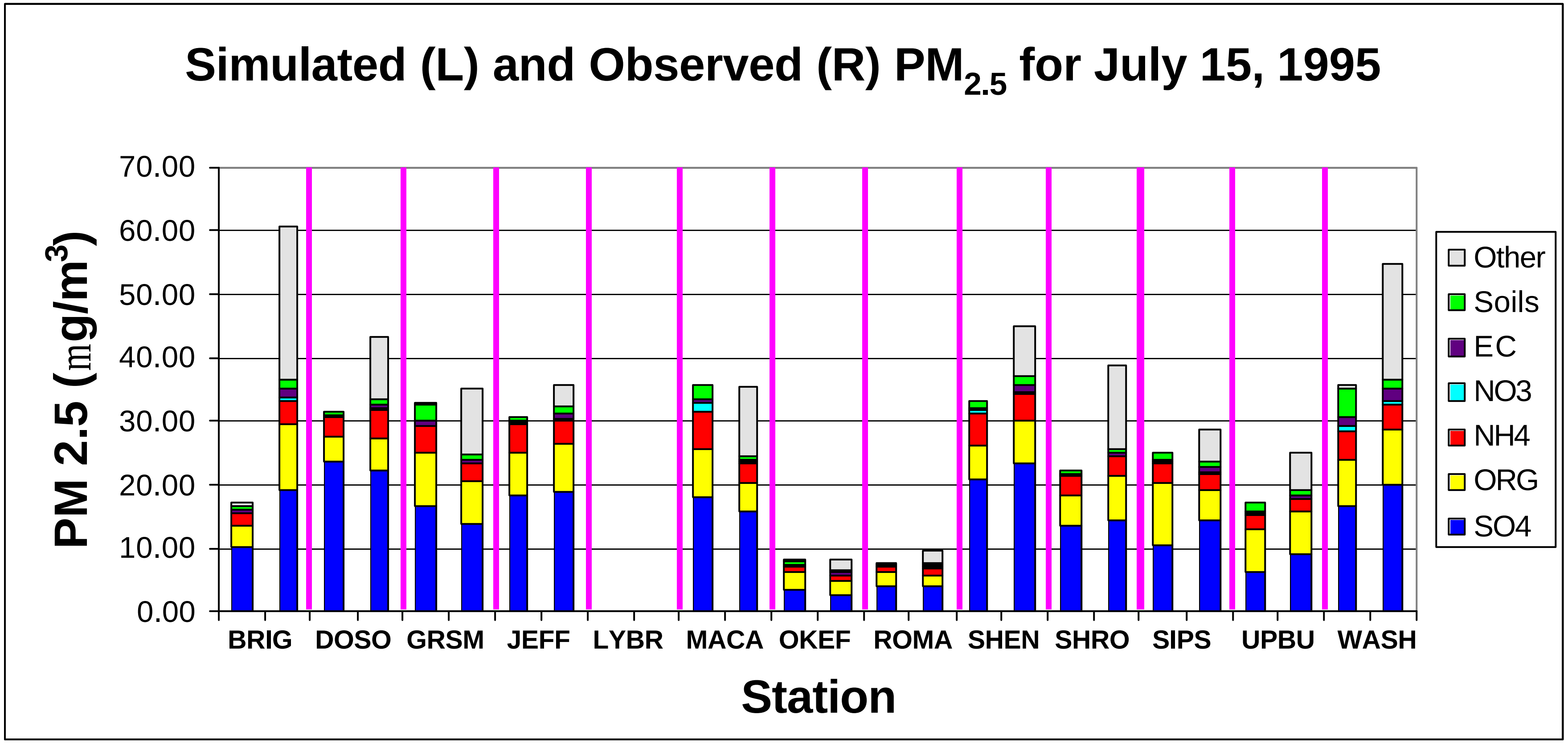








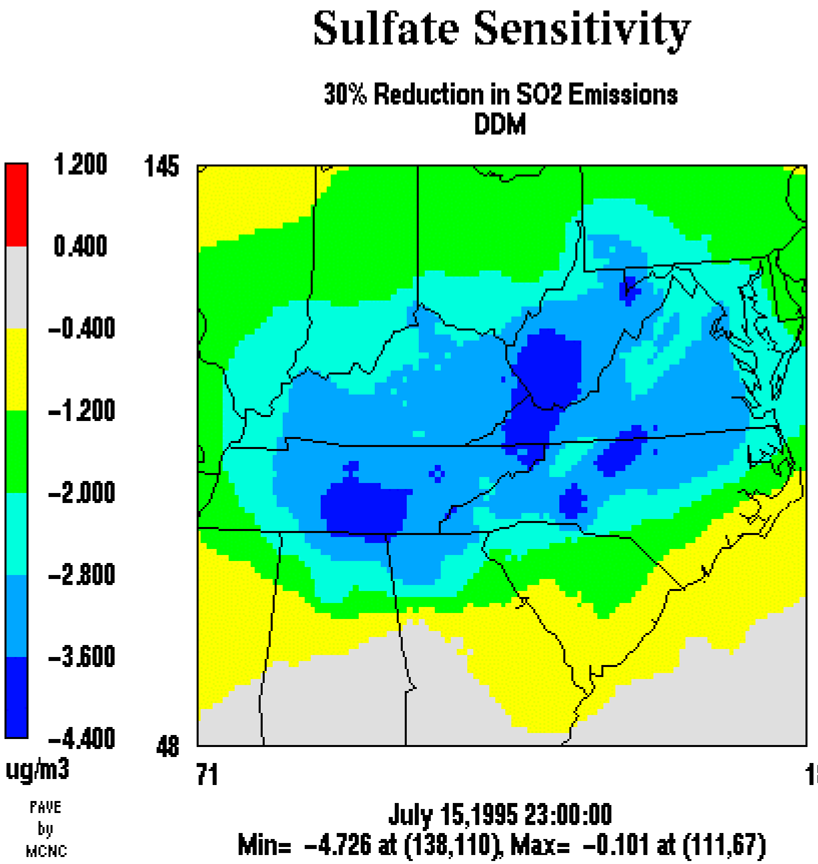
Performance on July 15, 1995

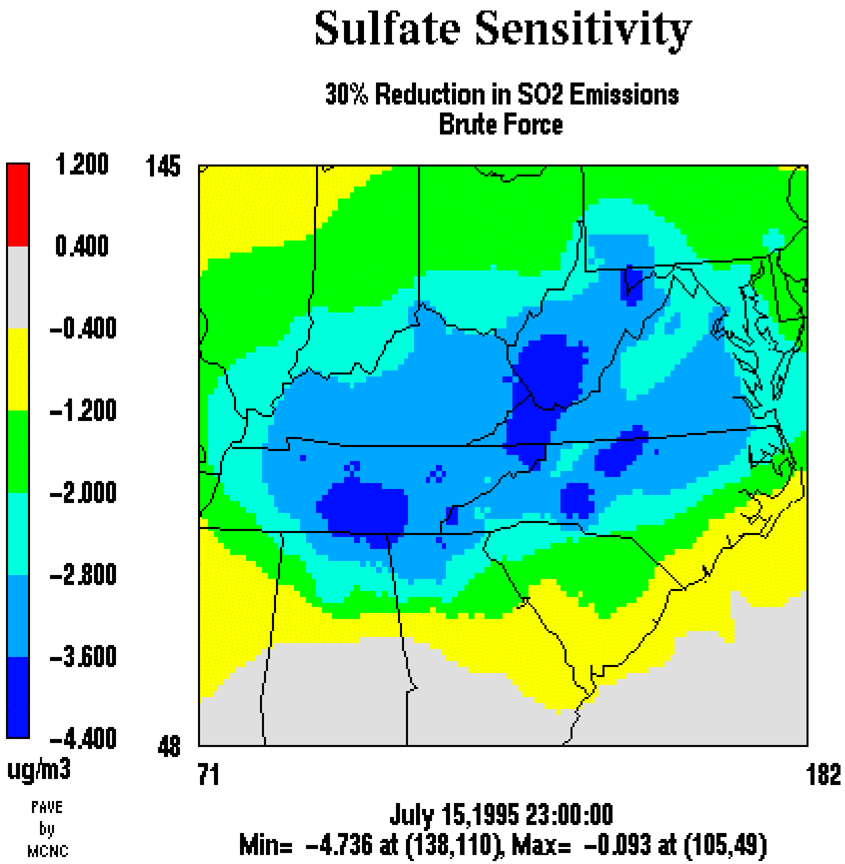


Sensitivity Analysis to Emissions

