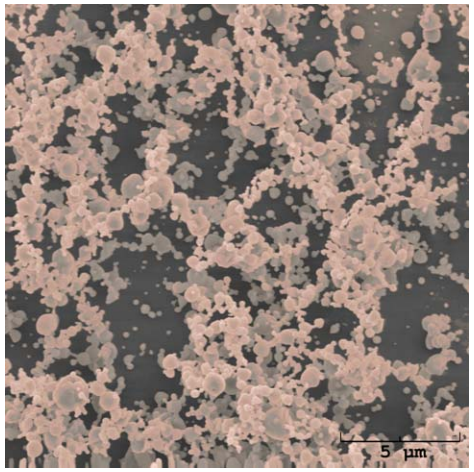
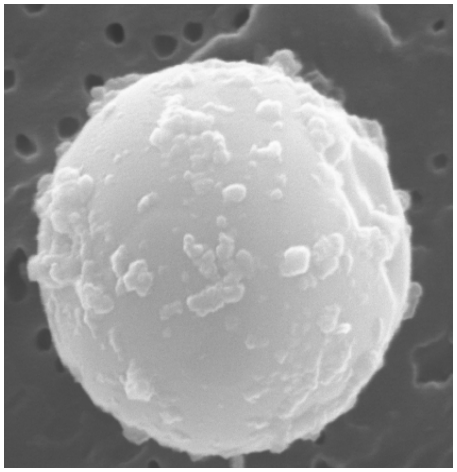
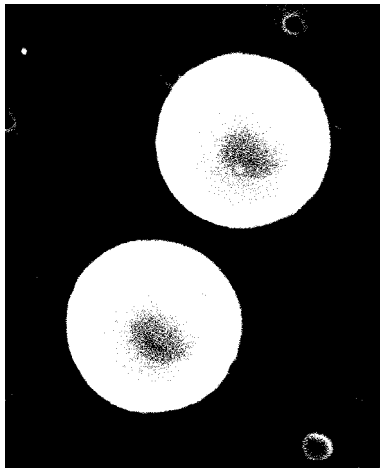
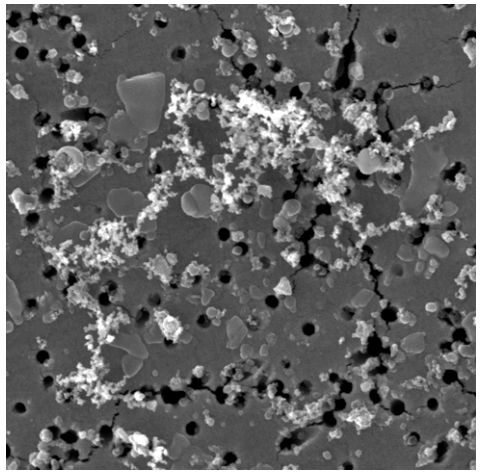
Atmospheric Formation of Ultrafine Particles

Charles Stanier, Assistant Professor
University of Iowa
Department of Chemical and
Biochemical Engineering
cstanier@engineering.uiowa.edu





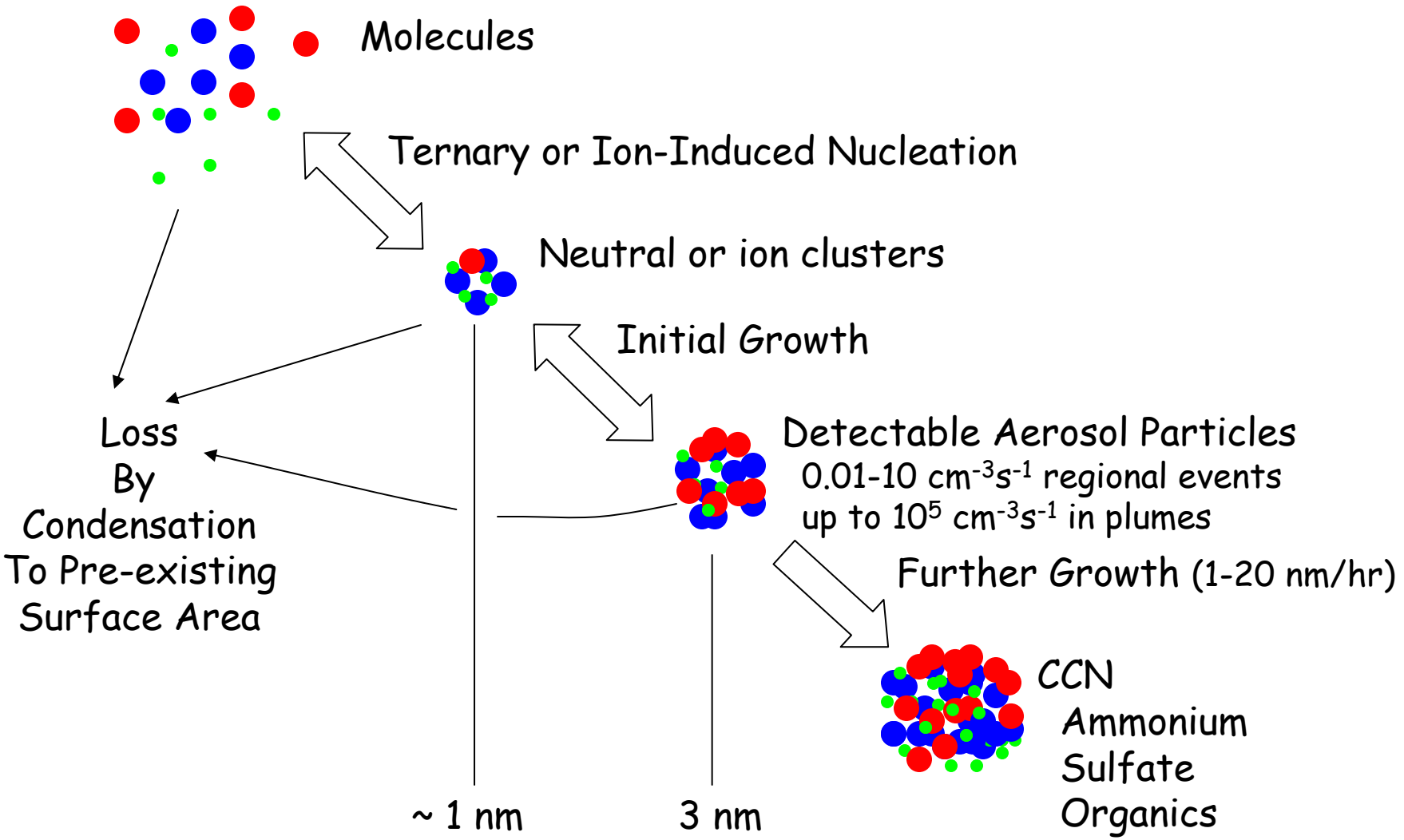




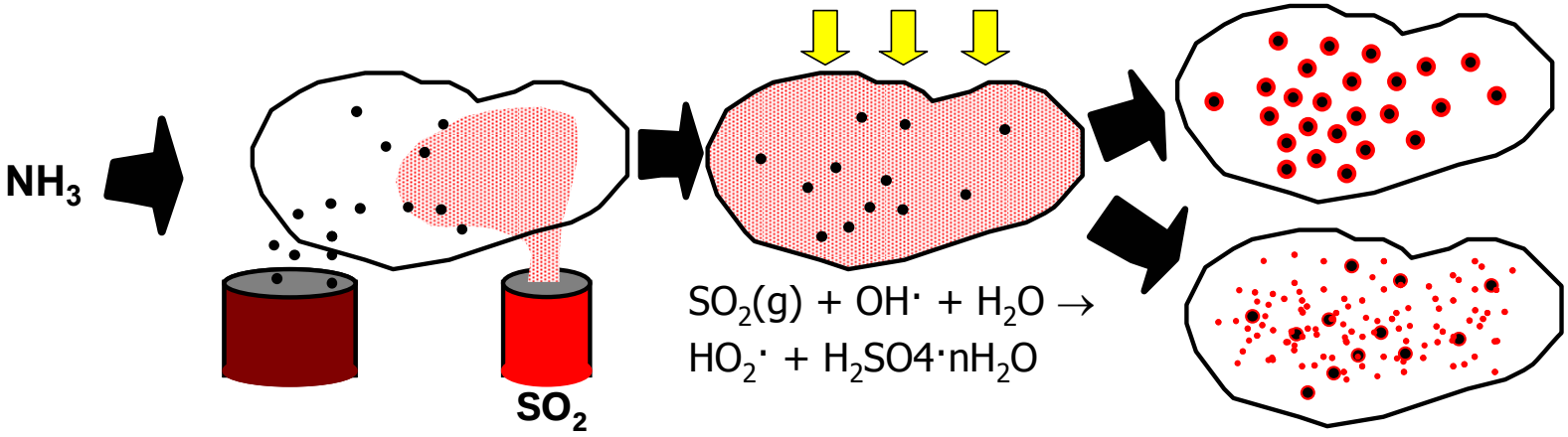
Outline

- What is atmospheric new particle formation
- Some examples
  - Physical measurements
  - Chemical measurements
  - Modeling
- What fraction of particles are from new particle formation vs. combustion?

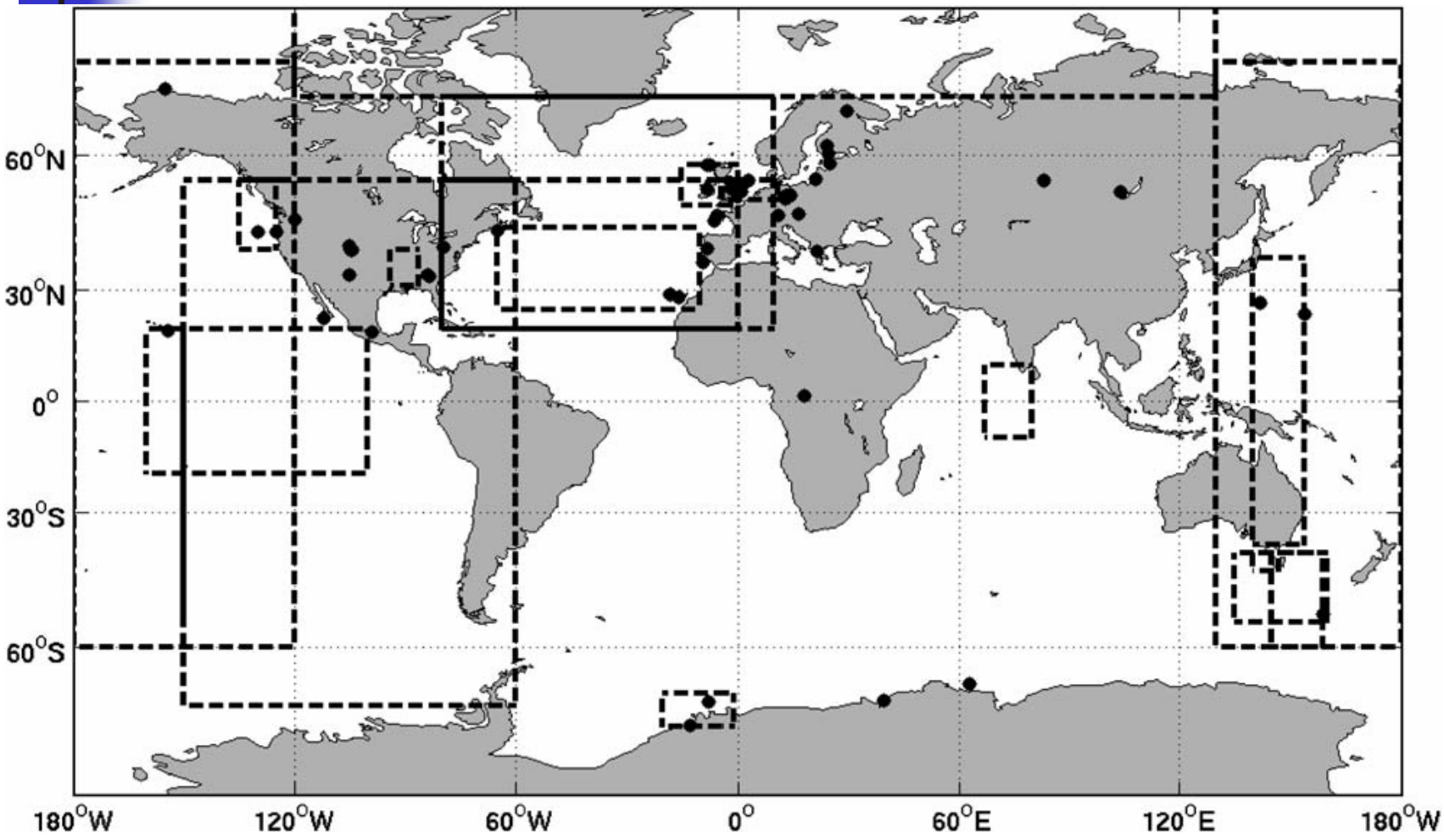
What is Nucleation?



Nucleation Overview

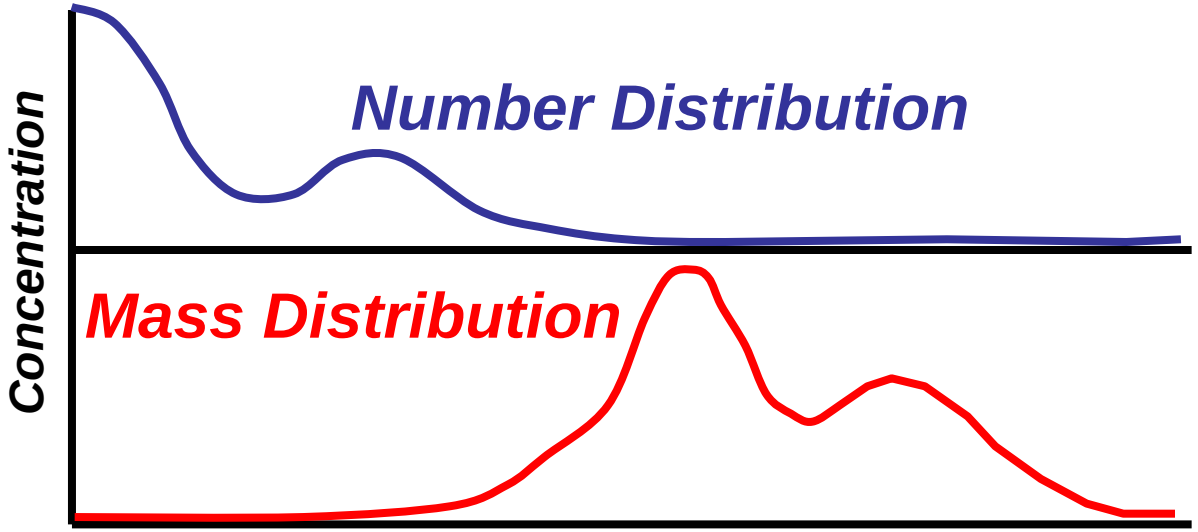


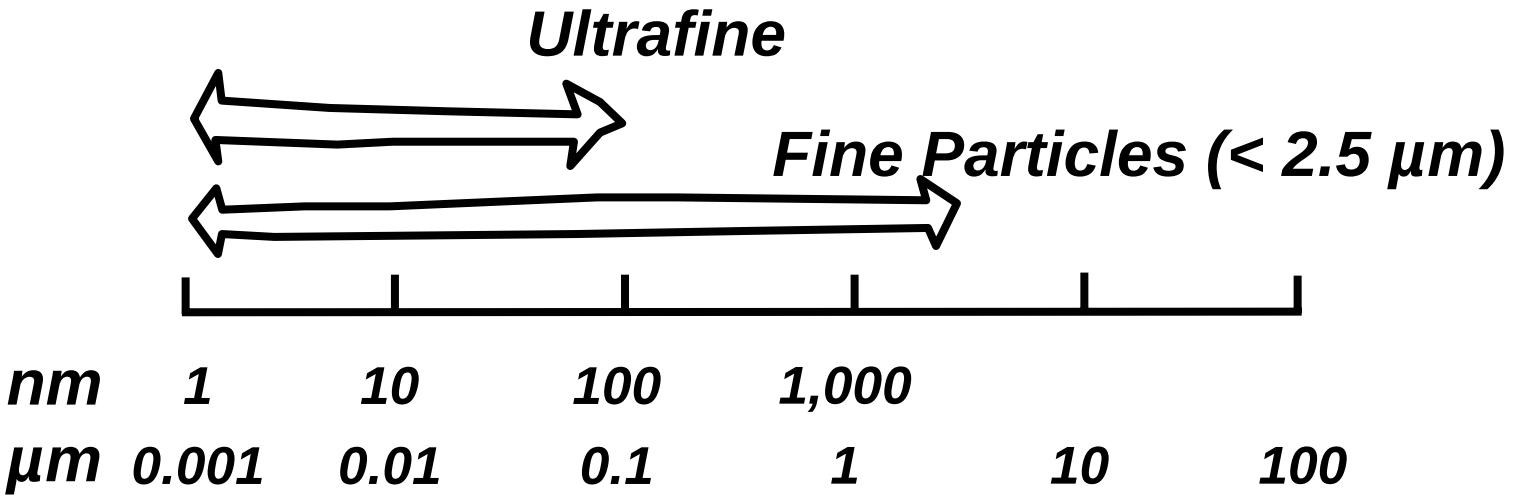
Nucleation Observations



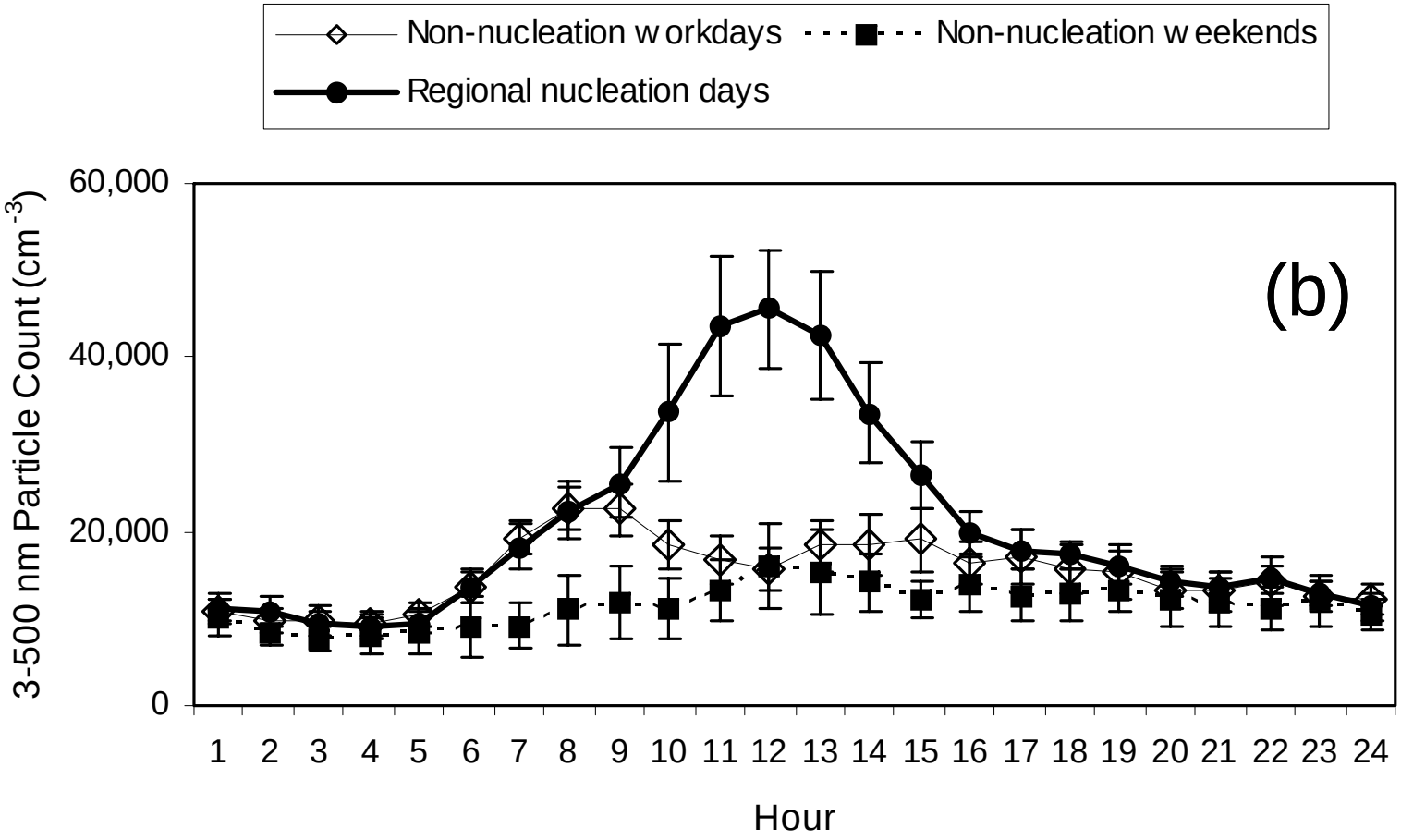
Kulmala, McMurry, et al. (2004) J. Aerosol Sci. 35 pp. 143-176

Particle Size

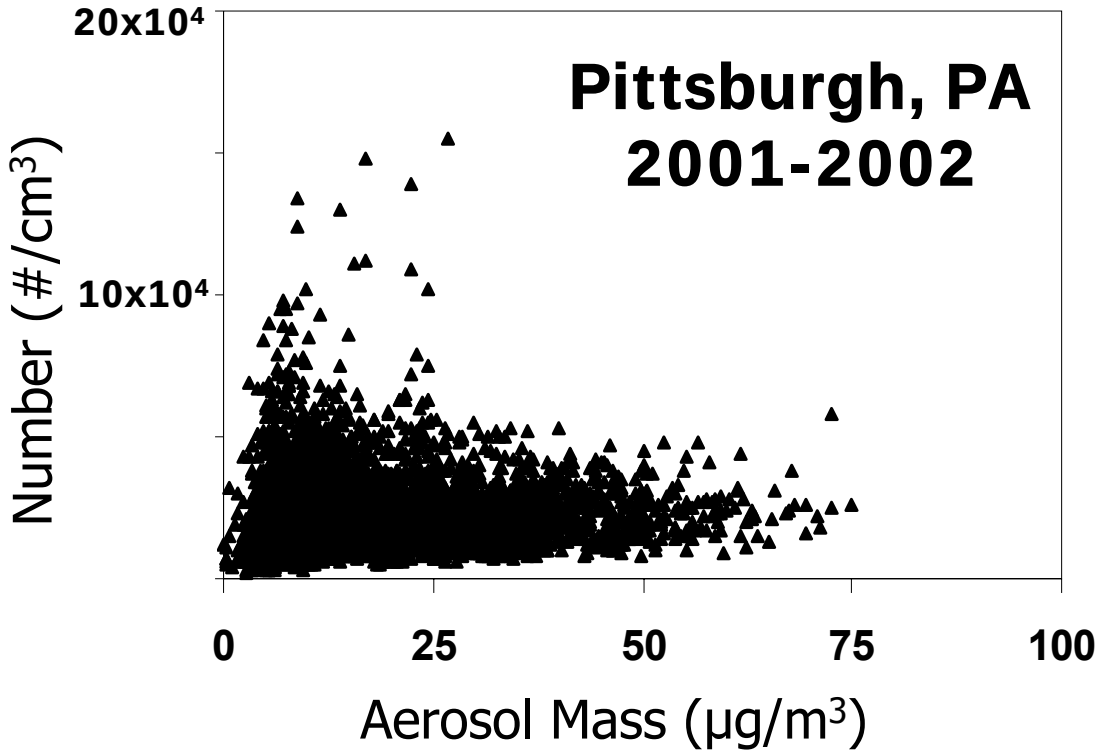




Diurnal Pattern

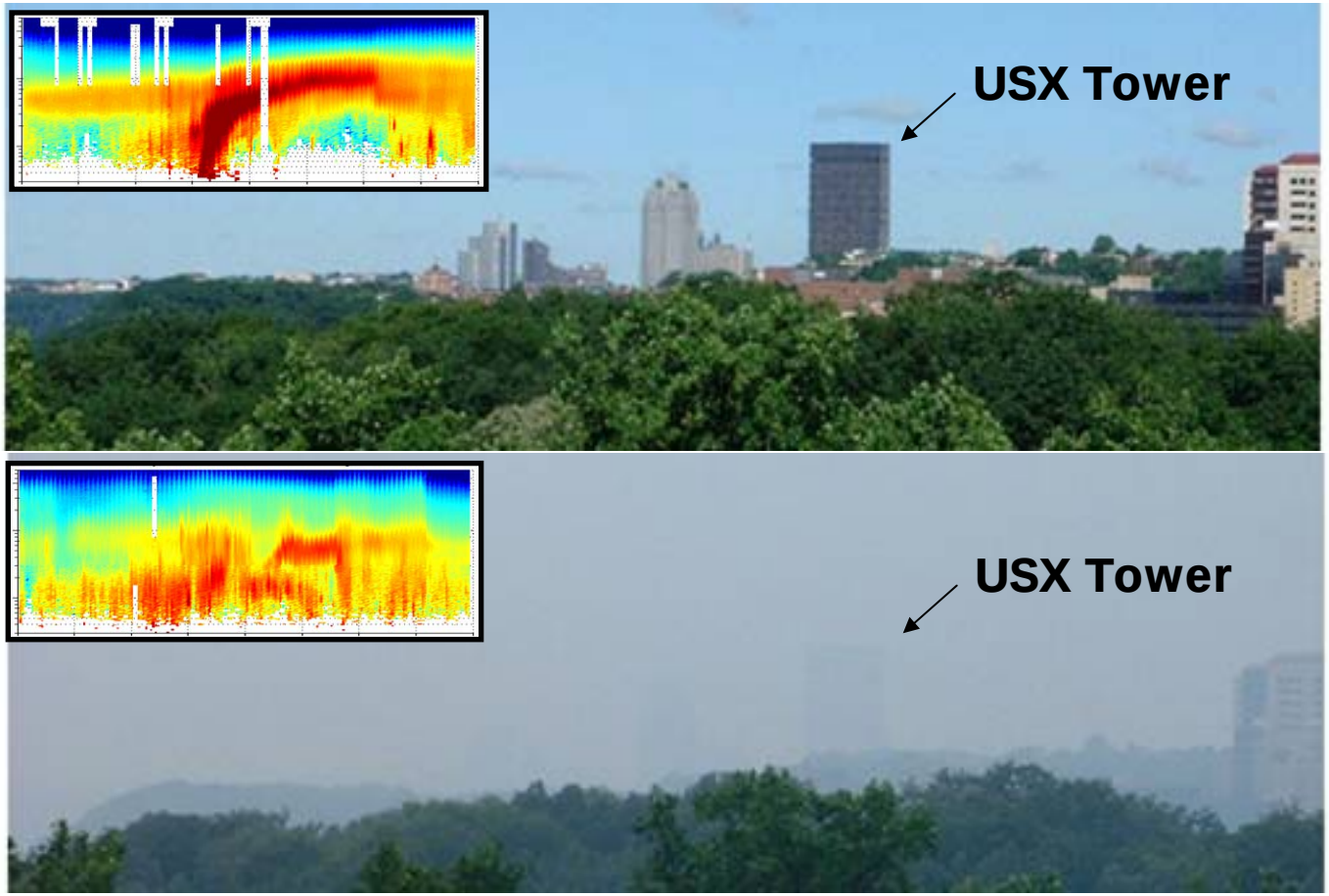


Number vs. Mass Distribution

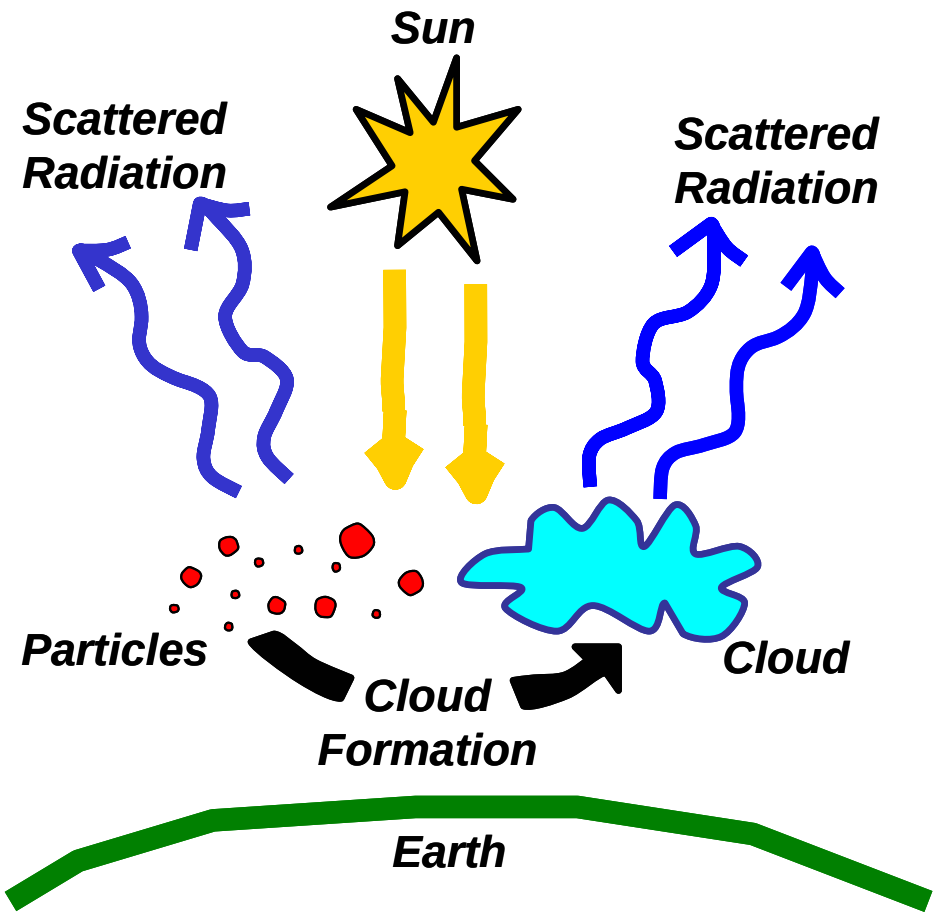


- Negative correlation
- Related to nucleation activity
- Occurring over wide area

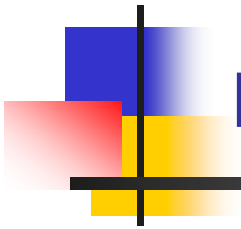
New Particle Formation vs. Visibility



Other Aerosol Impacts: Visibility & Climate

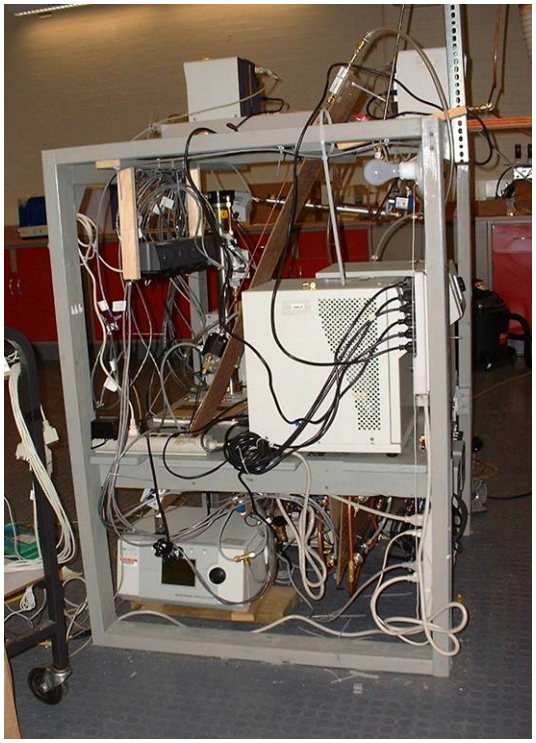
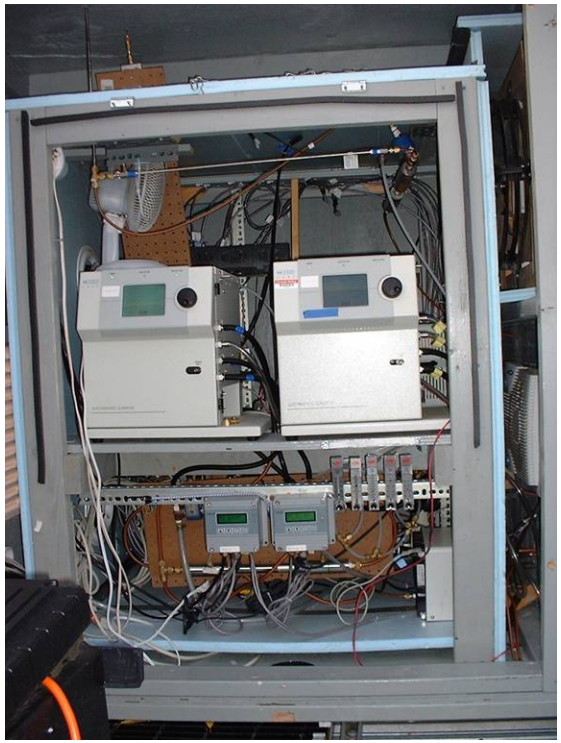


EPA (2001) National Air Quality: Status and Trends



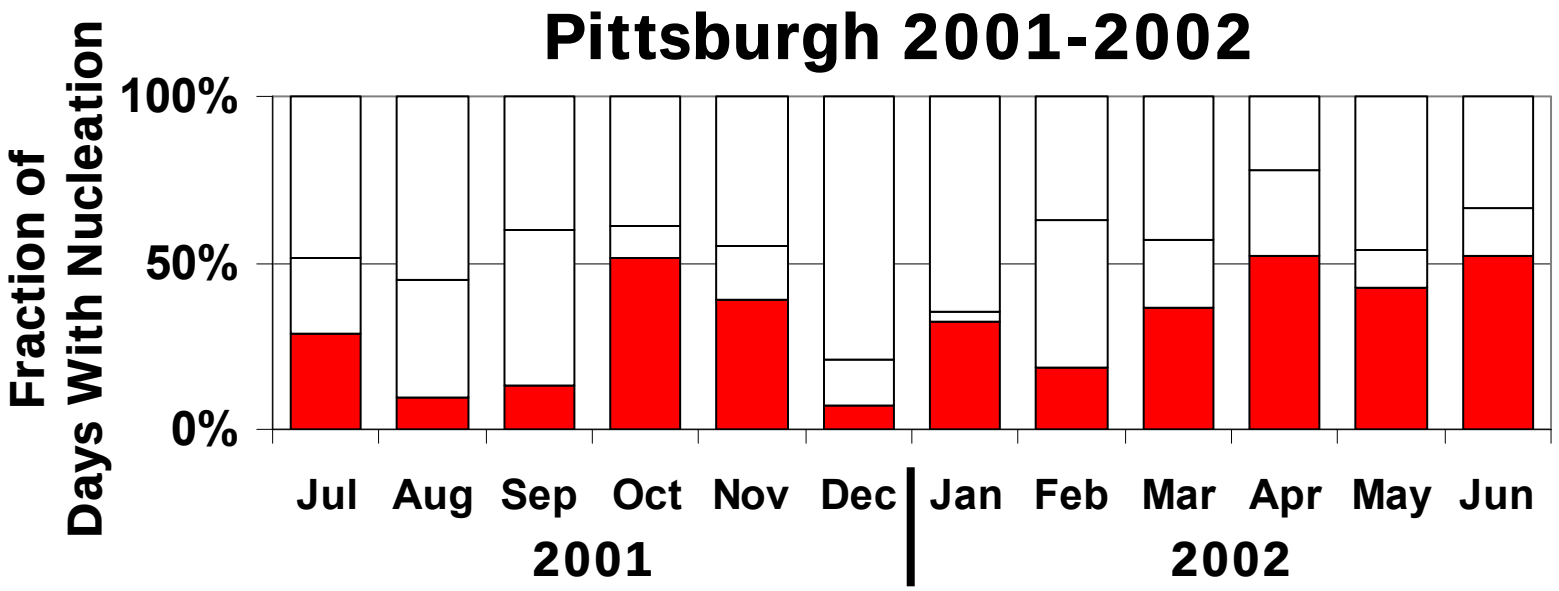
Physical Measurements

Dry-Ambient Aerosol Size Spectrometer

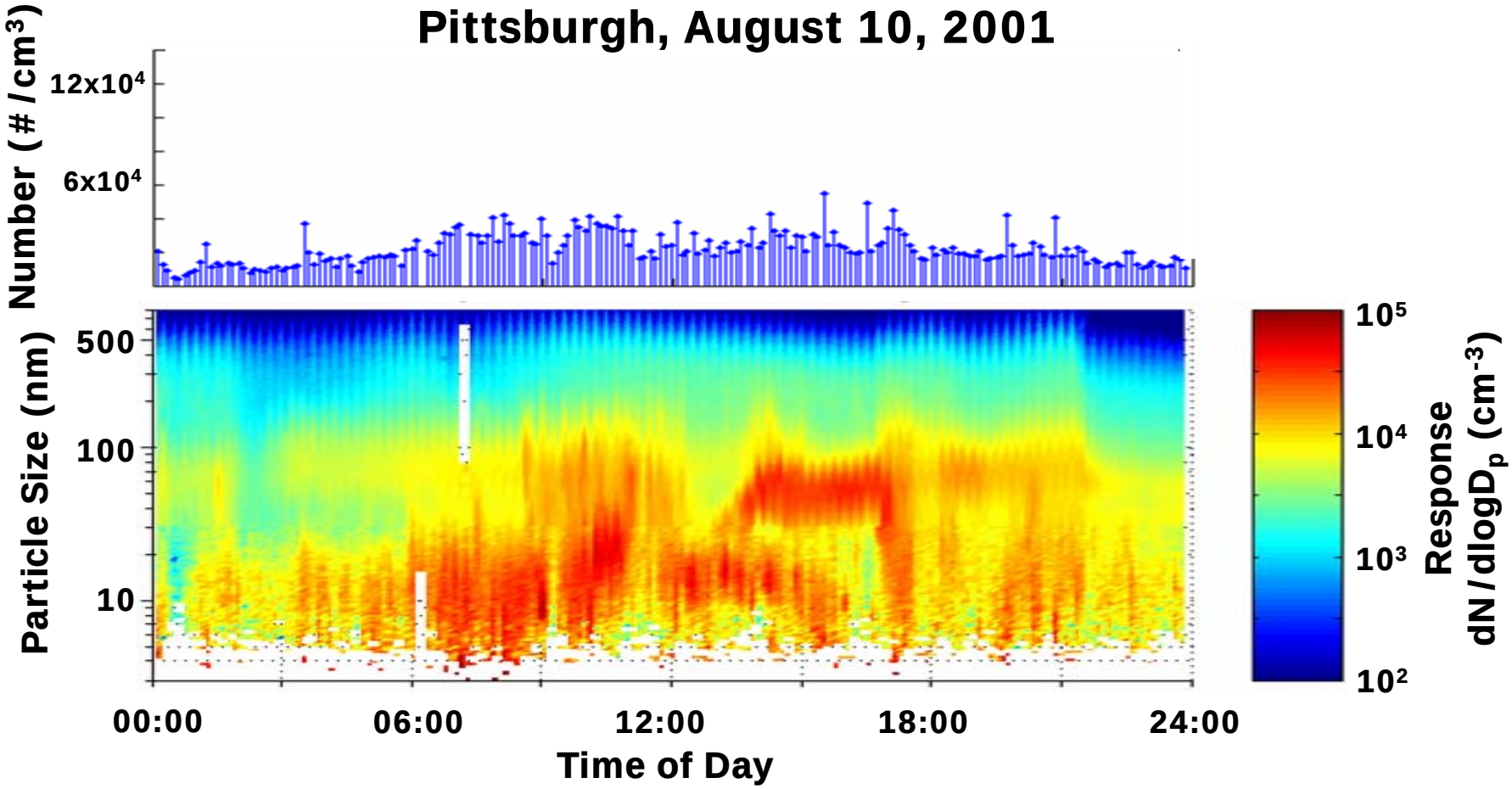

- Reconfigured commercial instruments
- RH control system
- Inlet particle losses characterization
- Custom control, data acquisition, and data reduction software