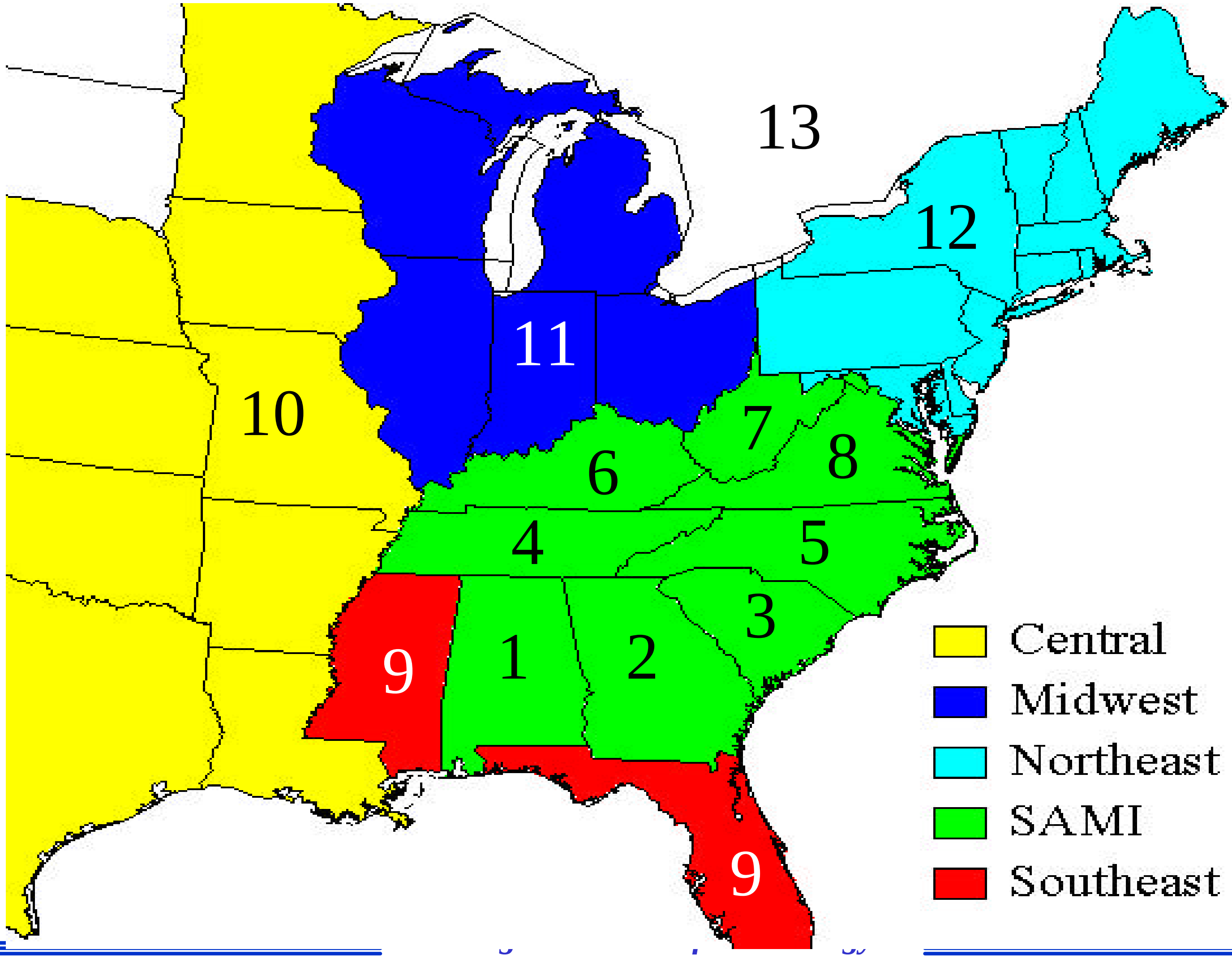
- DDM - Decoupled Direct Method: Extended to Particulate Matter
  - Use direct derivatives of governing equations
  - Perform numerous sensitivity calculations in one model run.
  - Inaccurate sensitivities may result due to non-linear response
  - Assessed response of PM to emissions
    - Regionally
    - By source region

Sulfate Sensitivity to SO_2 Emissions

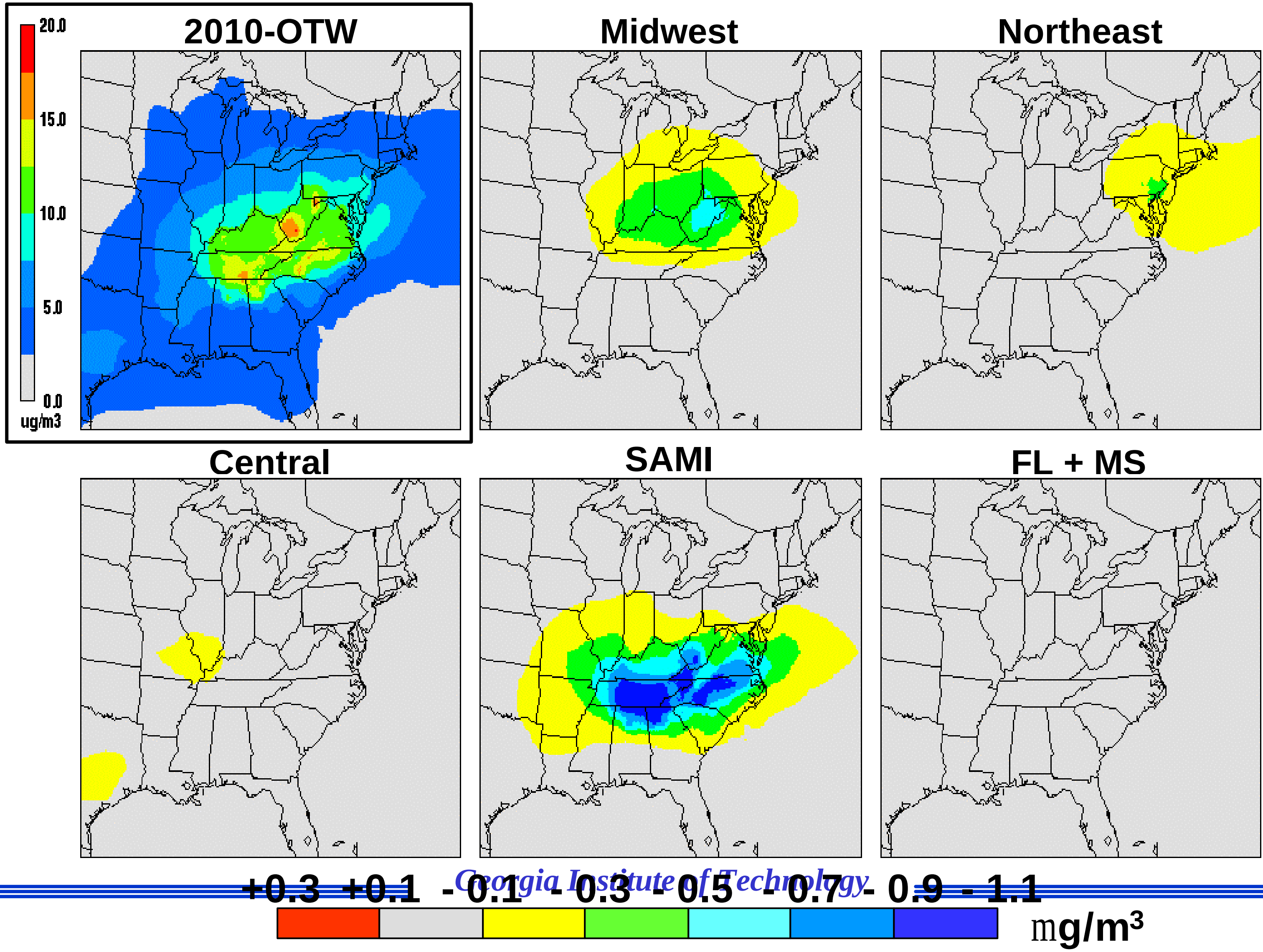




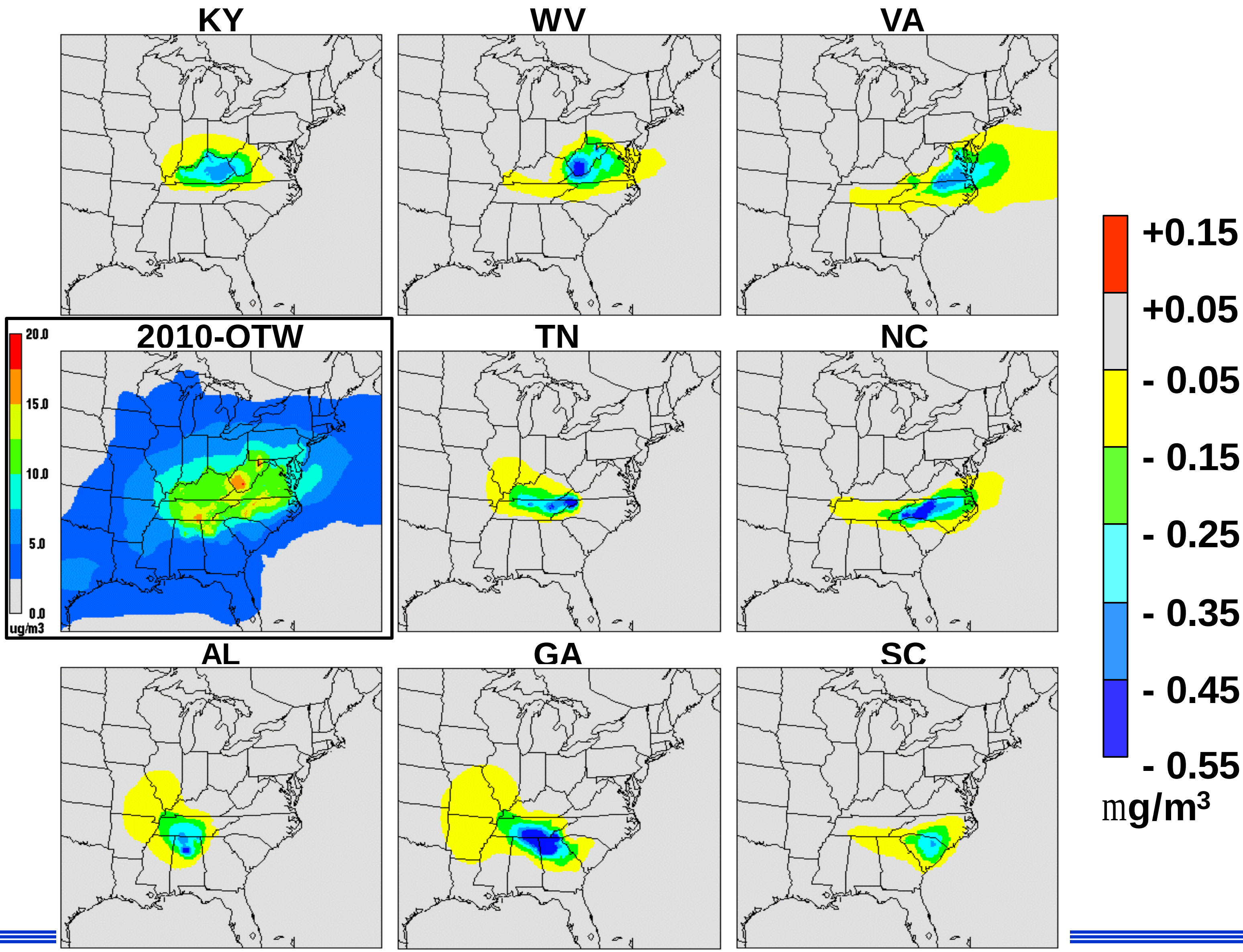
Geographic Sensitivity Regions