Nucleation Frequency by Month

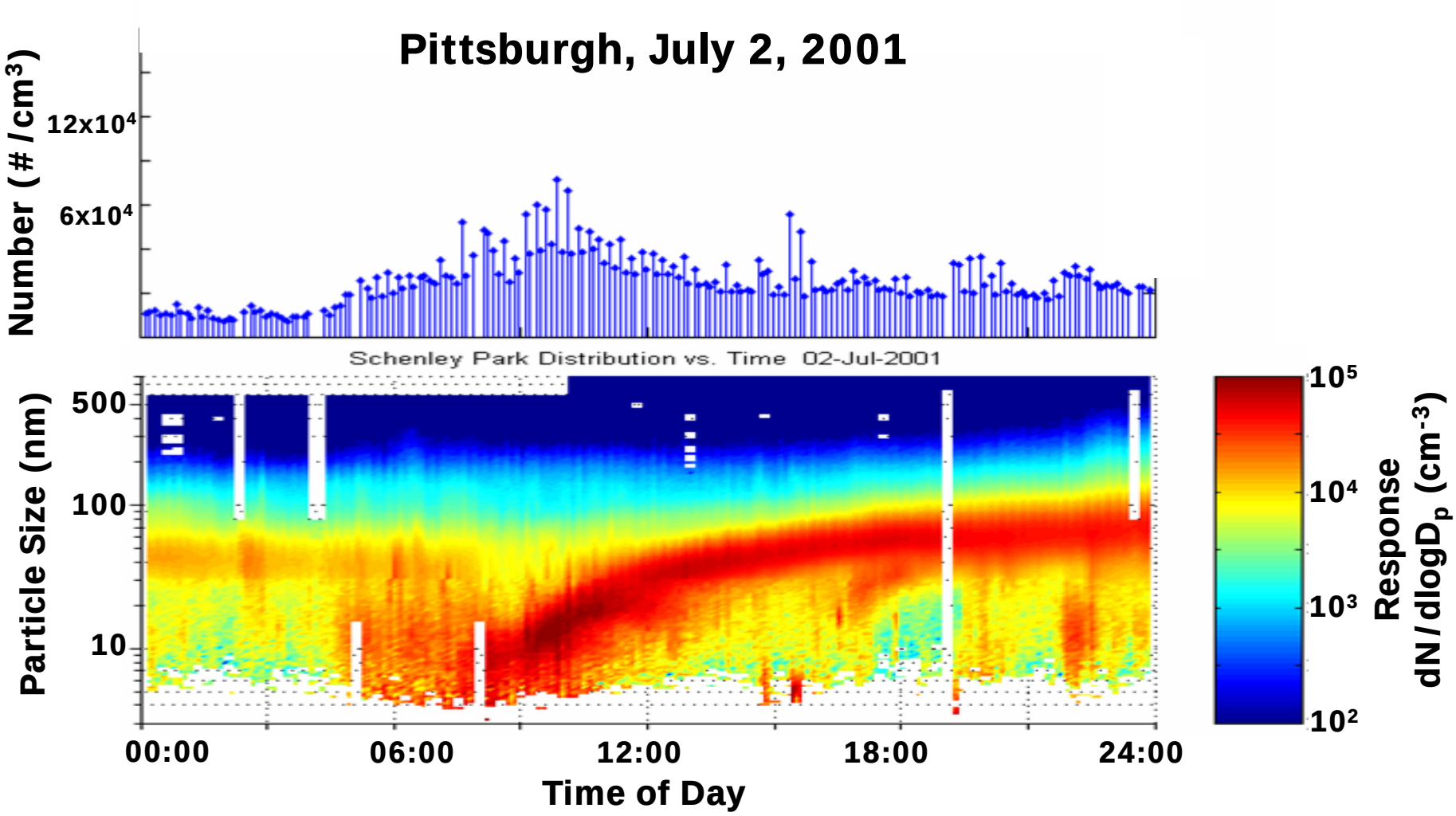


- Significant fraction of days (30%+)
- Most prevalent in spring, fall

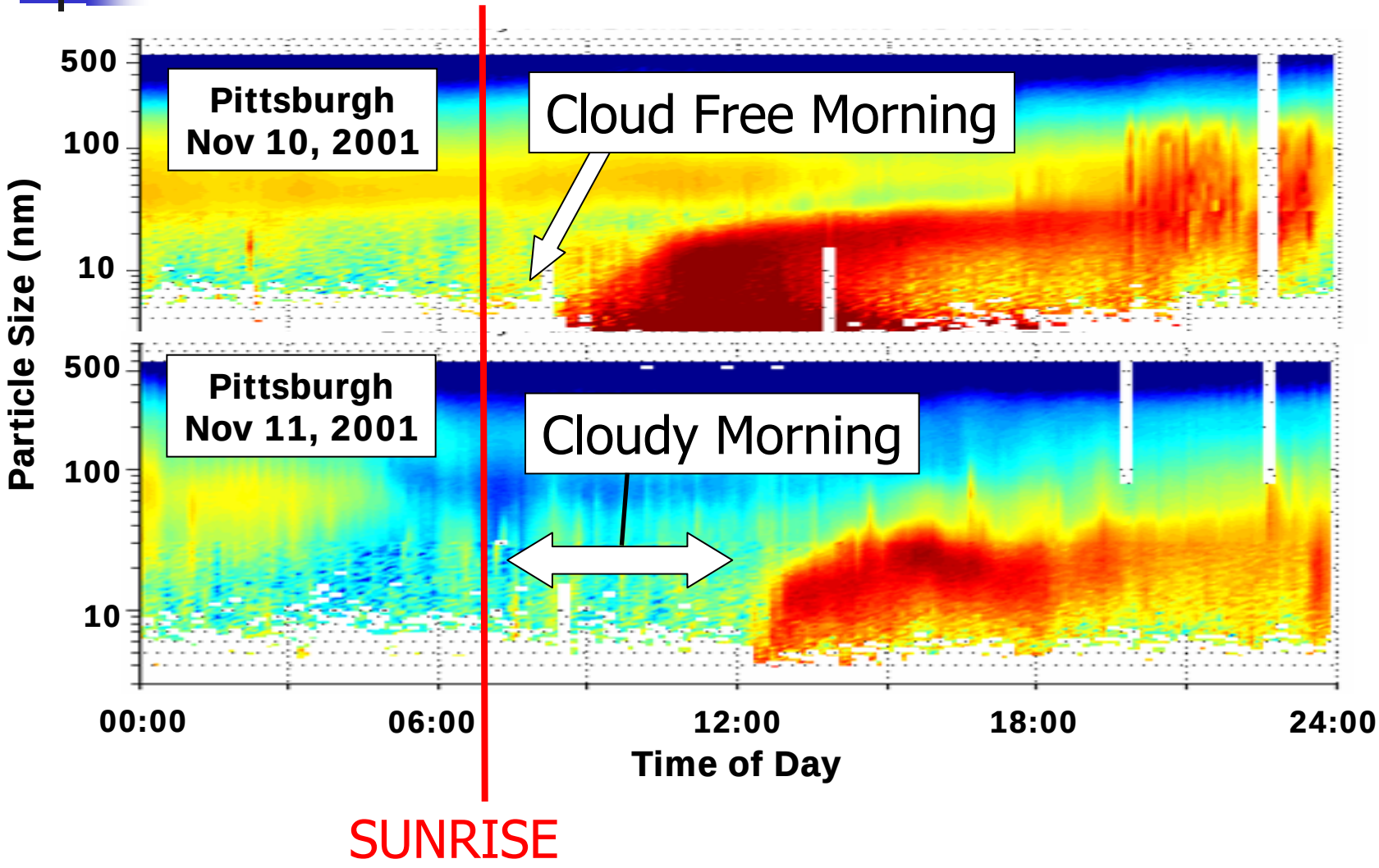
Example: No Nucleation



Example: Weak Nucleation

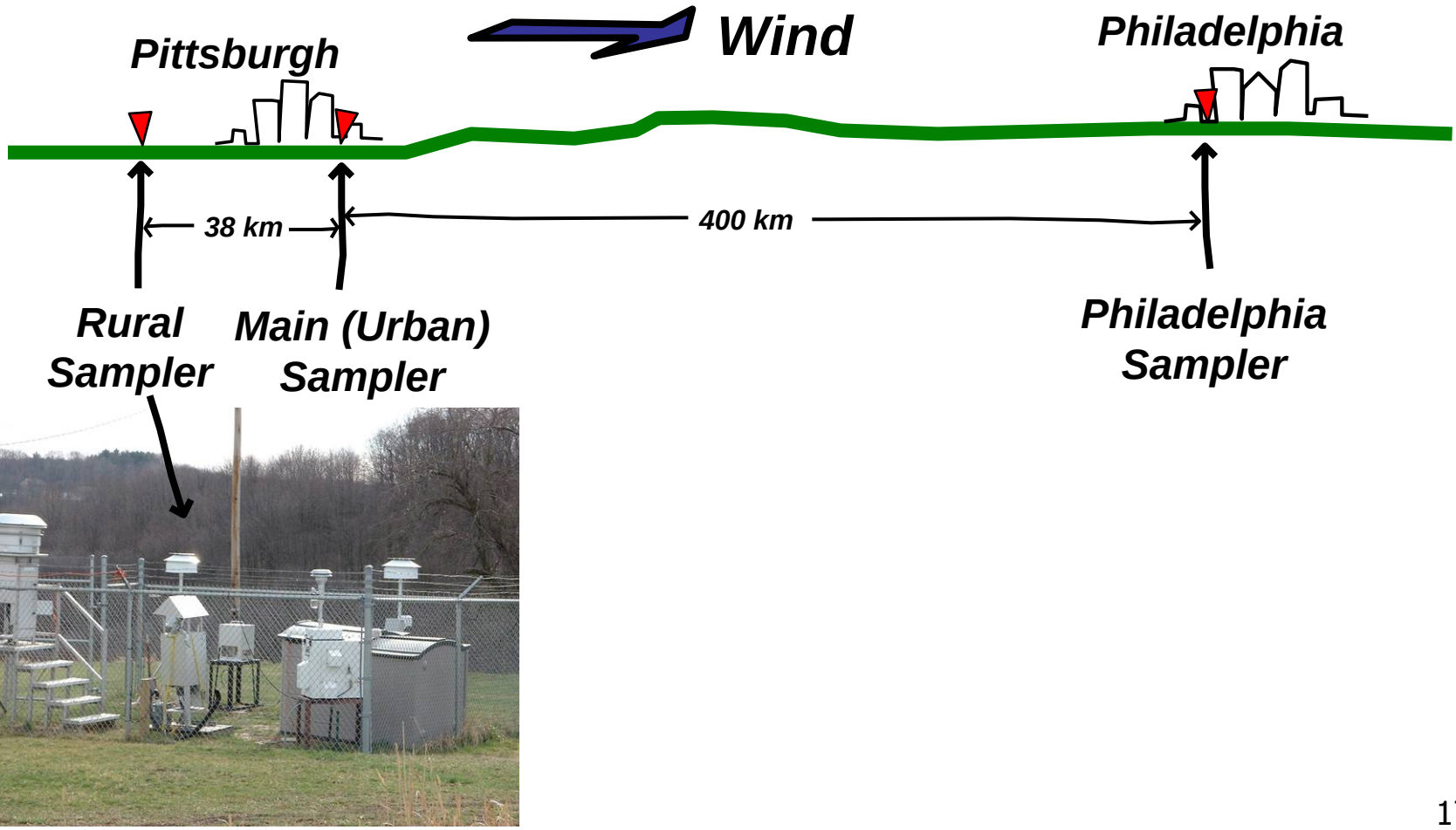


Sunlight and New Particle Formation

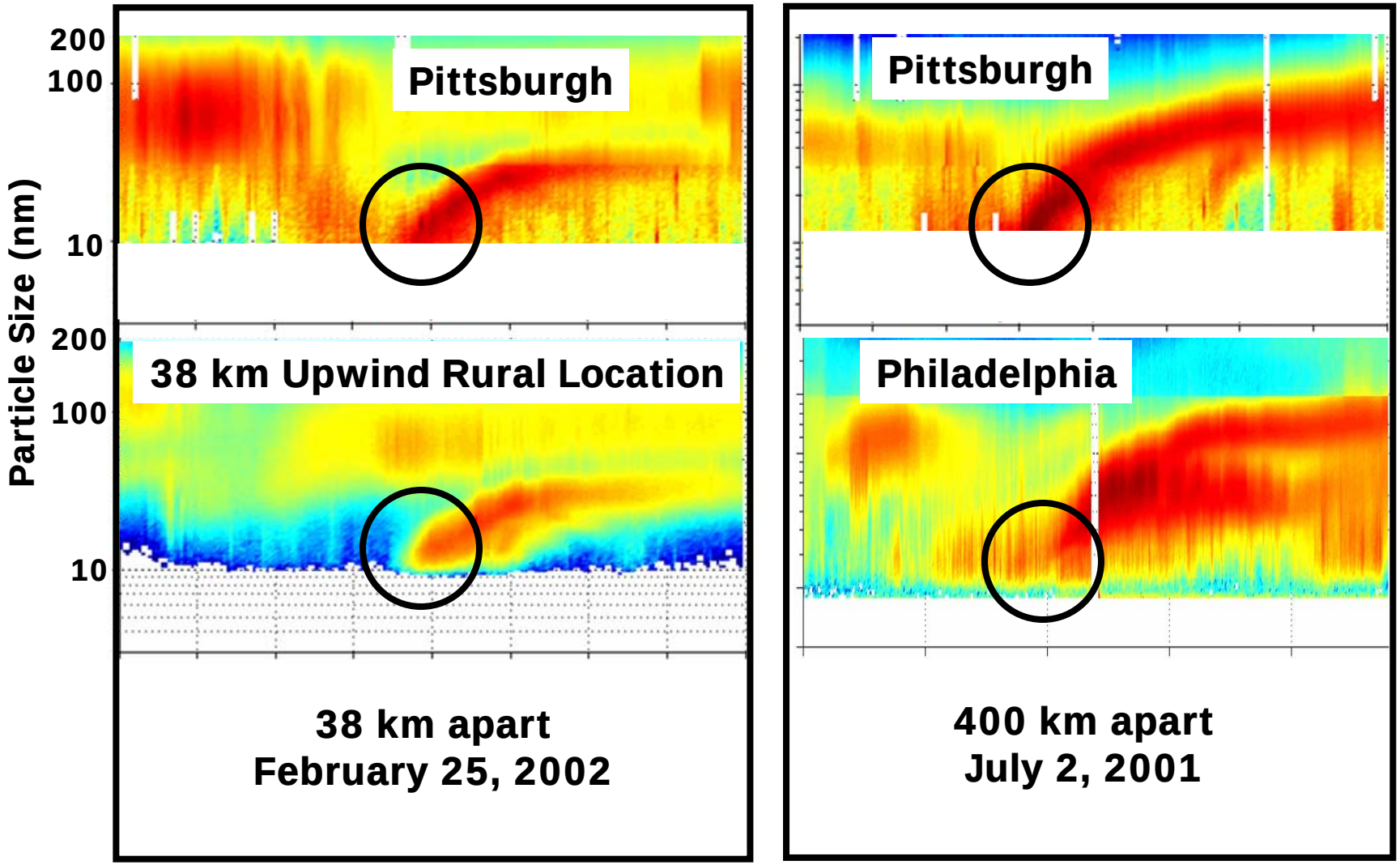


Nucleation's Spatial Coverage

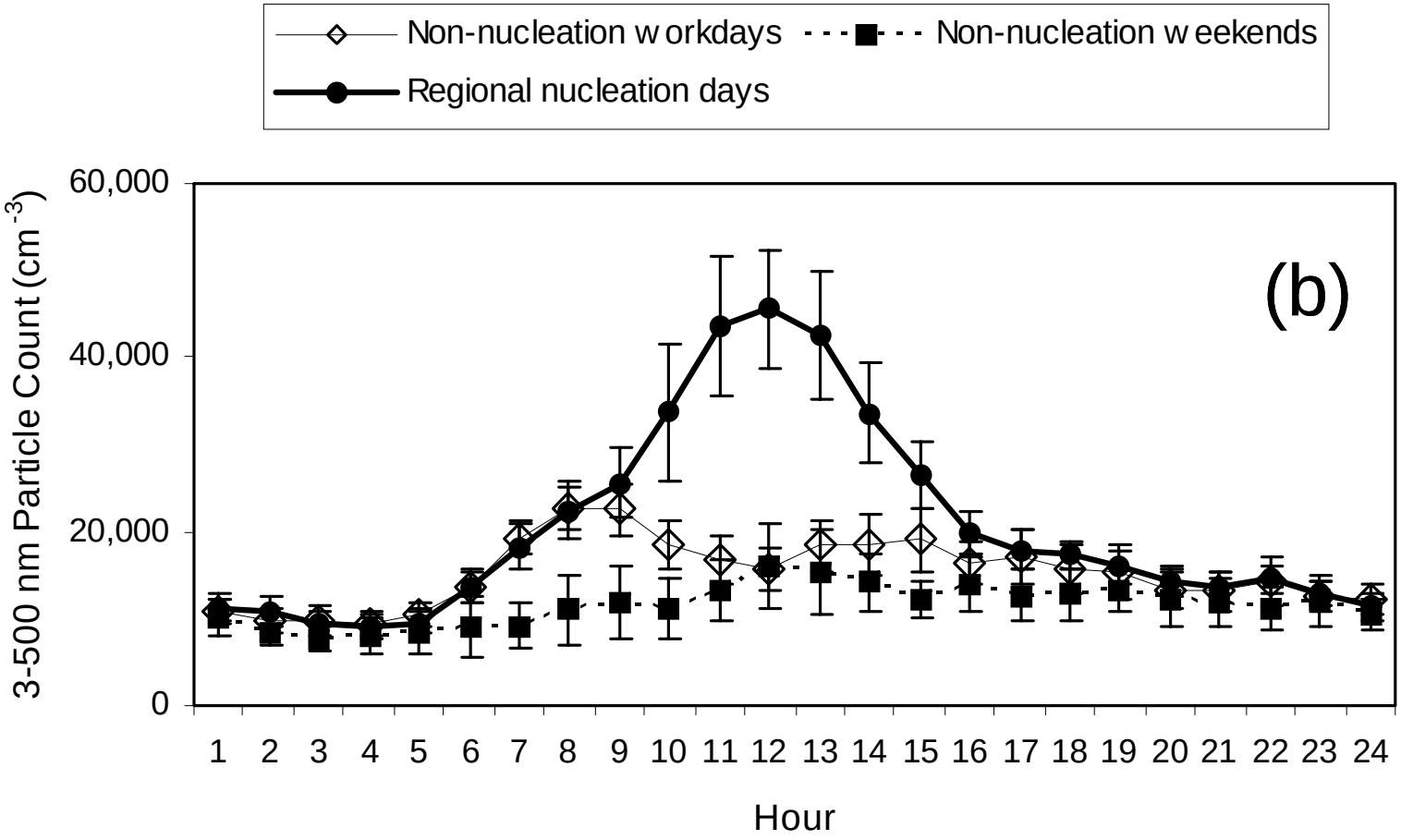
- Method: simultaneous sampling

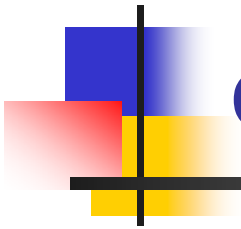


Spatial Coverage Result



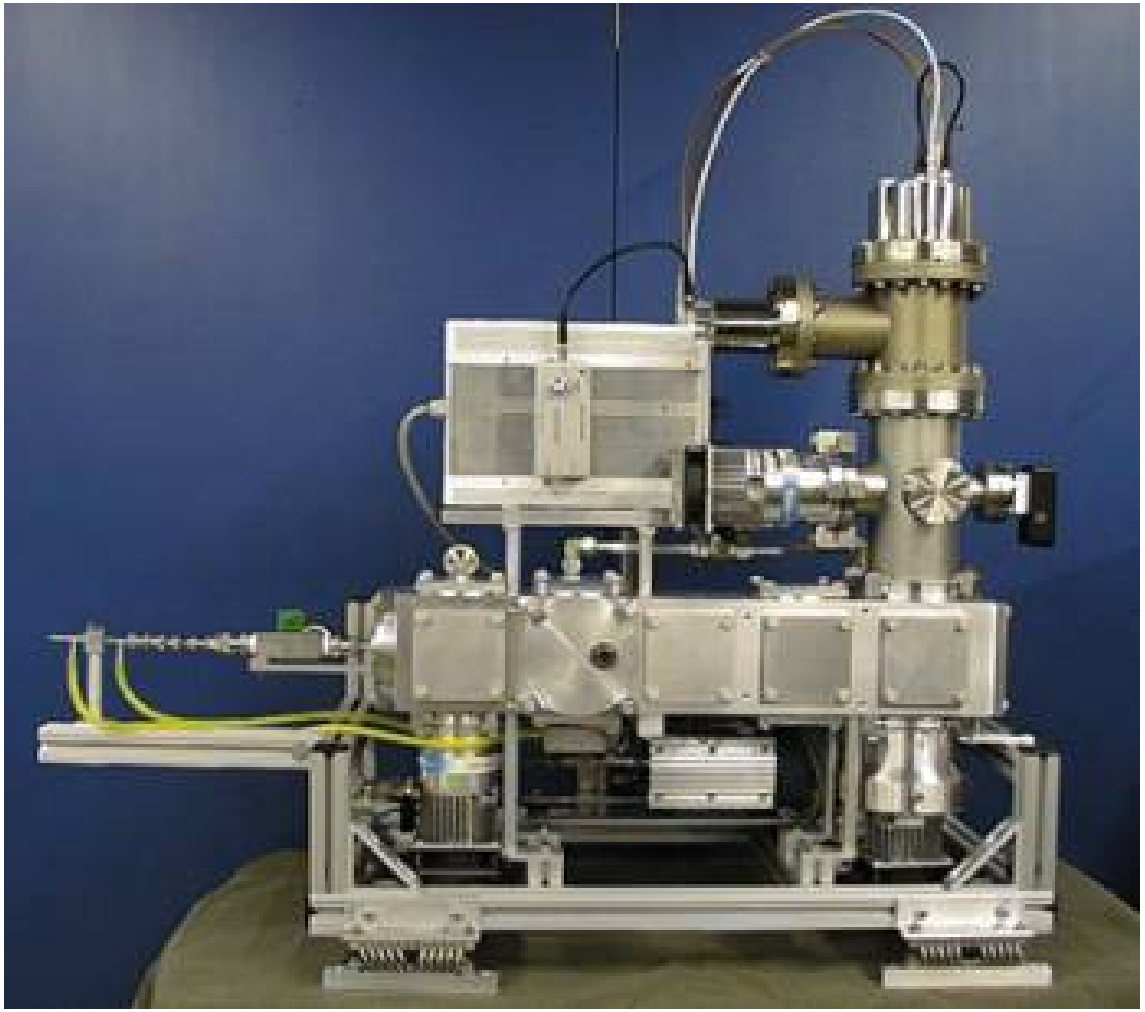
Diurnal Pattern





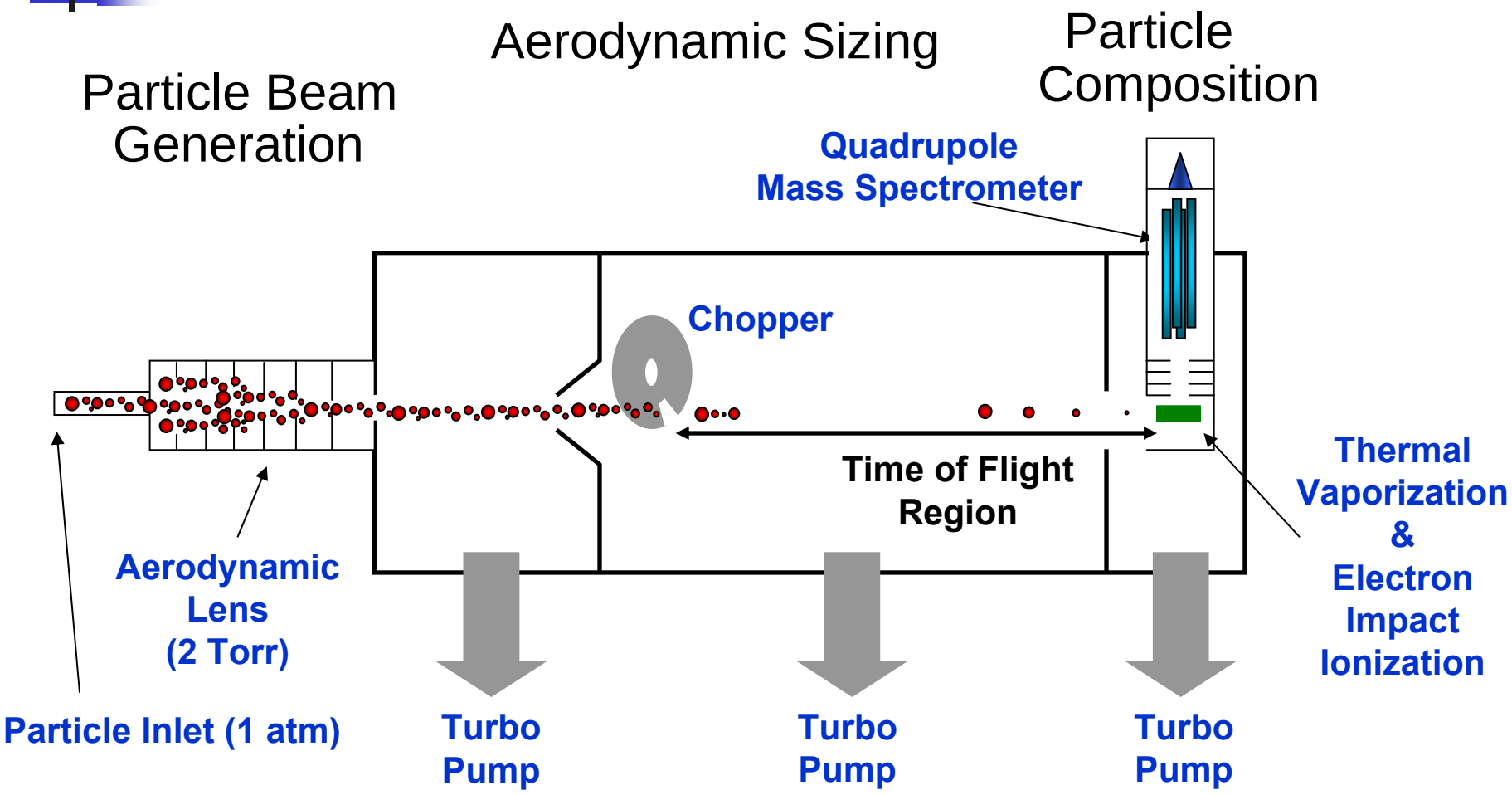
Chemical Measurements

Aerosol Mass Spectrometer



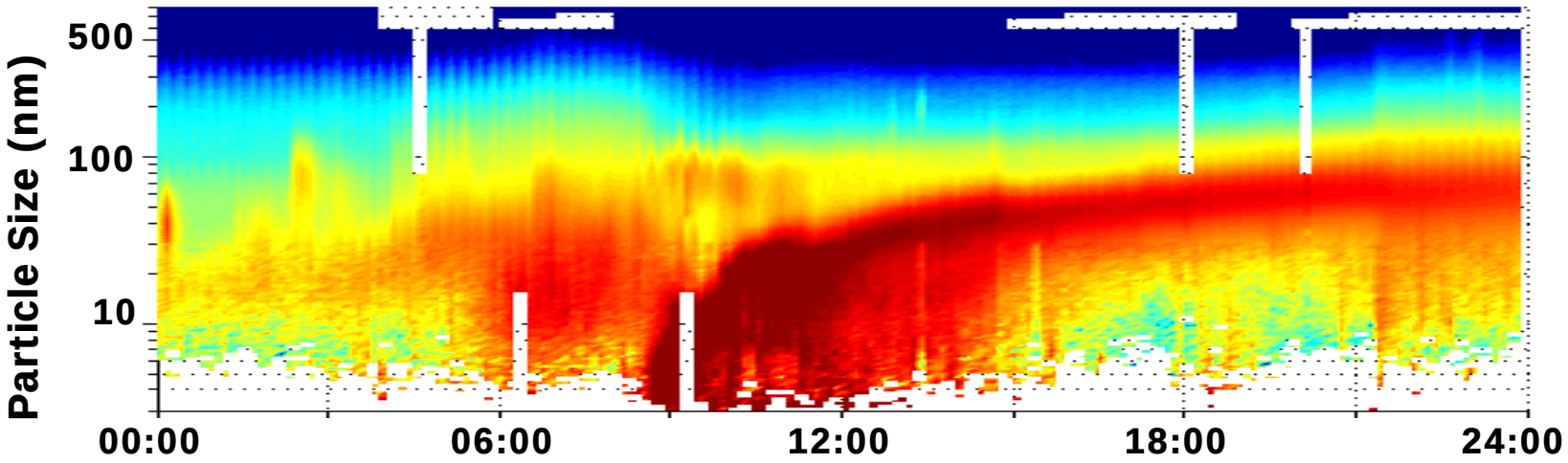
Zhang, Q.; Jimenez, J.L.; Caragaratna, M.; Worsnop, D.

Aerosol Mass Spectrometer

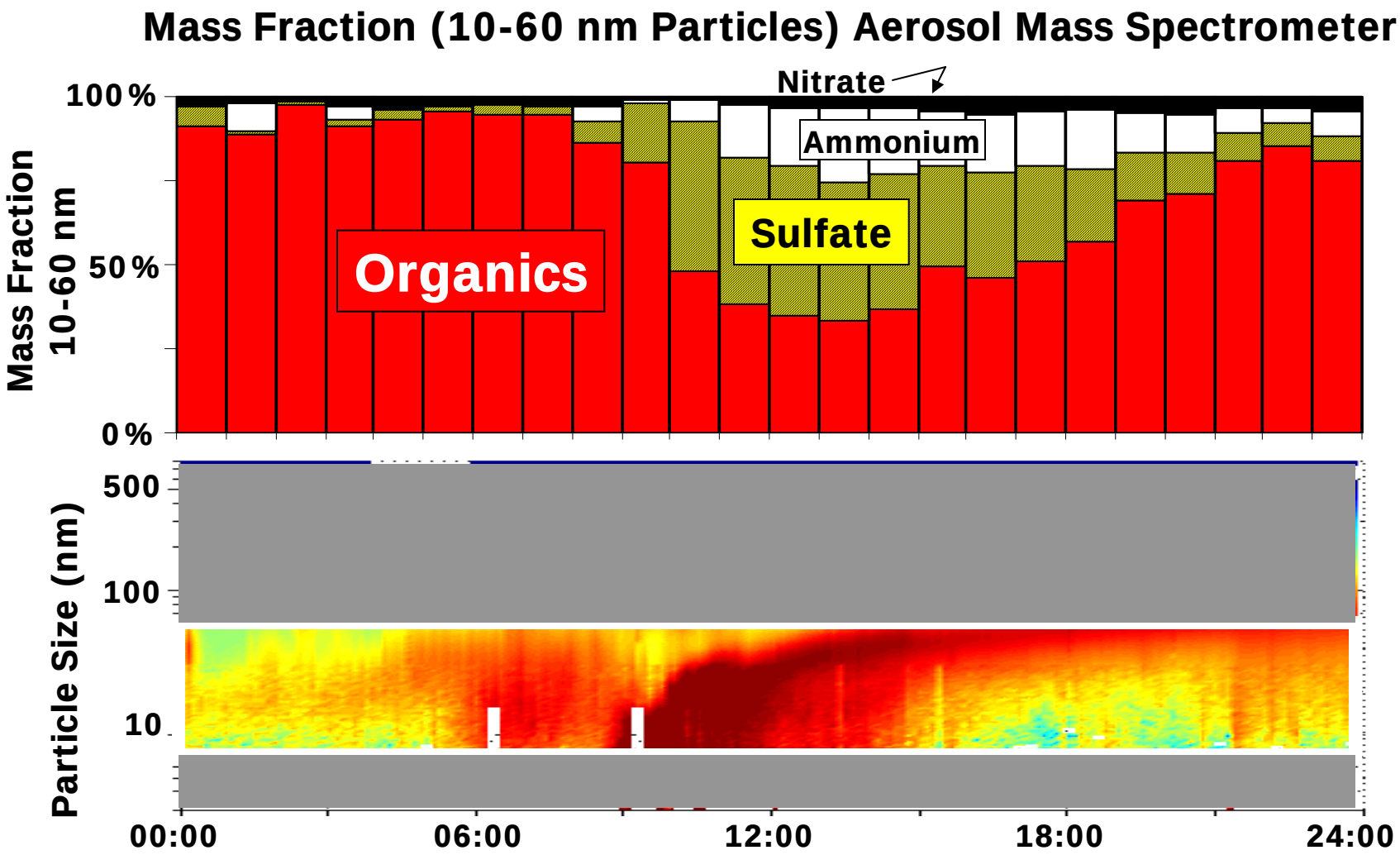


Jayne et al., Aerosol Science and Technology 33:1-2(49-70), 2000.
Jimenez et al., Journal of Geophysical Research, in press, 2002.