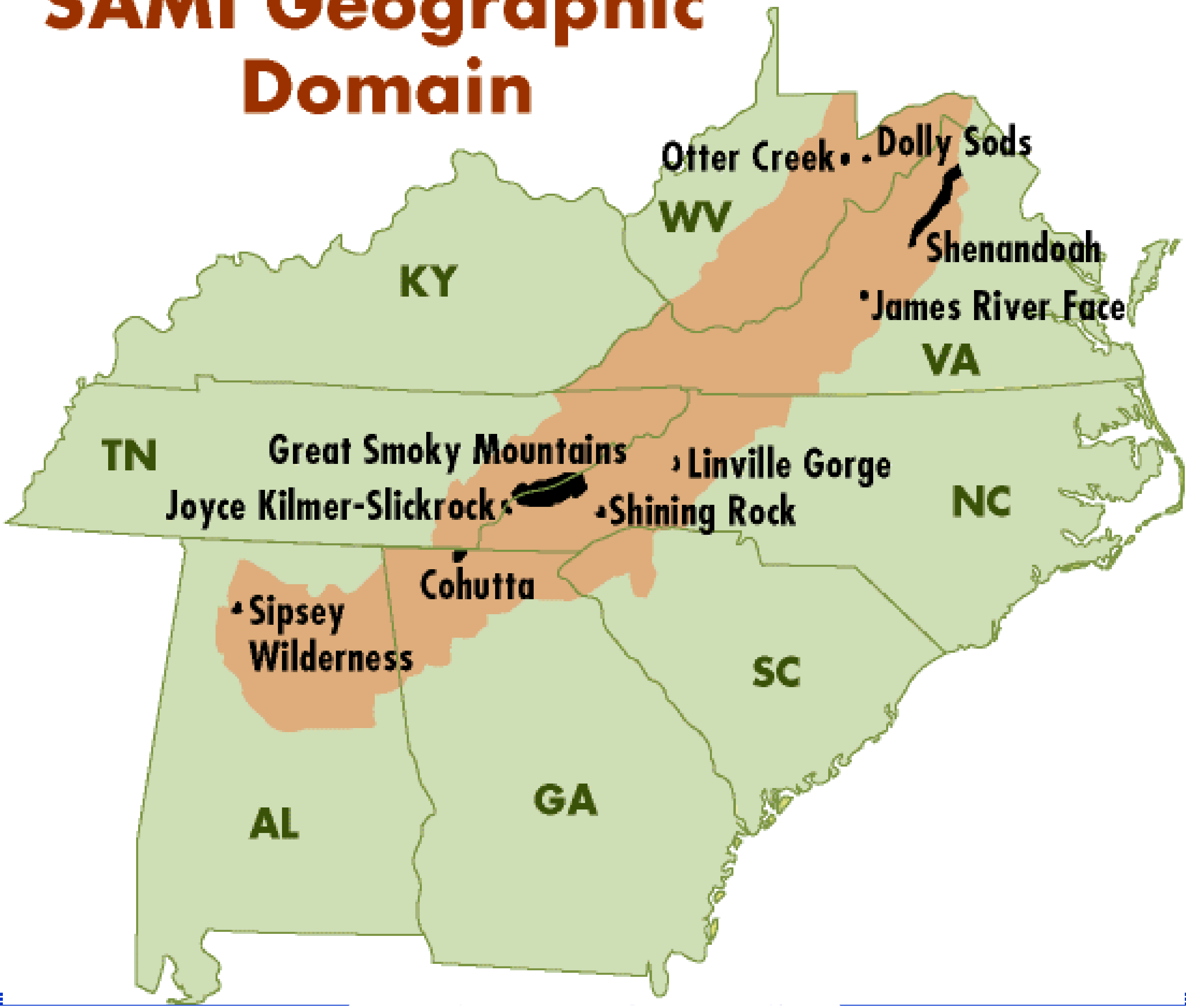
SO_4 & its Change on July 15, 1995 for a 10% Reduction of 2010-OTW SO_2 Emissions from Different Regions