September 12, 2002 Nucleation Event

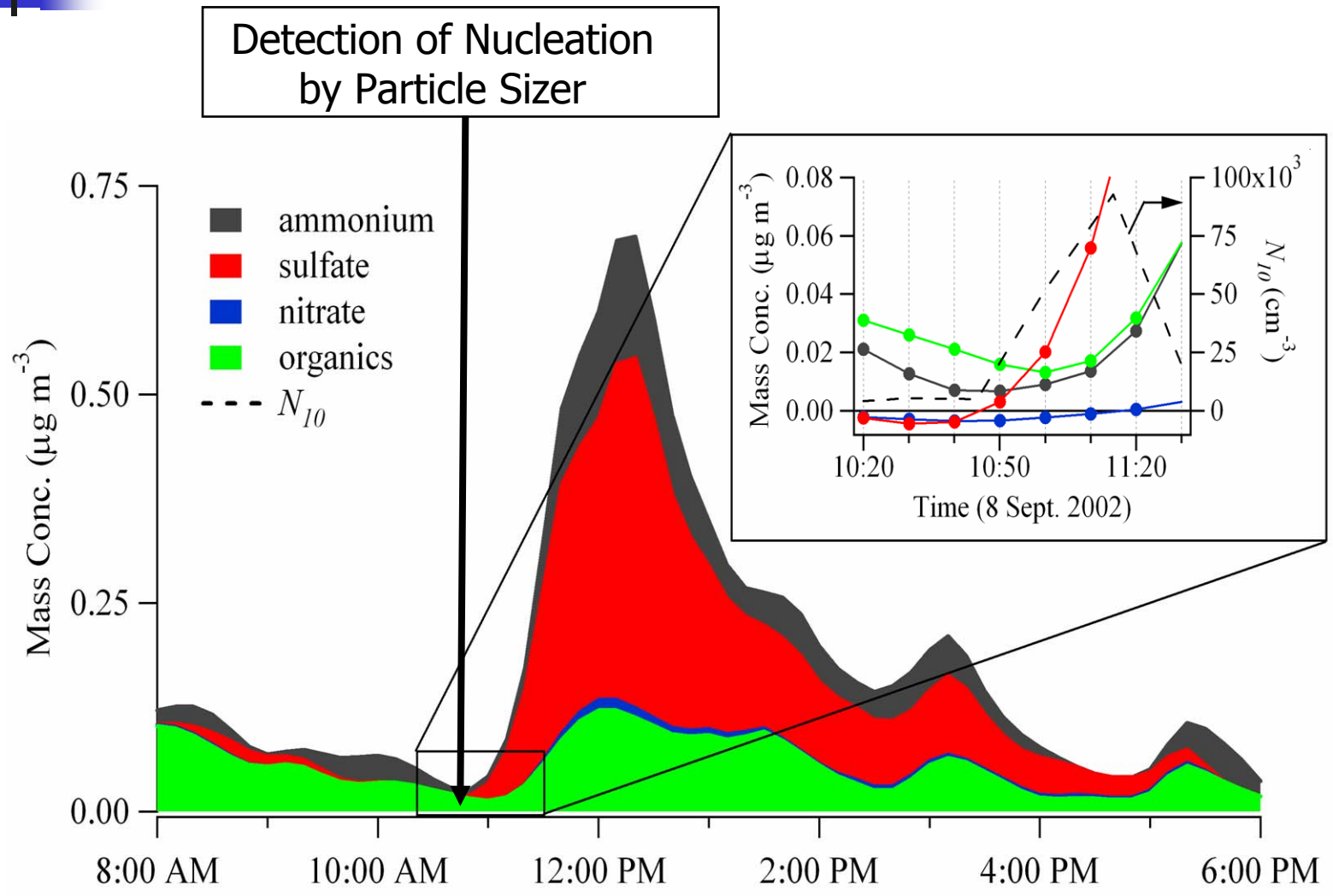


September 12, 2002 Nucleation Event

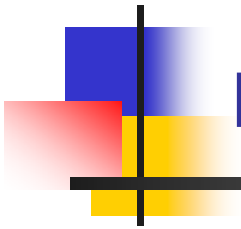


*Zhang & Jimenez (Univ. Colorado-Boulder)

Chemistry of Growth: Particle Mass Spectra at 20-33 nm



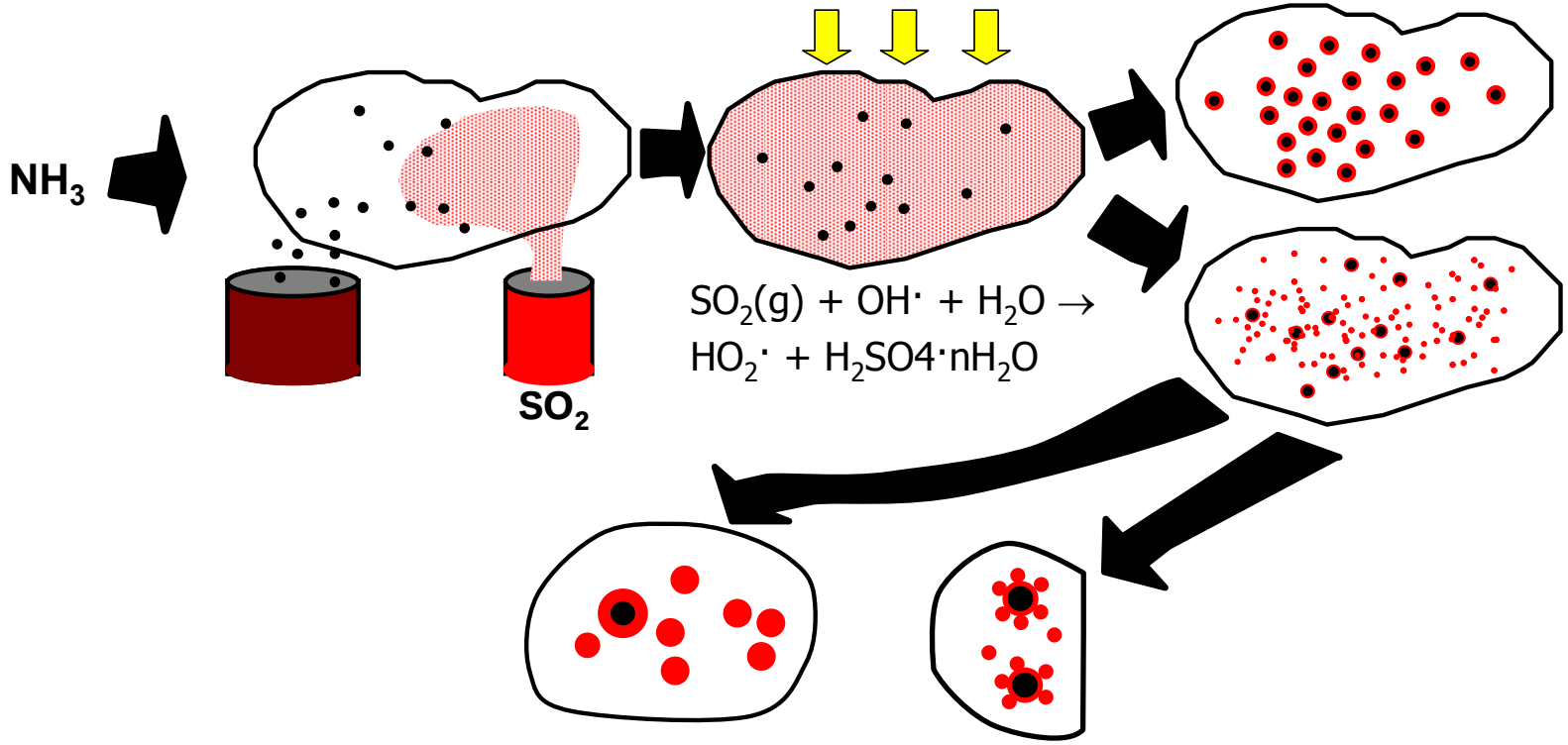
Zhang, et. al. Insights into the Chemistry of Nucleation Bursts and New Particle Growth Events in Pittsburgh based on Aerosol Mass Spectrometry. Environ. Sci. Technol., in press.



Modeling

Chemistry of Nucleation: Simulation[1]

Inputs	***Processes Modeled***	***Output***
Preexisting Aerosol Distribution	**SO_2 Oxidation to H_2SO_4**	**Predicted Aerosol Distribution**
SO_2 Concentration	**H_2SO_4-H_2O-NH_3 Nucleation**	
NH_3 Concentration	**H_2SO_4 Condensation**	
UV Light Intensity	**Particle Coagulation**	
Temperature & RH		



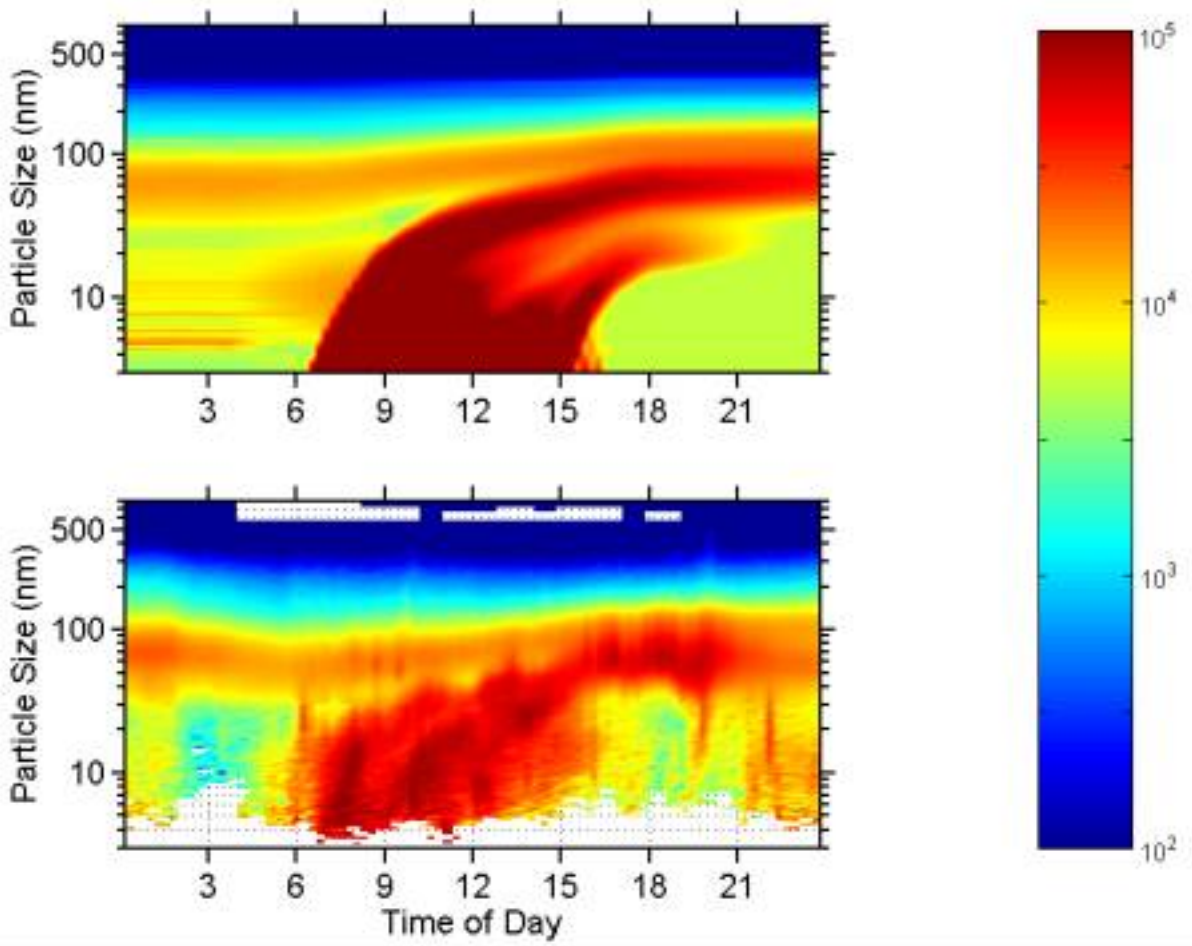
[1]Model adapted from Capaldo, Kasibhatla, Pandis. J. Geophys. Res., 1999.

Modeling H_2SO_4 Nucleation

- Photochemical box model
- Modeled gas-phase species:
  - SO_2, H_2SO_4, OH, NH_3
  - SO_2 measured, OH and NH_3 calculated from measurements
- 220 fixed size sections ranging in size from 0.8 nm to 10 μm
- T, RH, SO_2 and UV radiation from measurements
- Initial distribution available from dry size distributions
- Maximum OH concentration assumed for each month, scaled based on UV
  - 5×10^6 molecules/cm^3 in summer[1]
  - 1×10^6 molecules/cm^3 in winter[2]

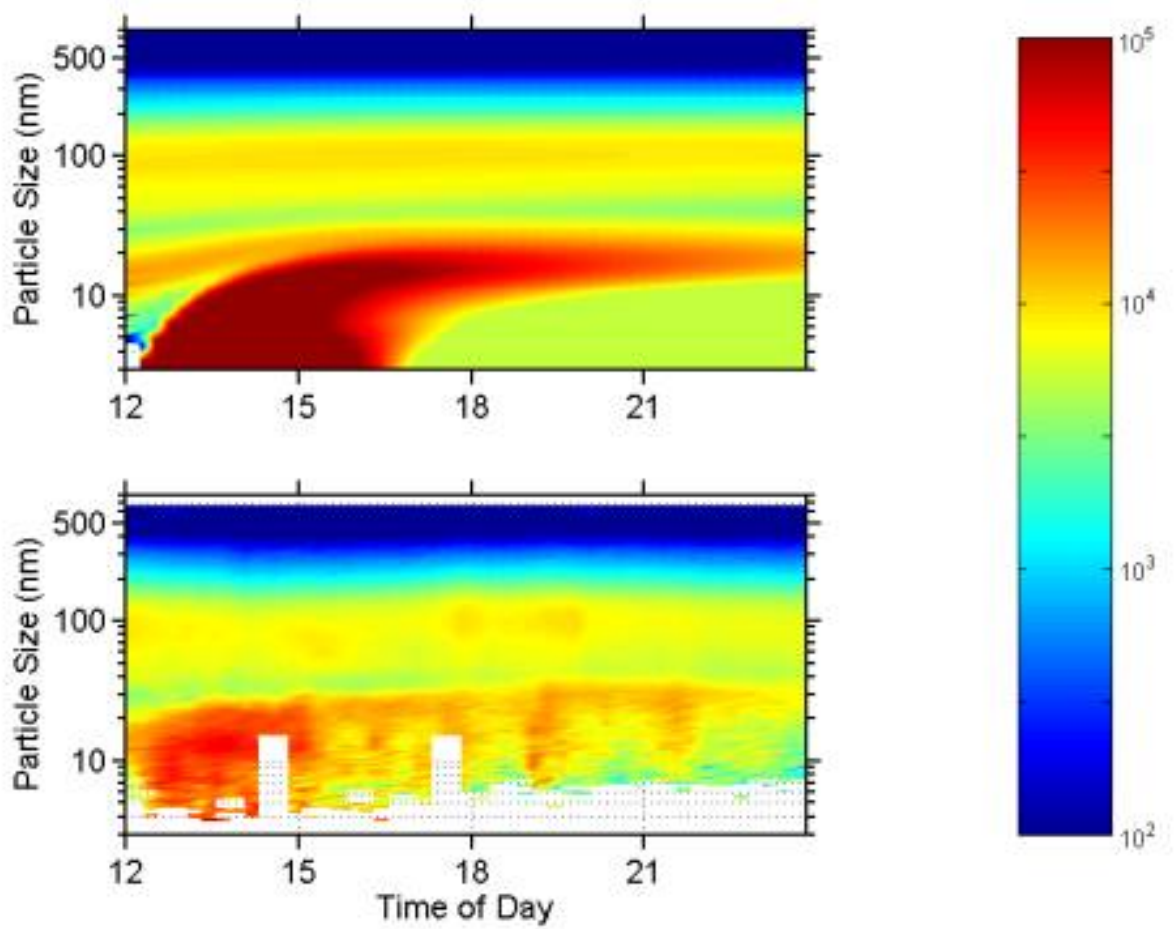
[1]Ren et al. (2003)
[2]Heard et al. (2001)

Comparison on July 27, 2001



- Model predicted presence or lack of nucleation on all 19 days
- Timing of onset of nucleation within one hour of observations for all 13 events
- Size and shape of growth curve consistent with observations
- High number concentrations predicted

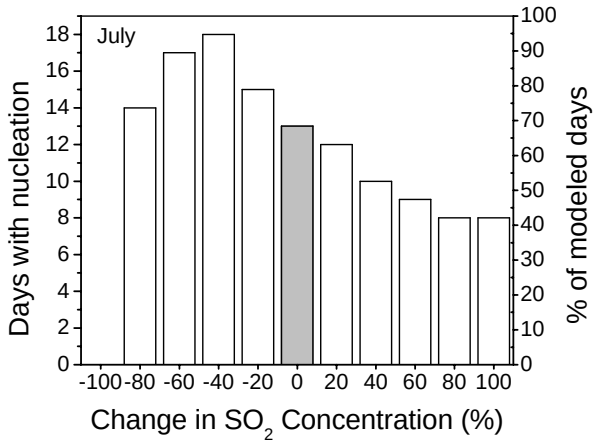
Comparison on January 28, 2002



- 25 out of 29 days predicted correctly
- Timing of onset of nucleation not as good (6 of 12 within one hour)
- Growth generally underpredicted with two exceptions
- High number concentrations predicted

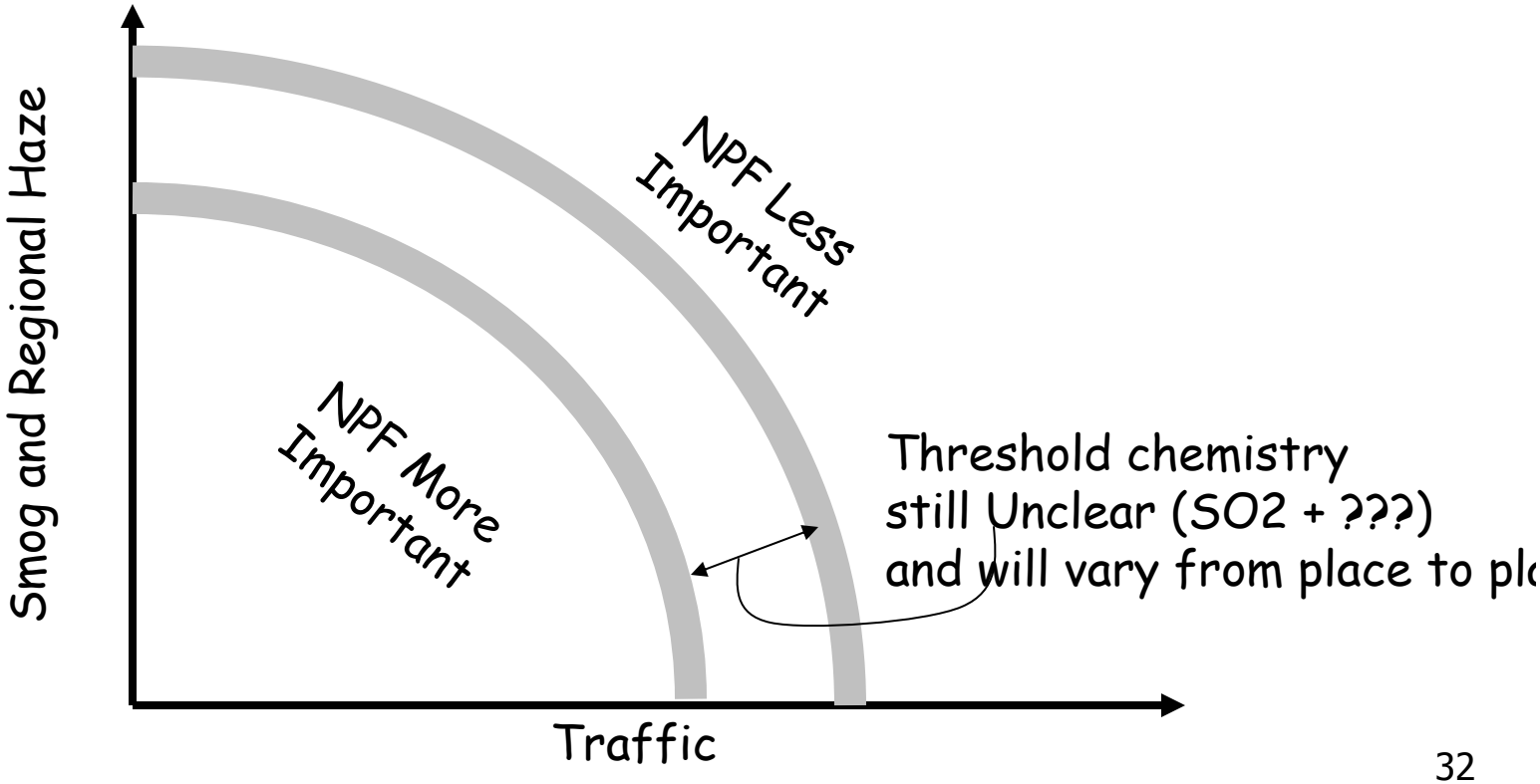
Sensitivities

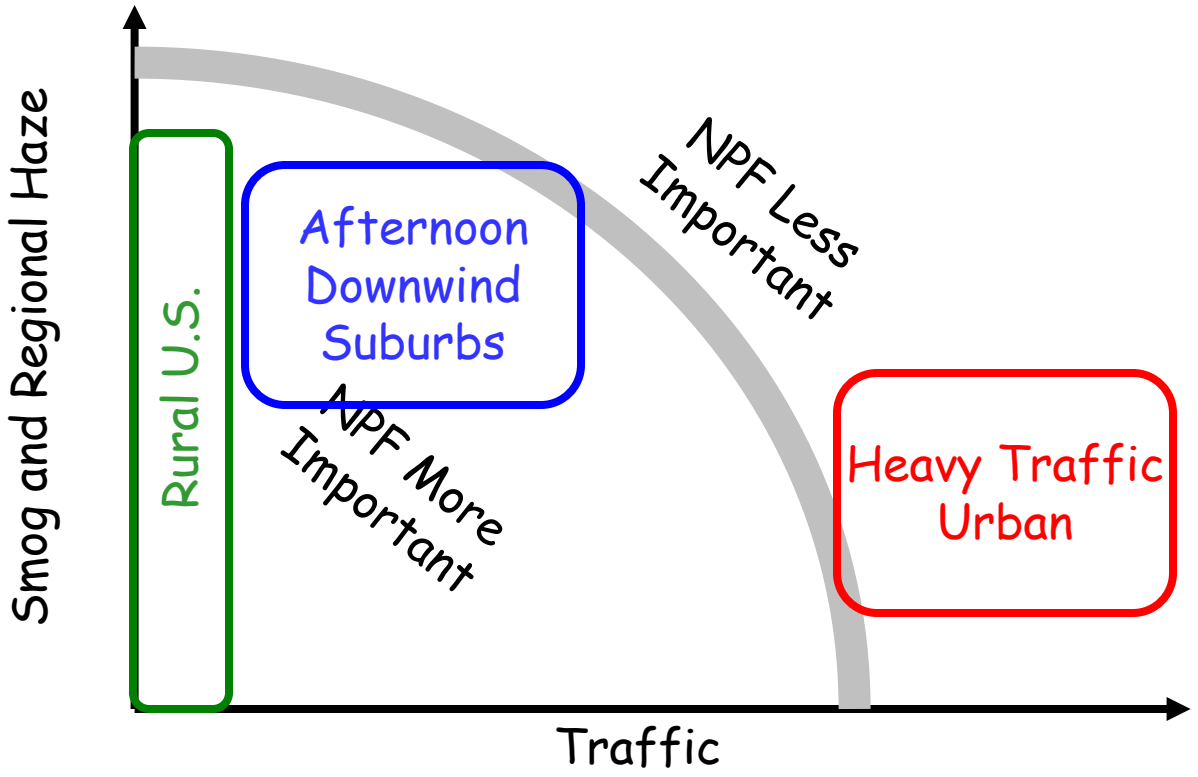
- NPF is thought to be sensitive to:
  - $PM_{2.5}$ ↓ NPF ↑
  - Ammonia ↑ NPF ↑ (but not sure how strong this effect)
  - SO_2 ↓ NPF ↓ (if NH_3 in excess … that covers most locations)
  - SO_2 ↓ NPF ↑ (if NH_3 limited, e.g. northeast U.S. in summer)
  - Reactive VOCs ↓ NPF ? – but growth of particles will be limited – so they will not last as long in the atmosphere



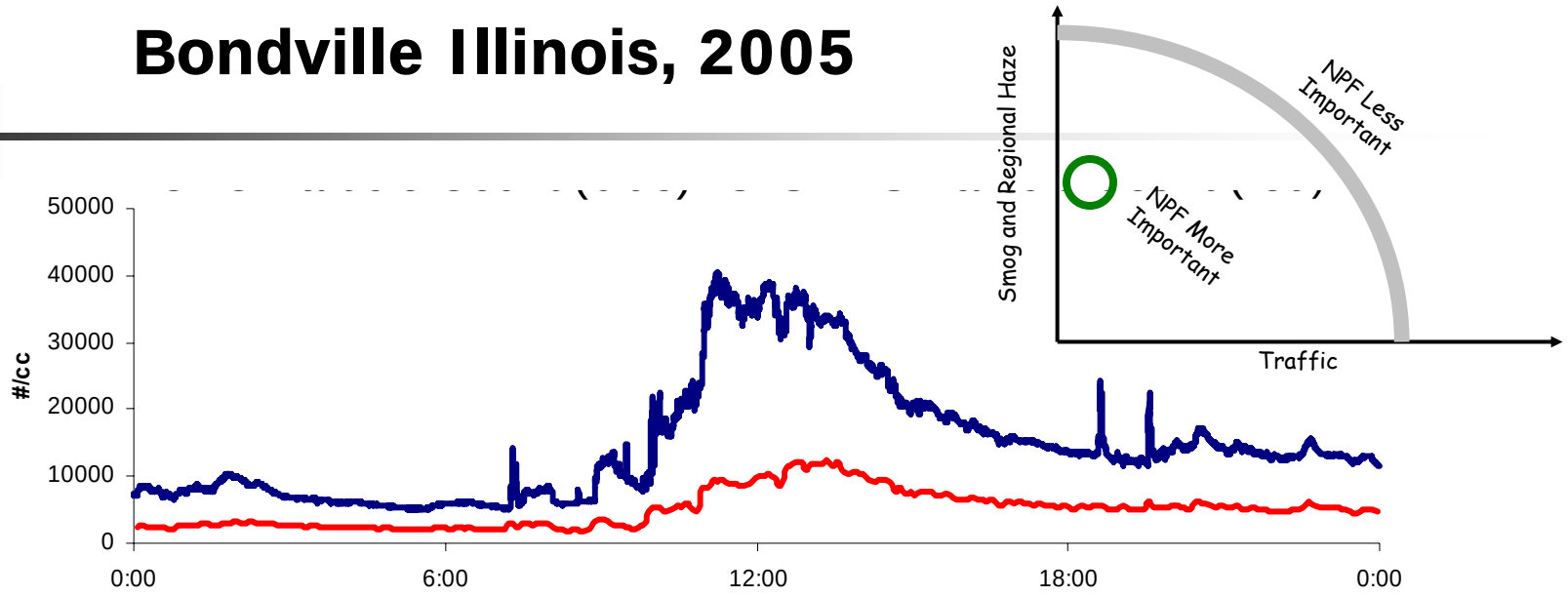
What fraction of ultrafines are from NPF?

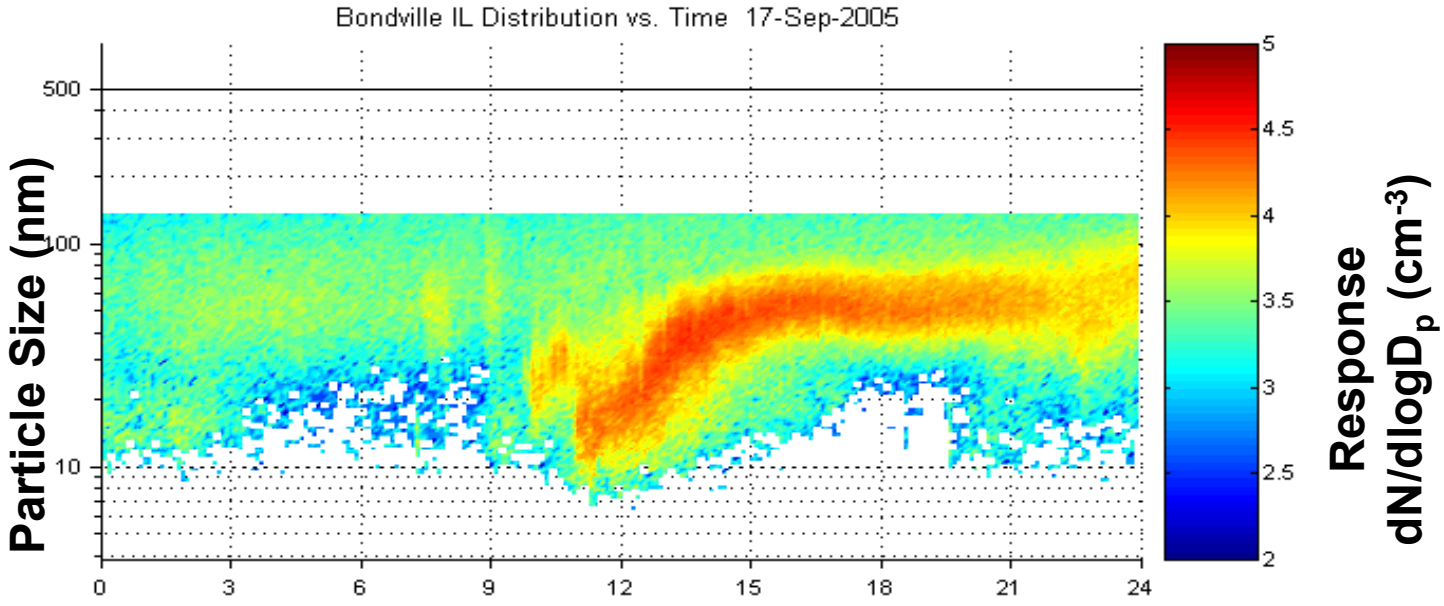
- To a large extent, we do not know
- Will vary by location
- NPF most important at midday and afternoons



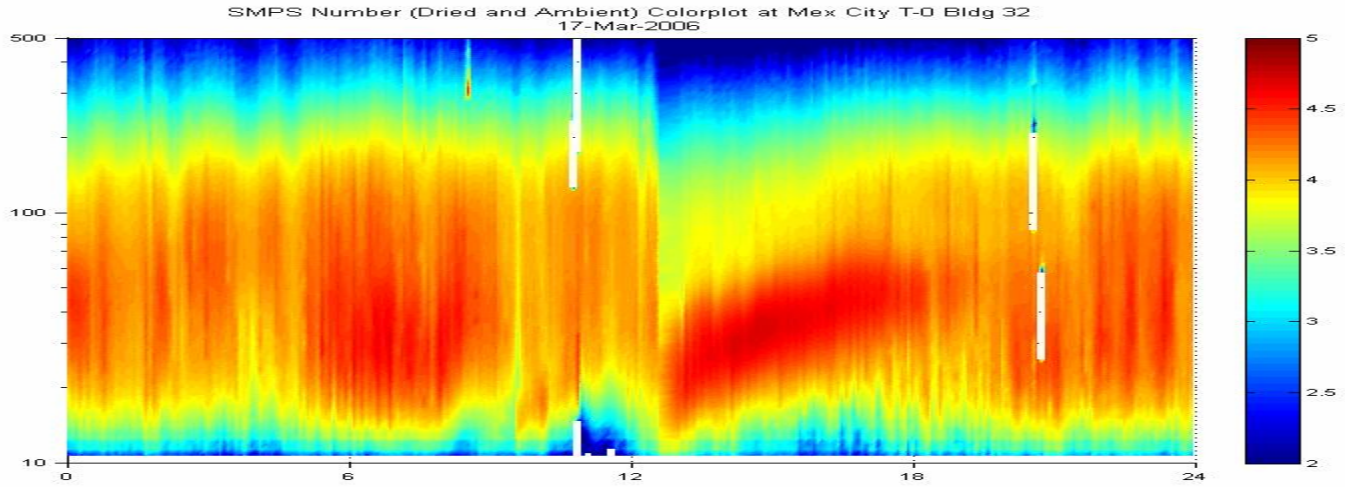

Smog and Regional Haze
Rural U.S.
Afternoon Downwind Suburbs
NPF More Important
NPF Less Important
Heavy Traffic Urban
Traffic