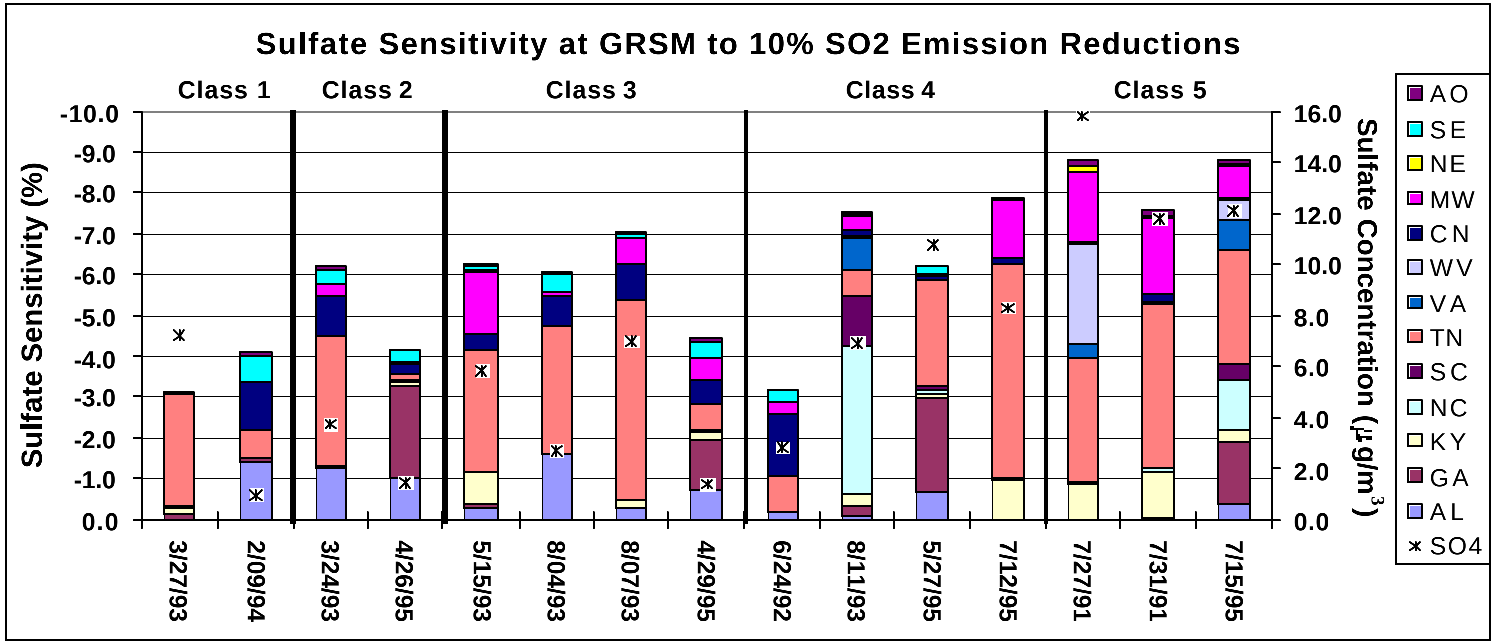


SO_4 & its Change on July 15, 1995 for a 10% Reduction of 2010-OTW SO_2 Emissions from SAMI States



SAMI Geographic Domain




Sulfate Sensitivity at GRSM to 10% SO2 Emission Reductions
Class 1
Class 2
Class 3
Class 4
Class 5
Sulfate Sensitivity (%)
Sulfate Concentration (µg/m3)
-10.0
-9.0
-8.0
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
3/27/93
2/09/94
3/24/93
4/26/95
5/15/93
8/04/93
8/07/93
4/29/95
6/24/92
8/11/93
5/27/95
7/12/95
7/27/91
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KY
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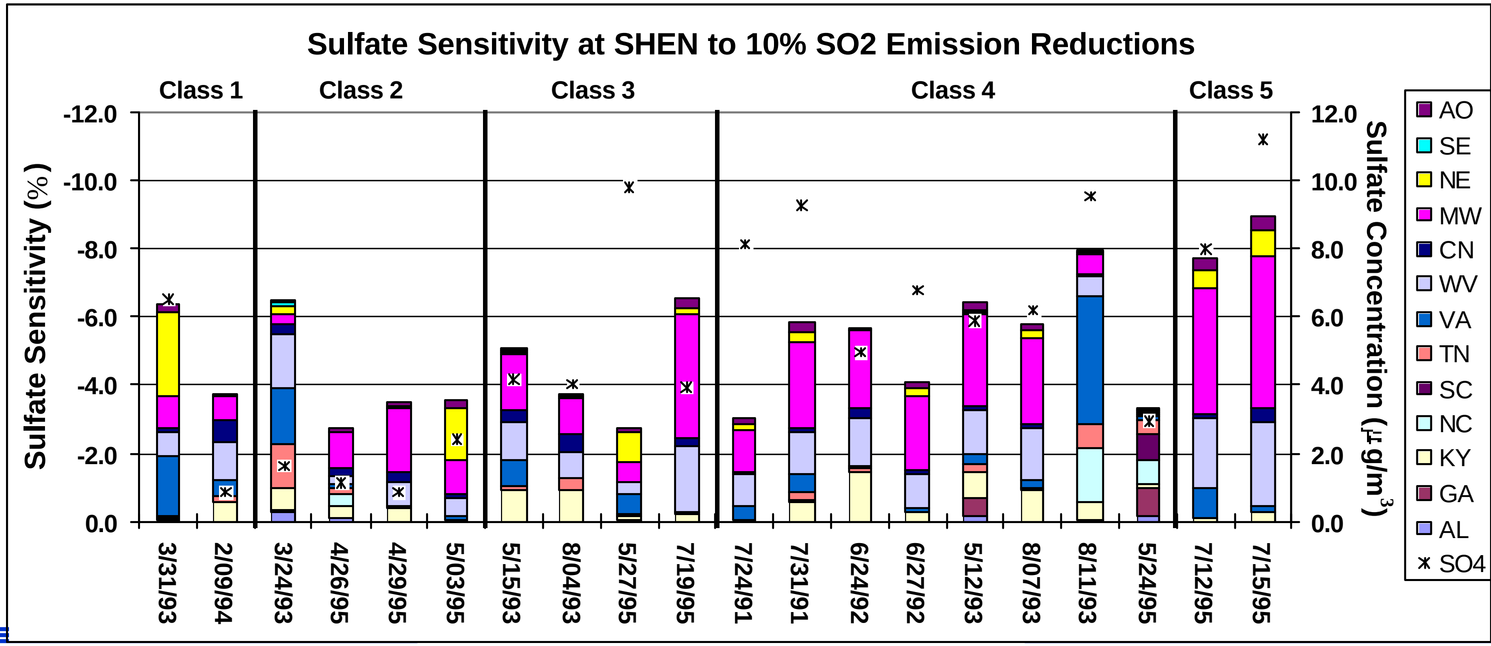
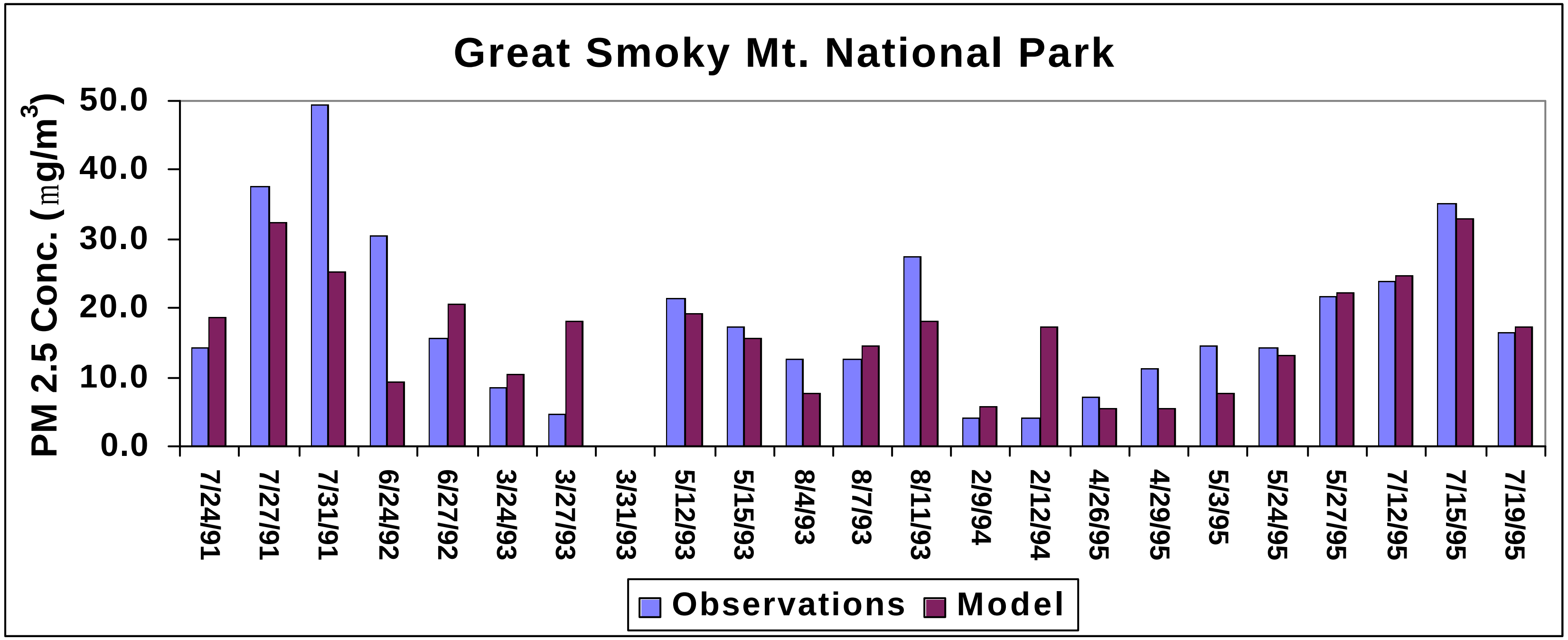
AL
SO4