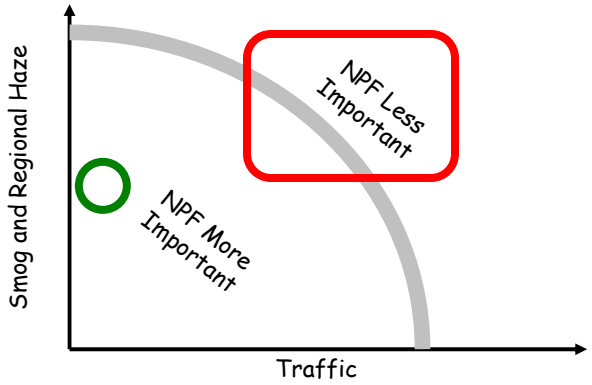
Bondville Illinois, 2005



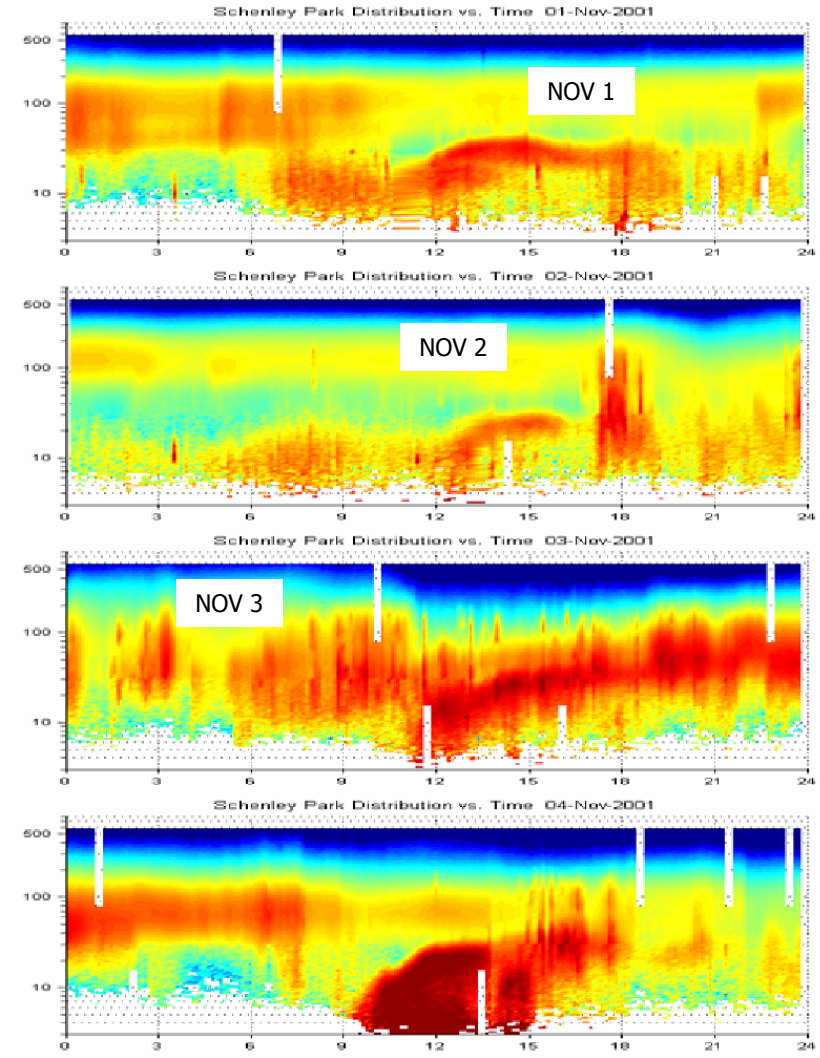


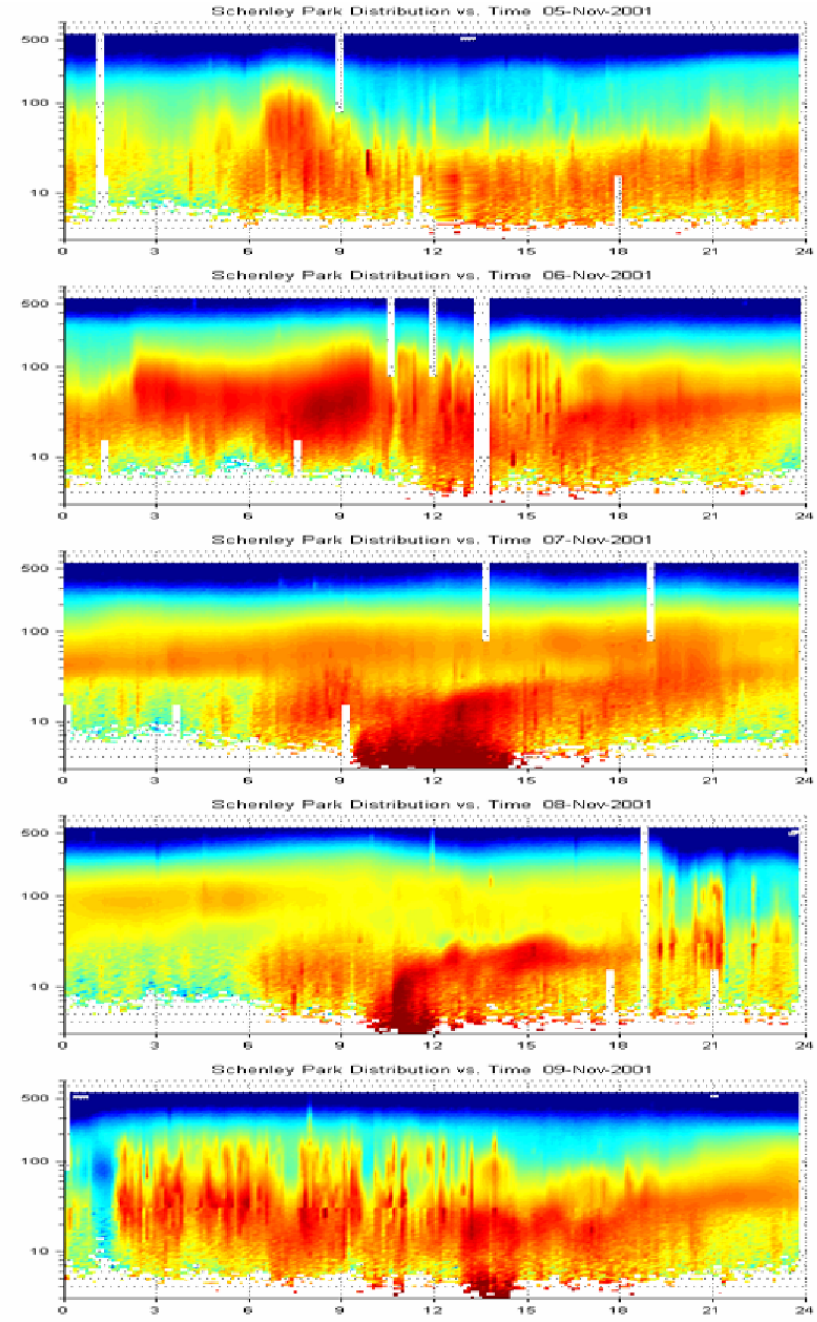
Mexico City Mar 17, 2006



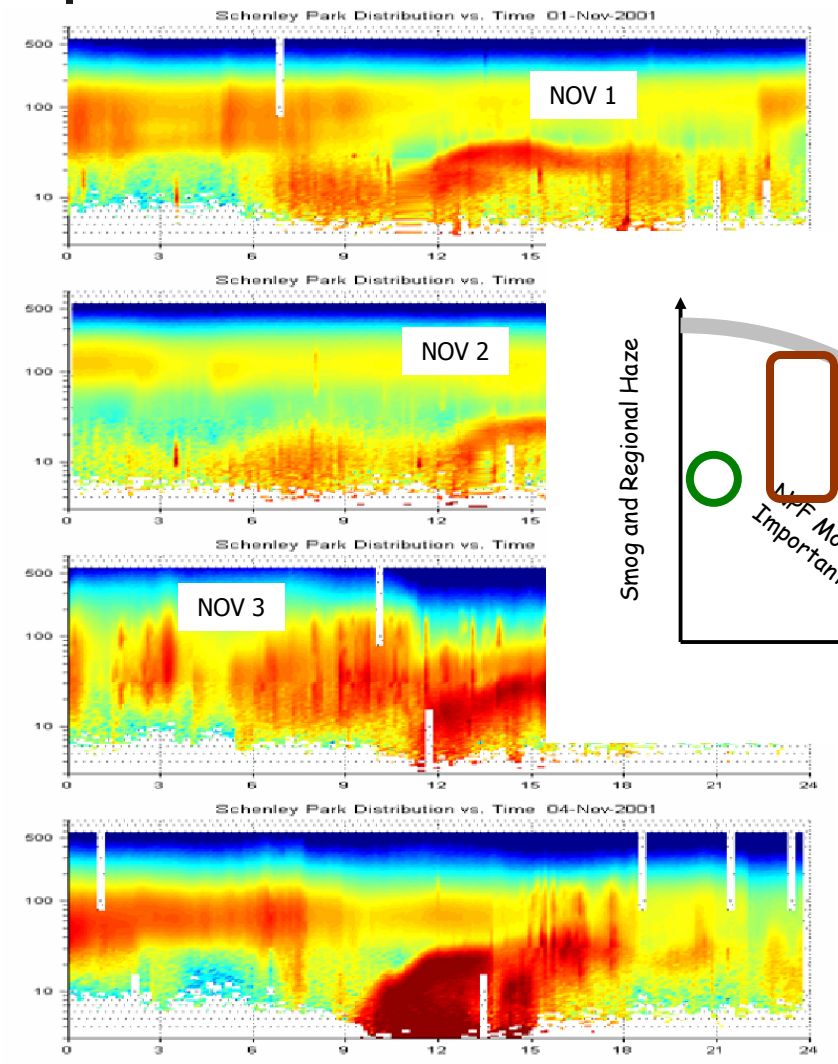


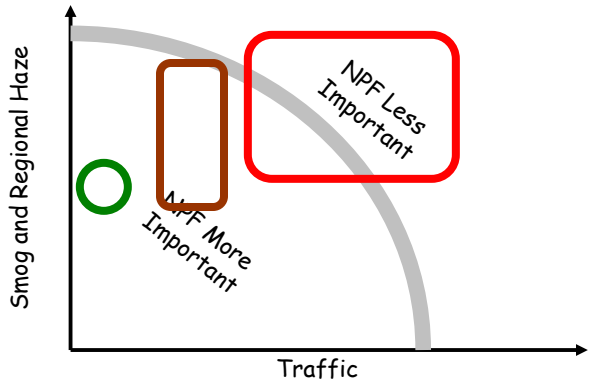
Pittsburgh PA



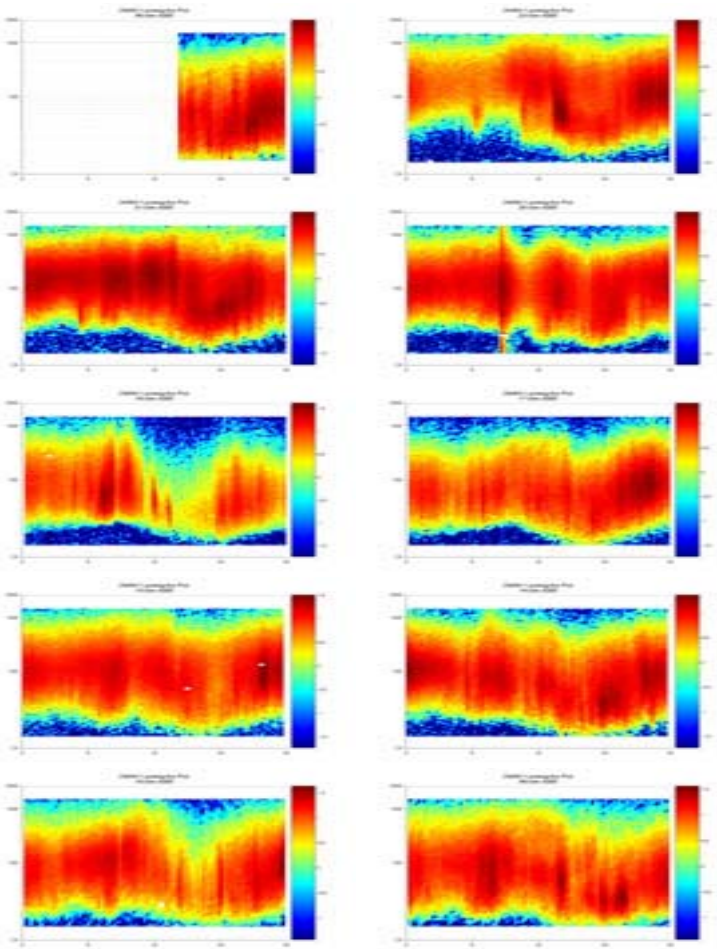


Pittsburgh PA

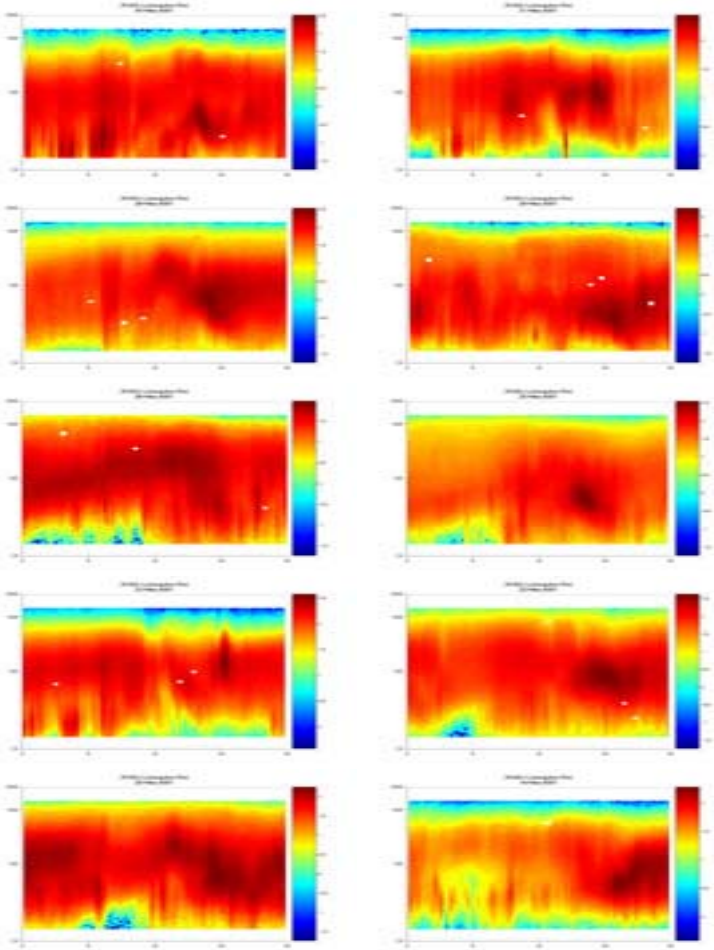




DOWNY DEC 2000

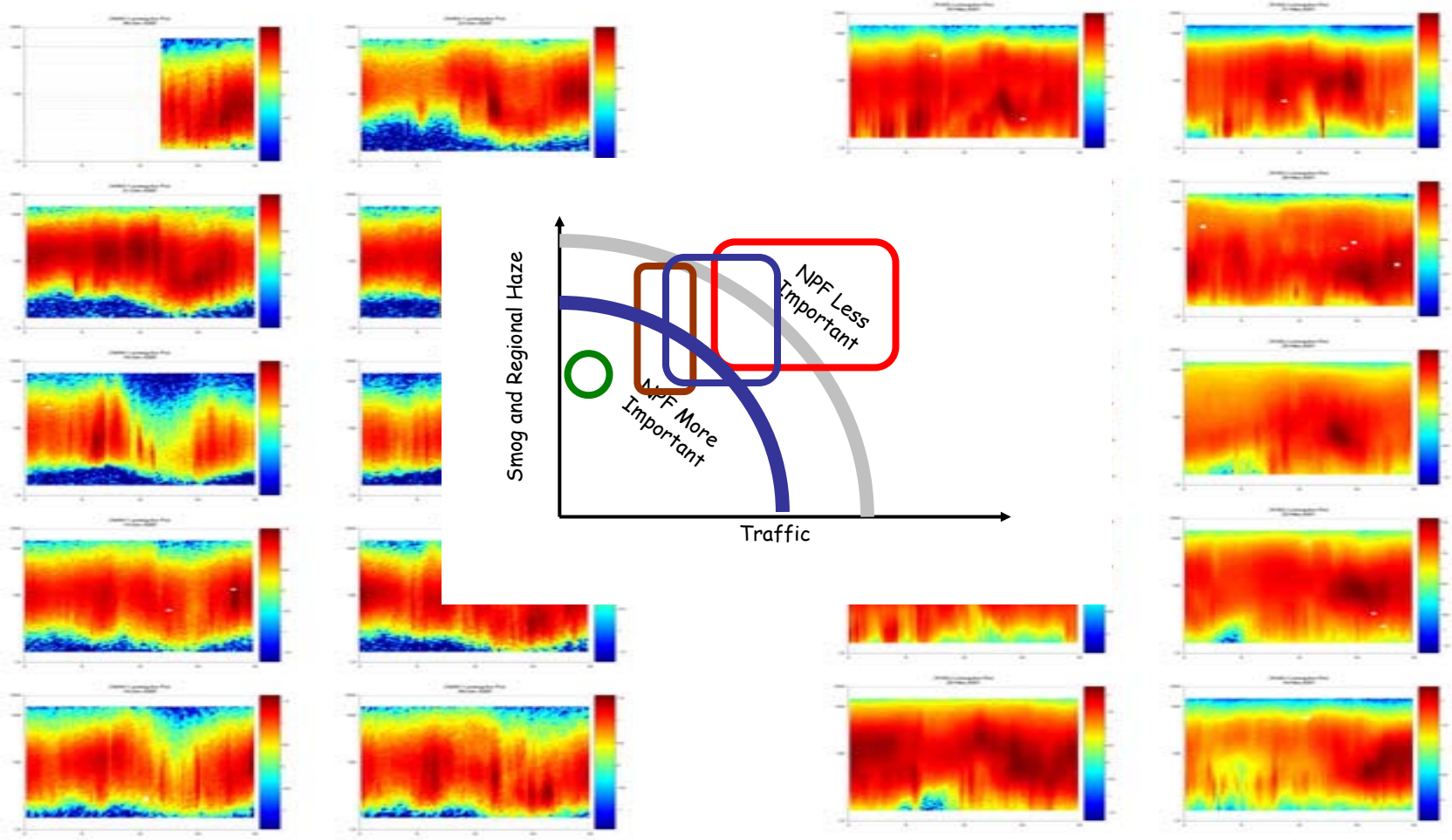


RIVERSIDE MAY 2001



DOWNY DEC 2000

RIVERSIDE MAY 2001



Future Work

- In the process of summarizing comparisons between Pittsburgh, Rochester, New York City, Atlanta, LA, and St. Louis.
- Unify measurements, detailed modeling, and a "screening" model that attributes ultrafines to traffic vs. new particle formation
- Sort out some details of chemistry and meteorology
- Monitor how implementation of further sulfur reductions from power plants, and advanced diesel influence new particle formation

Acknowledgements

Students:

Alicia Kalafut – Ultrafine Particle Sampling

Kazeem Olanrewaju – Ultrafine Particle Modeling

University of Iowa Callaborators:

Greg Carmichael, Jerry Schnoor, Bill Eichinger

Carnegie Mellon Collaborators:

Spyros Pandis, Tim Gaydos, Andrey Khlystov,

Outside Collaborators:

Allen Williams

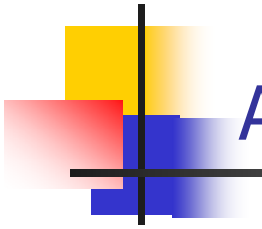
Illinois Soil and Water Survey

Peter McMurry

University of Minnesota

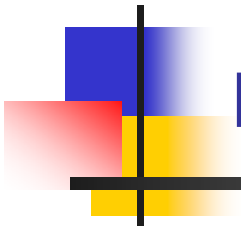
Jimenez Group, University of Colorado-Boulder

Jose-Luis Jimenez & Qi Zhang



Additional Material

- Modeling Framework
- Future Work
- Measurement Technique
- Traffic and Modeling
- Bondville
- Mexico
- Background on PM



Modeling framework

Modeling H_2SO_4 Nucleation

- Photochemical box model
- Modeled gas-phase species:
  - SO_2, H_2SO_4, OH, NH_3
  - SO_2 measured, OH and NH_3 calculated from measurements
- 220 fixed size sectoins ranging in size from 0.8 nm to 10 µm

$$\frac{\partial C_{H_2SO_4}}{\partial t} = R_{gas}\left(SO_2, OH, T, P\right) + n^* R_{nuc}\left(C_{H_2SO_4}, NH_3, T, RH\right)$$
$$+ R_{cond}^{H_2SO_4}\left(C_{H_2SO_4}, RH\right) - R_{dep}\left(C_{H_2SO_4}\right)$$

$$\frac{\partial N_i}{\partial t} = R_{nuc}\left(C_{H_2SO_4}, NH_3, T, RH\right)$$
$$+ R_{coag}\left(N_j, RH\right) + R_{cond}^{N_i}\left(C_{H_2SO_4}, RH\right) - R_{dep}\left(N_i\right)$$

Sulfuric Acid Nucleation Formation

$$SO_2 + OH^{\cdot} + M \rightarrow HOSO_2^{\cdot} + M$$

$$HOSO_2^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + SO_3(g)$$

$$SO_3(g) + H_2O + M \rightarrow H_2SO_4(g) + M$$

$$H_2SO_4(g) + nH_2O(g) \rightarrow H_2SO_4 \cdot nH_2O(aq)$$

$$SO_2(g) + OH^{\cdot} + O_2 + (n+1)H_2O \rightarrow HO_2^{\cdot} + H_2SO_4 \cdot nH_2O(aq)$$

Chemistry and deposition

- Sulfuric acid is produced from the reaction of SO_2 and OH[1]

$$R_{gas} = k_{SO_2}[SO_2][OH]$$

- Deposition:

$$R_{dep} = \frac{v_{dry,i} c_i}{H}$$

  - v_{dep} for aerosol dependent on particle size[2], 1.0 cm/s used for H_2SO_4 [3]

[1] k_{SO2} from DeMore et al. (1994)

[2] Hummelshoj et al. (1992)

[3] Brook et al. (1999)

Condensation

- Condensation rate:

$$J = 2\pi N_i D D_p F(Kn) A(p - p_0)$$

- Change in number concentration:

$$R_{cond}^{N_i} = F_{i-1} N_i C_{H_2SO_4} - F_i N_i C_{H_2SO_4}$$

- Flux between fixed sections:

$$F_i = \frac{6 M_{H_2SO_4} K_{mt}^i D_p}{RT\rho\pi\left[\left(D_p^{i+1}\right)^3 - \left(D_p^i\right)^3\right]}$$

Coagulation

- Coagulation rate:

$$R_{coag} = \frac{1}{2}\sum_{j=1}^{k} f_k K_{j,k-j} N_j N_{k-j} - N_k \sum_{j=1}^{\infty} K_{k,j} N_j \quad , \quad k \geq 2$$

- Generalized coagulation coefficient*

$$K_{12} = 2\pi\left(D_{p1} + D_{p2}\right)\left(D_1 + D_2\right)\beta$$

- Linear interpolation to preserve mass, number:

$$f_k = \frac{V_{k+1} - V_p}{V_{k+1} - V_k}$$

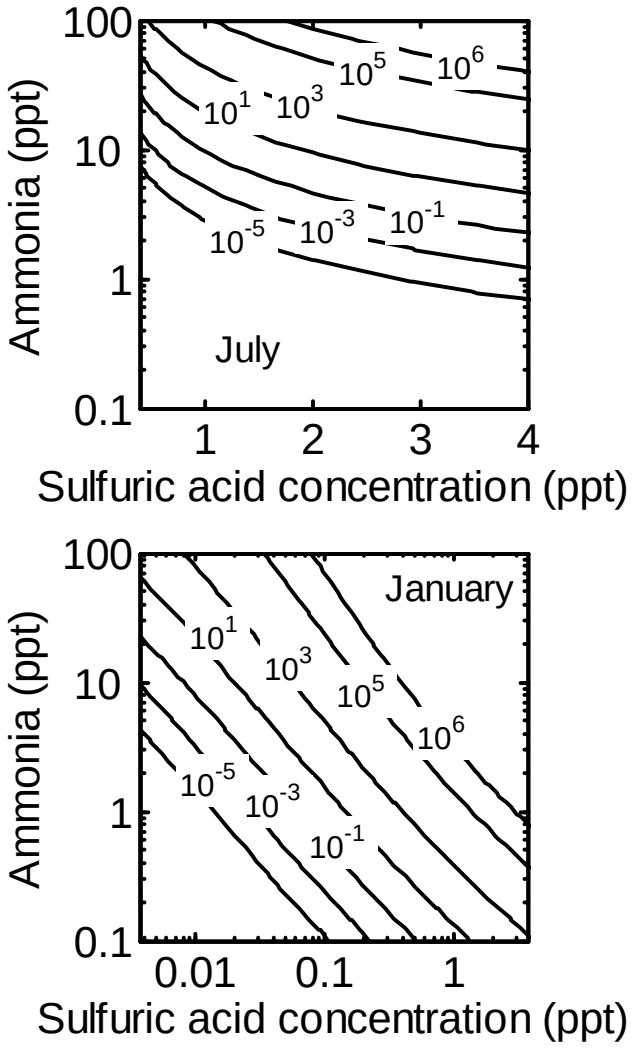
$$f_{k+1} = \frac{V_p - V_k}{V_{k+1} - V_k}$$

*β calculated using method of Fuchs, (1964)

Ternary nucleation correlation

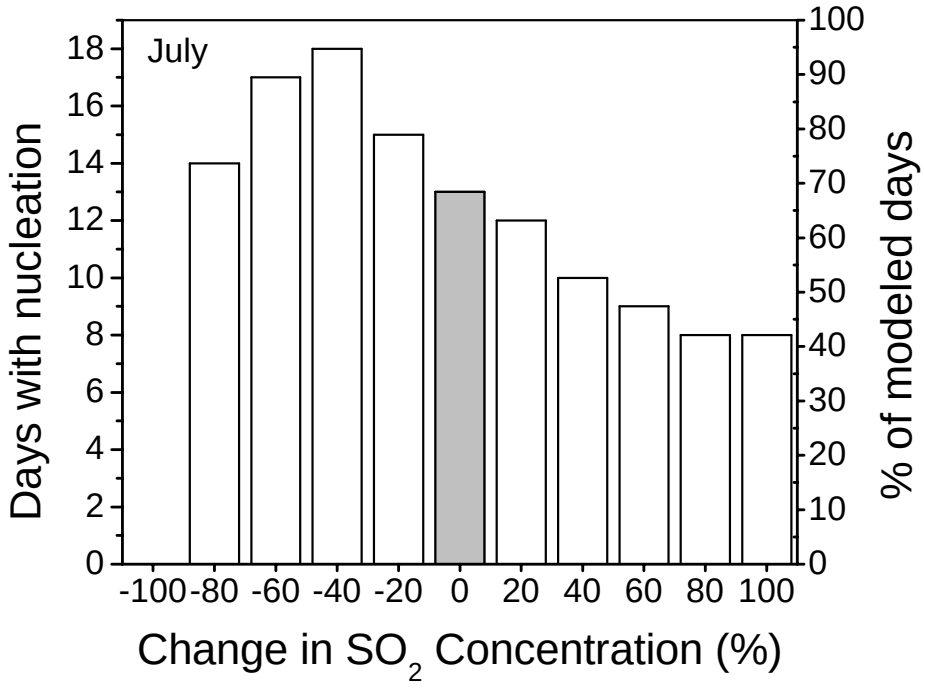
- Parameterization from Napari et al. (2002)
  - Calculates nucleation rate using parameters of T, RH, NH_3, H_2SO_4
- Approximation for initial nuclei size dependent on nucleation rate and T
  - 1 nm under typical July conditions
  - 0.8 nm under typical January conditions
- Approximation for composition of initial nuclei, also dependent on nucleation rate and T
  - Approximately 4 molecules of sulfuric acid, 4 of ammonium in July
  - 2 molecules of sulfuric acid, 2 of ammonium in January

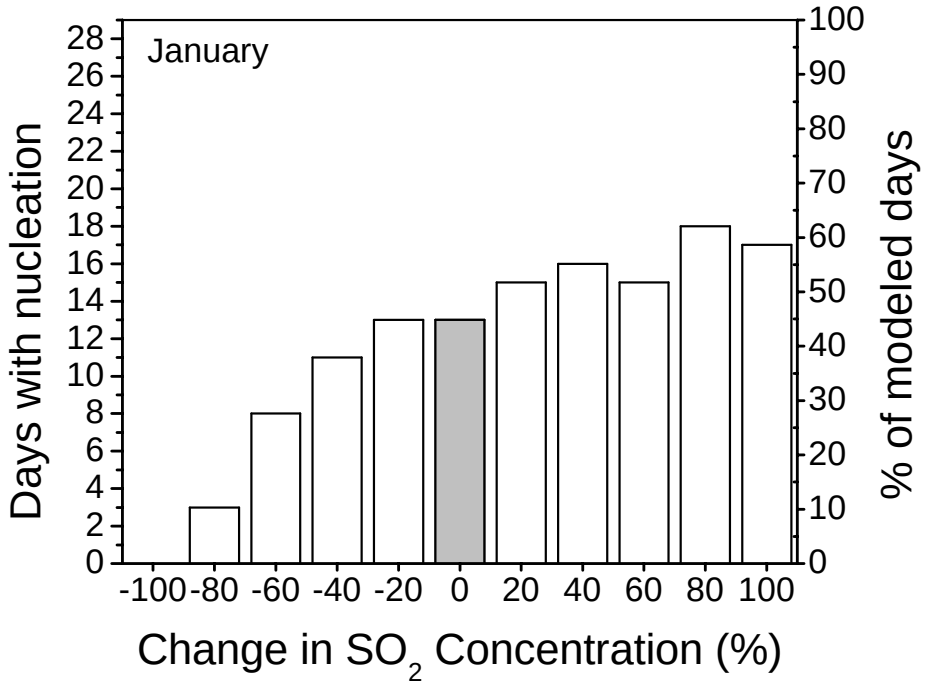
Nucleation rates



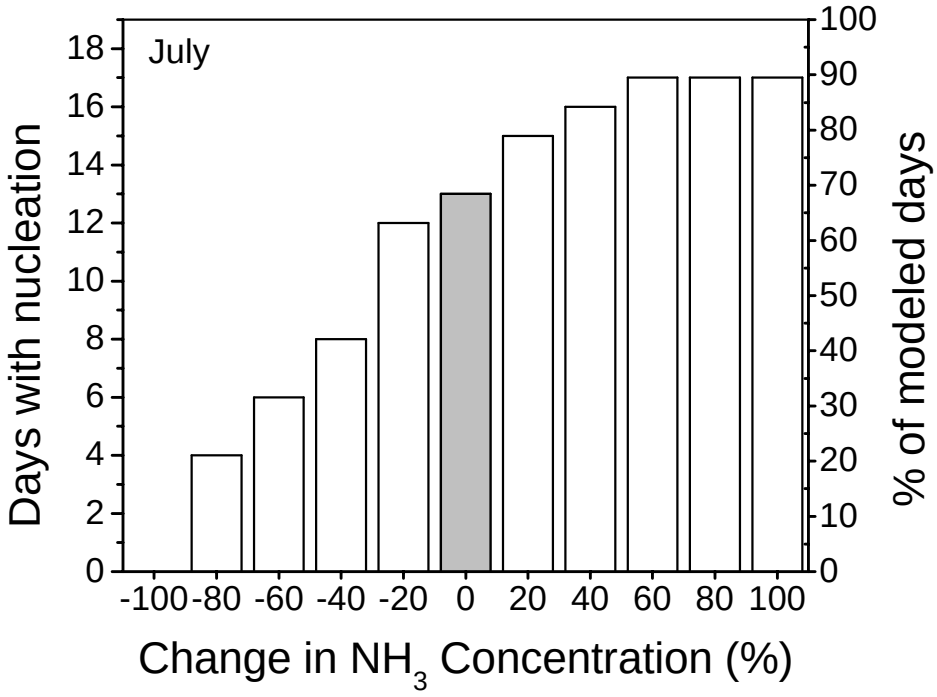
- Presence of gas-phase ammonia necessary for nucleation in July
  - 10 ppt generally enough
- Both ammonia and sulfuric acid play important role in January
  - Cloud cover, weaker UV radiation limit production of sulfuric acid

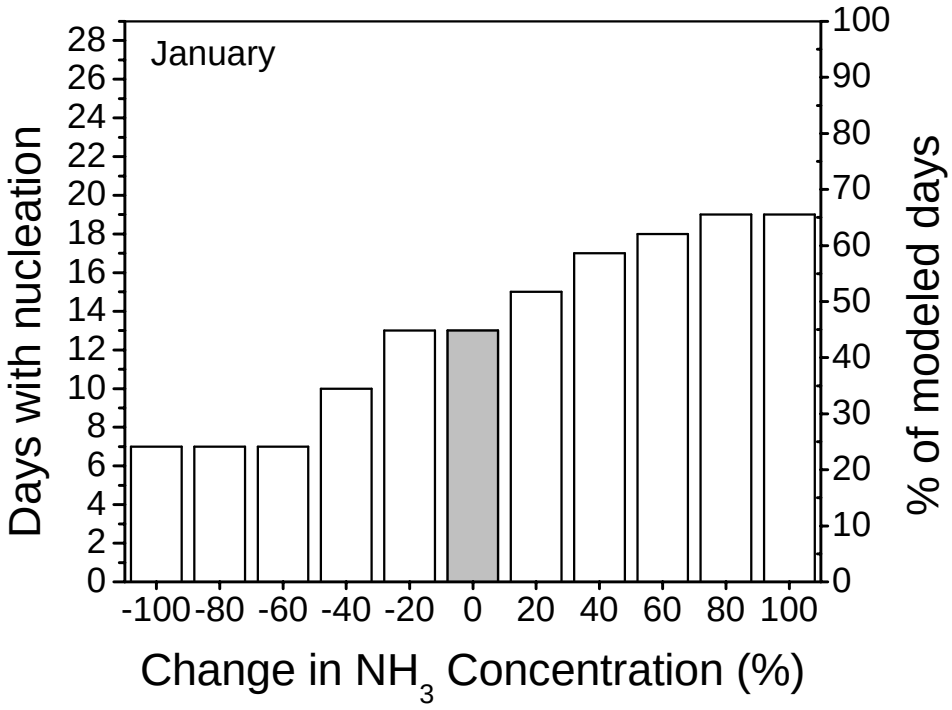
Sensitivity to SO_2 Emissions

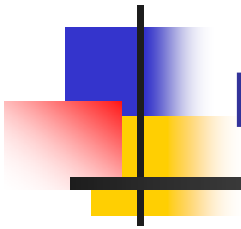




Sensitivity to NH_3 Emissions





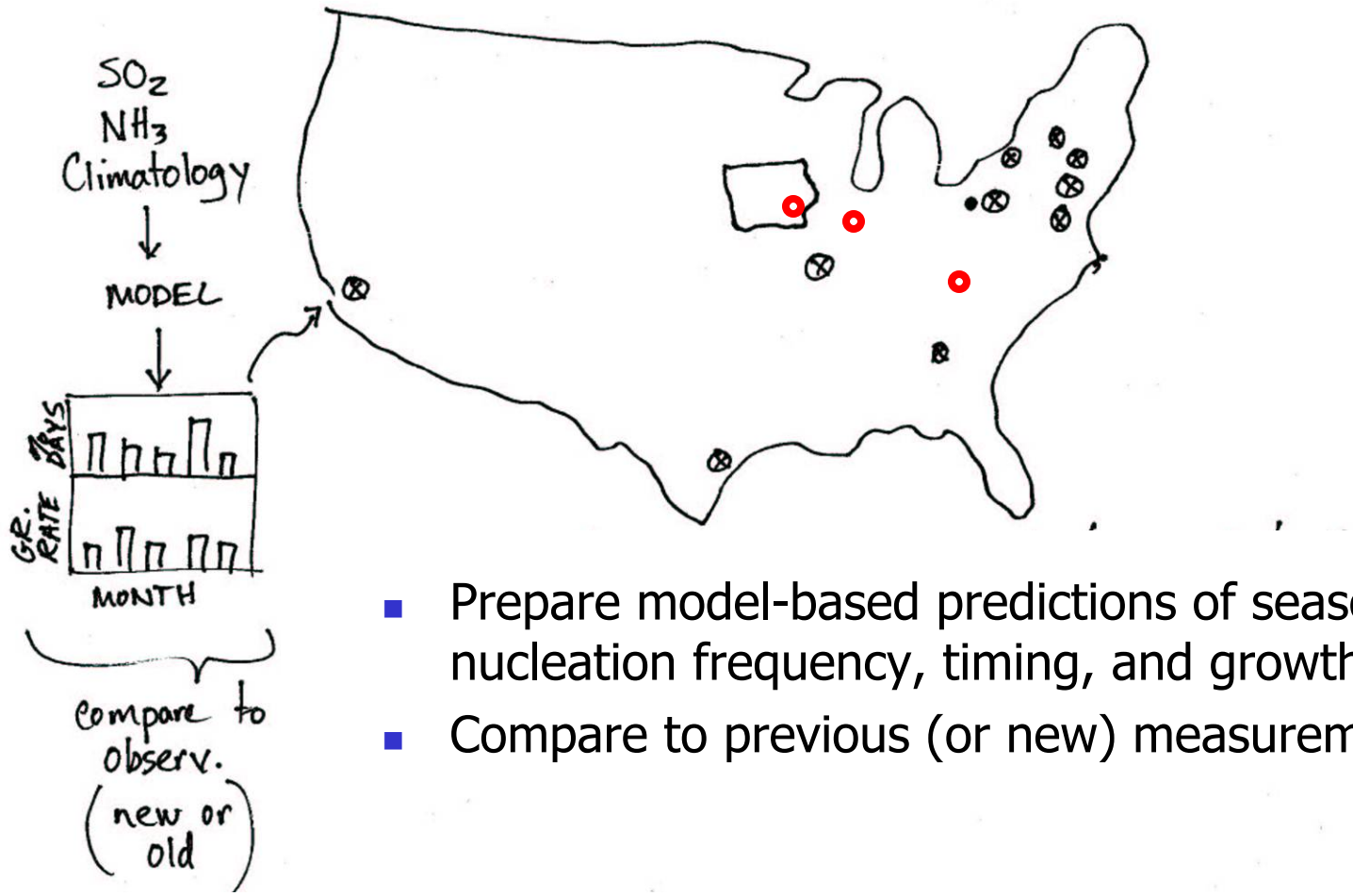


Future Work

Observational Analysis

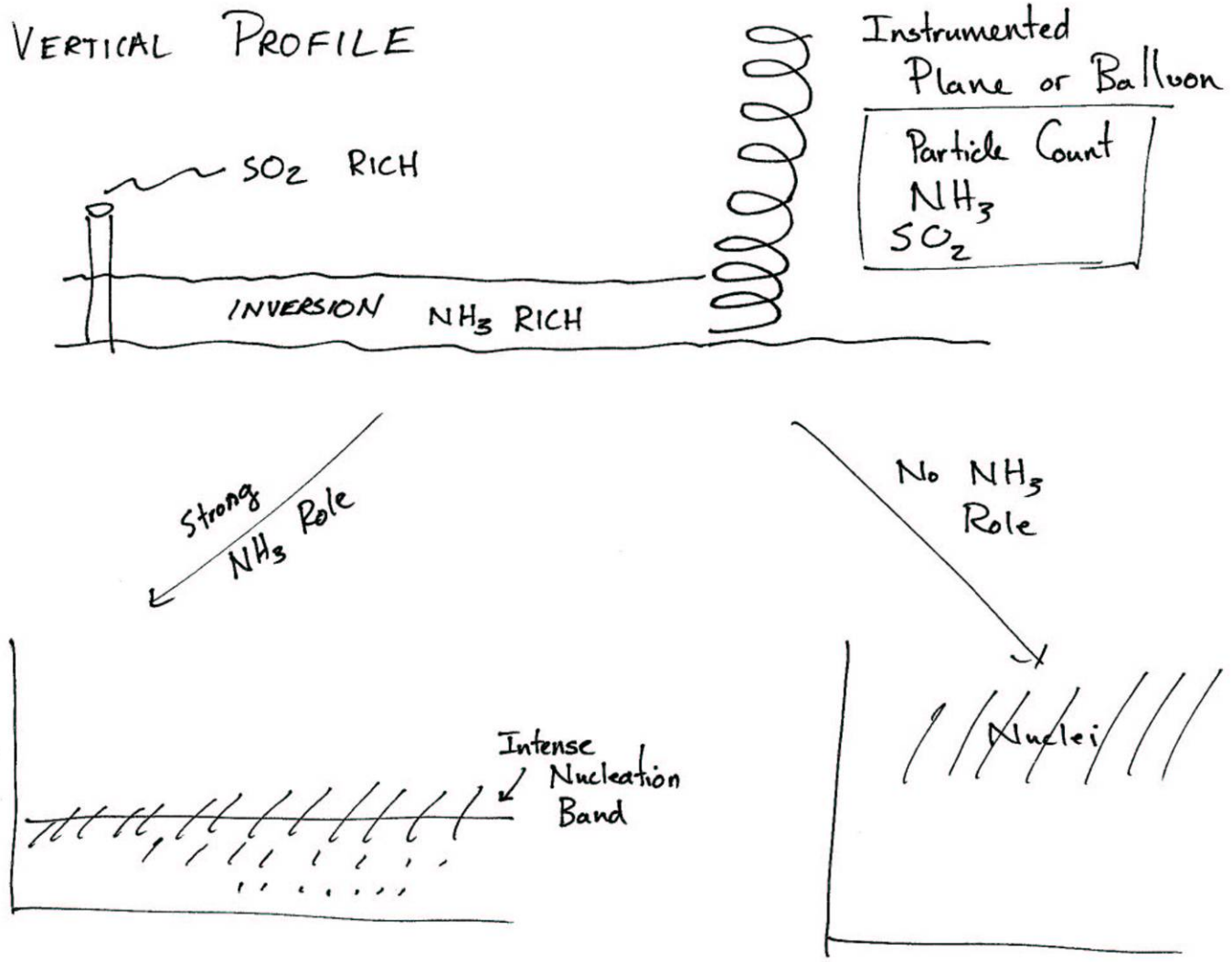
- Determine spatial extent of nucleation from "Supersite" 2001 observations and compare to SO_2 and NH_3 maps.