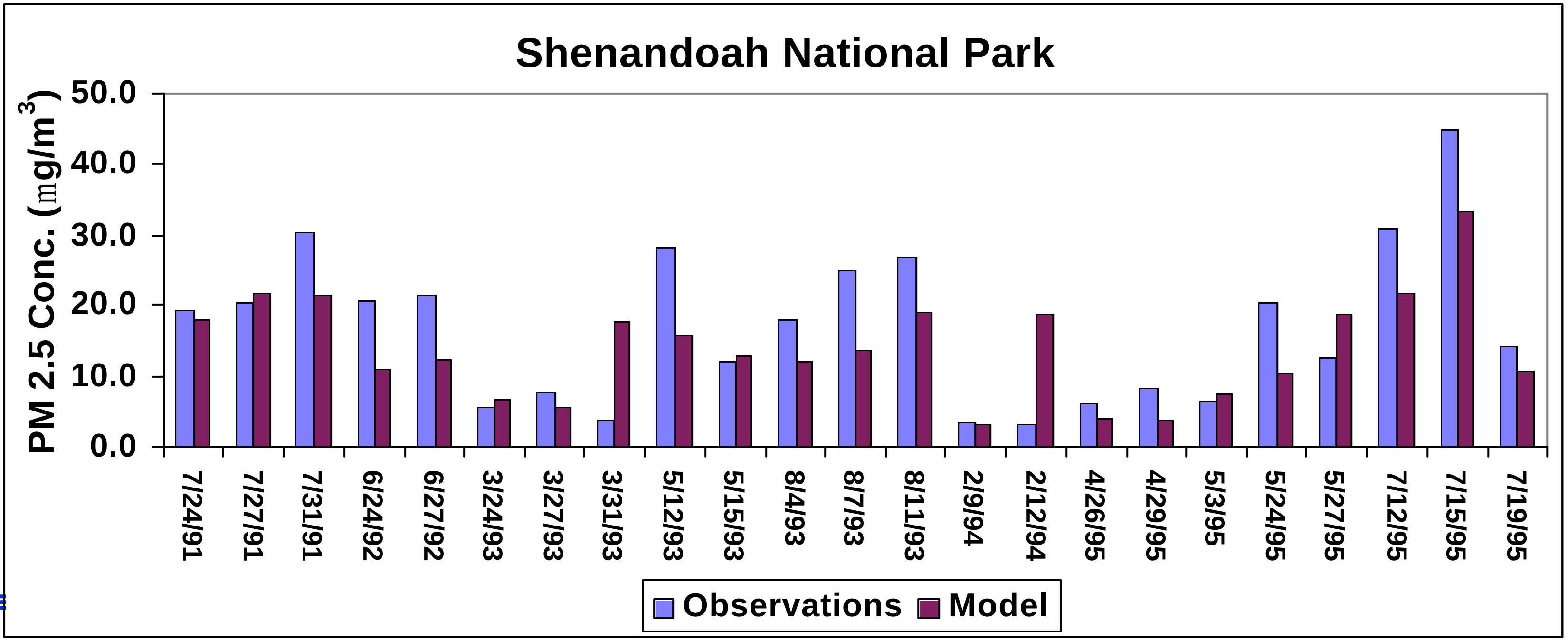

Sulfate Sensitivity at SHEN to 10% SO2 Emission Reductions
Class 1
Class 2
Class 3
Class 4
Class 5
Sulfate Sensitivity (%)
Sulfate Concentration (µg/m3)
-12.0
-10.0
-8.0
-6.0
-4.0
-2.0
0.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
3/31/93
2/09/94
3/24/93
4/26/95
4/29/95
5/03/95
5/15/93
8/04/93
5/27/95
7/19/95
7/24/91
7/31/91
6/24/92
6/27/92
5/12/93
8/07/93
8/11/93
5/24/95
7/12/95
7/15/95
AO
SE
NE
MW
CN
WV
VA
TN
SC
NC
KY
GA
AL
SO4

Summary

- Ozone models are “mature”
- PM Modeling is developing
  - Much more involved
  - More uncertainties
  - Performance is acceptable
- Main Features
  - Internal mixtures
    - External computationally huge
  - Sectional distribution
    - More flexible than modal
  - Inorganic thermodynamics
- Useful features
  - Direct sensitivity analysis
- Future
  - External mixture approach more common
  - more detailed organic chemistry



Great Smoky Mt. National Park
PM 2.5 Conc. (mg/m3)
50.0
40.0
30.0
20.0
10.0
0.0
7/24/91
7/27/91
7/31/91
6/24/92
6/27/92
3/24/93
3/27/93
3/31/93
5/12/93
5/15/93
8/4/93
8/7/93
8/11/93
2/9/94
2/12/94
4/26/95
4/29/95
5/3/95
5/24/95
5/27/95
7/12/95
7/15/95
7/19/95
Observations
Model



Shenandoah National Park
PM 2.5 Conc. (mg/m3)
50.0
40.0
30.0
20.0
10.0
0.0
7/24/91
7/27/91
7/31/91
6/24/92
6/27/92
3/24/93
3/27/93
3/31/93
5/12/93
5/15/93
8/4/93
8/7/93
8/11/93
2/9/94
2/12/94
4/26/95
4/29/95
5/3/95
5/24/95
5/27/95
7/12/95
7/15/95
7/19/95
Observations
Model