Observation-Model Hybrid

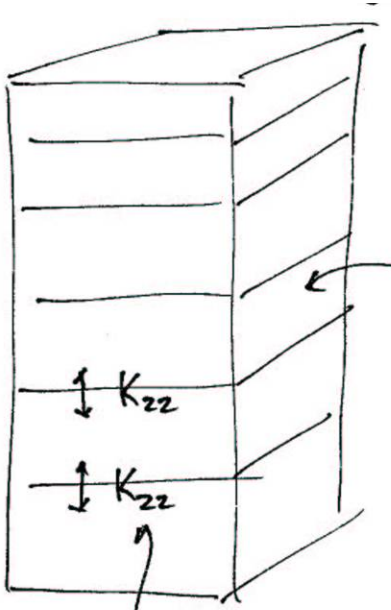


- Prepare model-based predictions of seasonal nucleation frequency, timing, and growth rate
- Compare to previous (or new) measurements

Vertical Profile Sampling



Vertical Mixing Models



$$\frac{\partial c}{\partial t} \propto \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial c}{\partial z}\right)$$

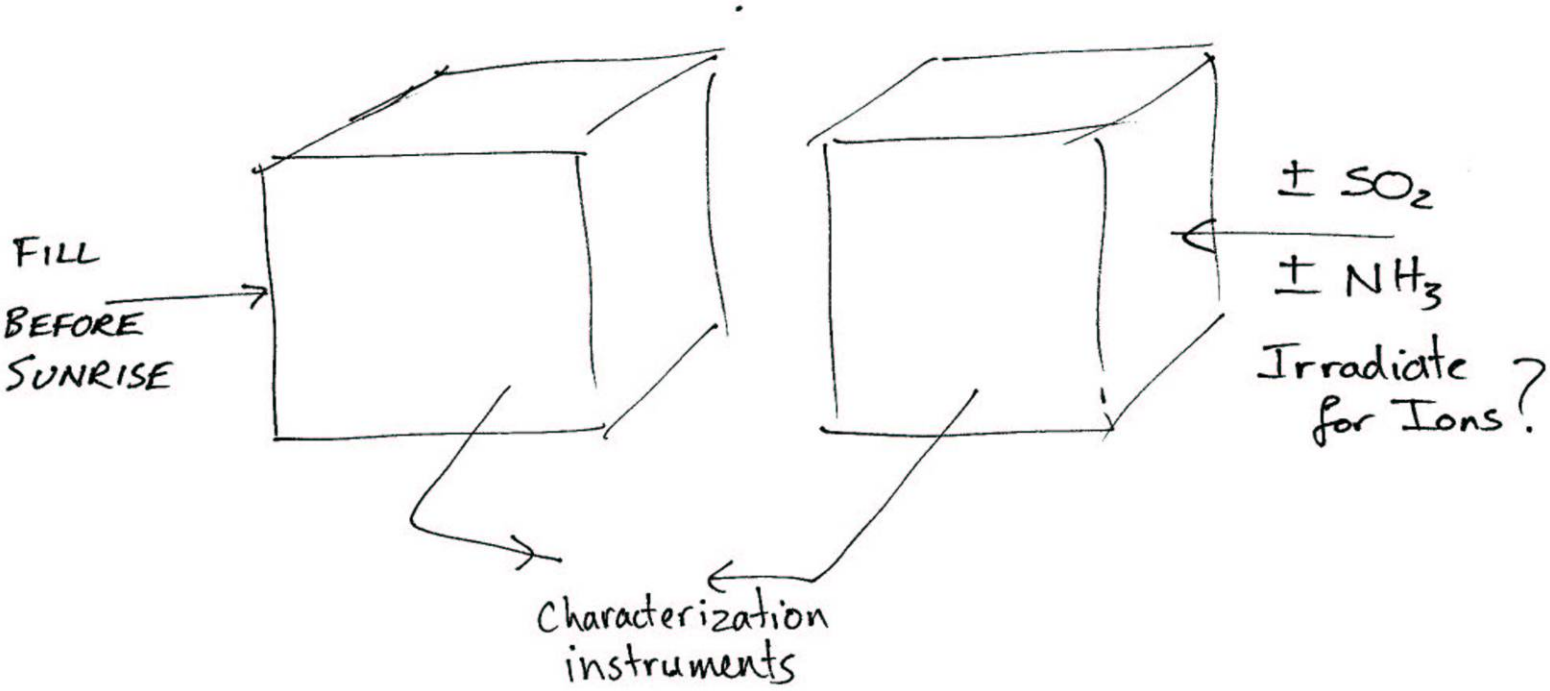
vertical eddy diffusion coefficient from Monin-Obukhov similarity theory

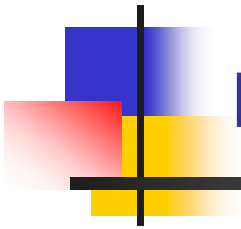
$$K_{zz} = \frac{k u_* z}{\phi(z/L)}$$

Function Dependent on Stability Class

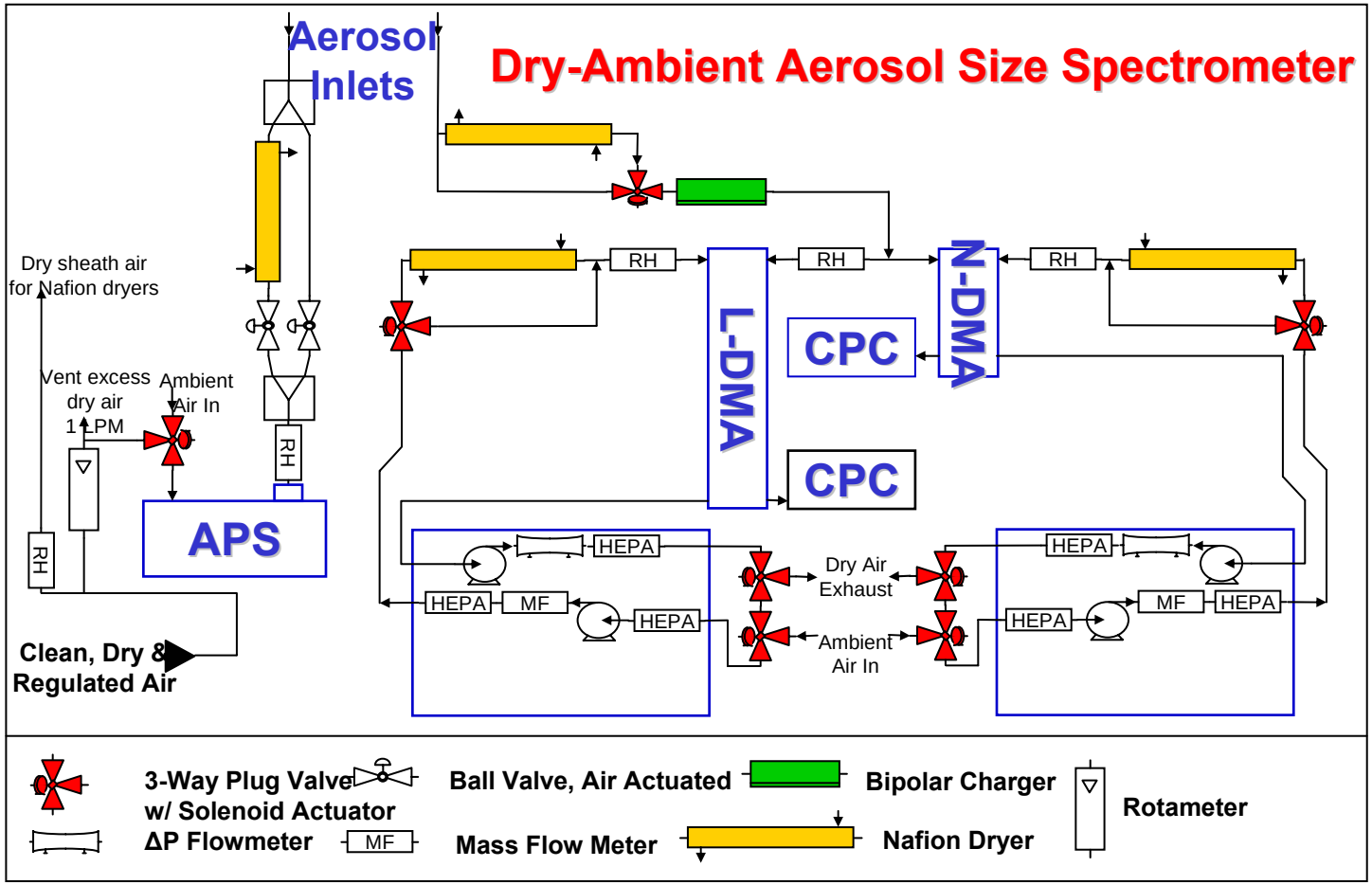
Monin-Obukhov Length

Perturbed Real Air Samples



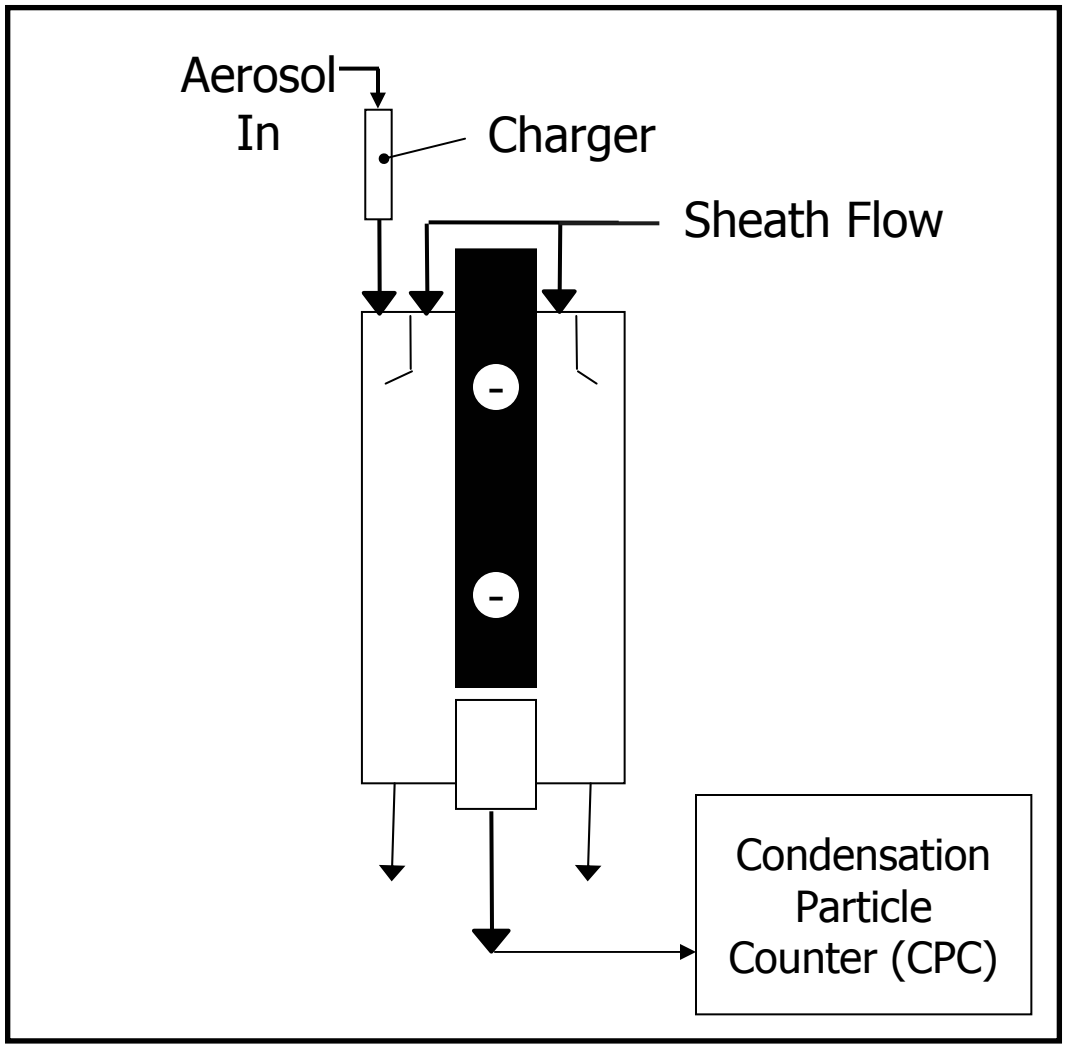


Measurement technique

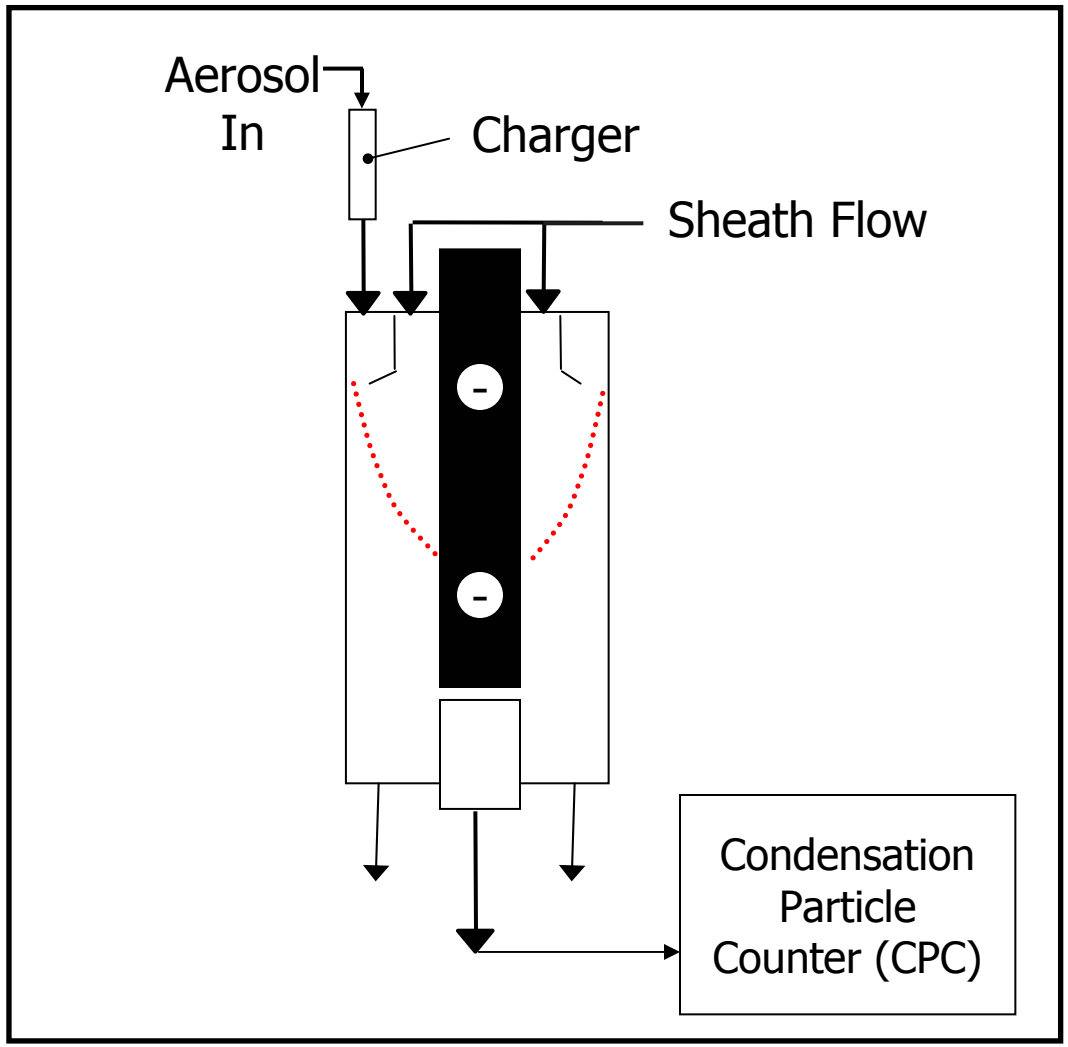


- Add RH controlled inlets (aerosol water measurement)
- Control & data acquisition hardware and software
- Data processing software to make 6 instruments behave like 1
- Extensive calibration
- Synthesis with other instruments and web-based data visualization

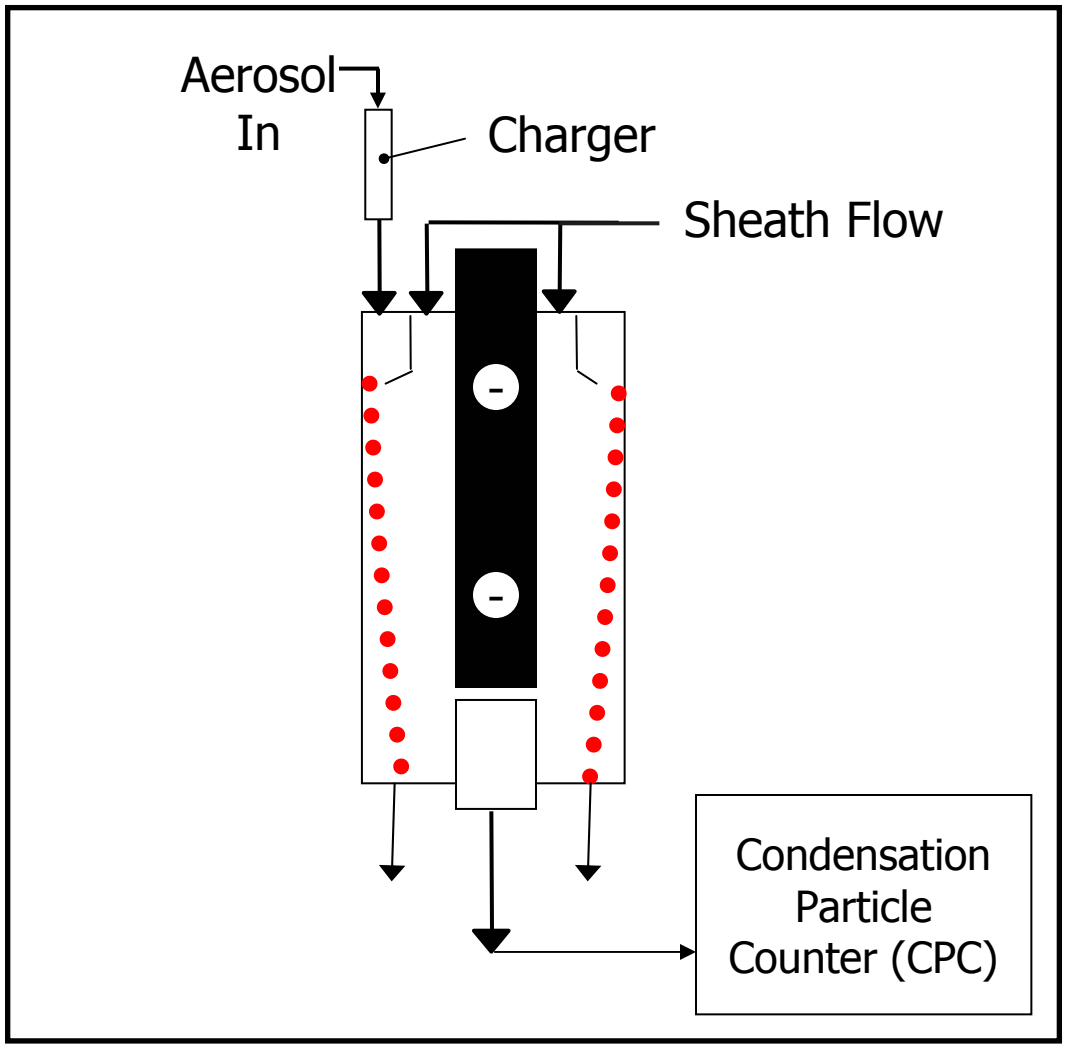
Scanning Mobility Particle Sizer



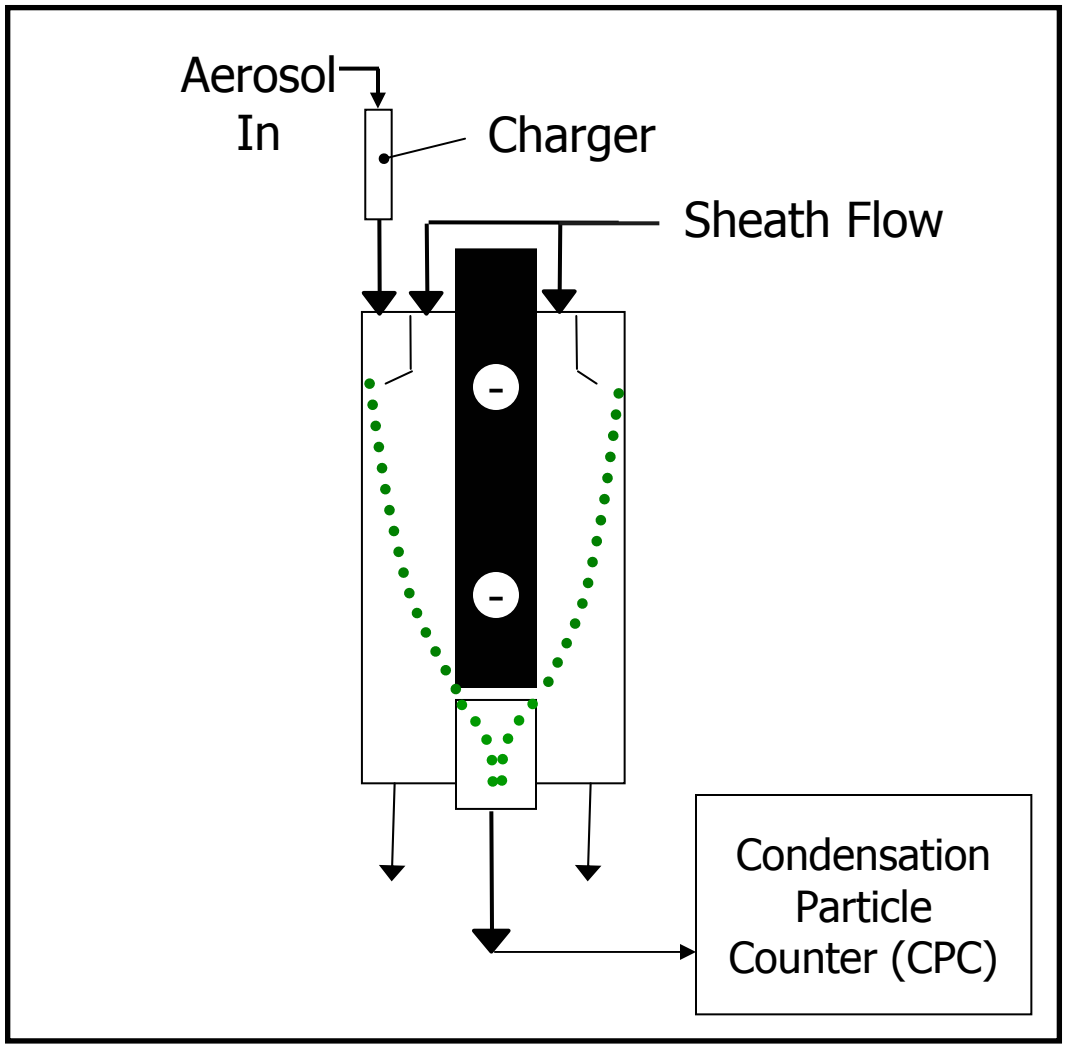
Scanning Mobility Particle Sizer

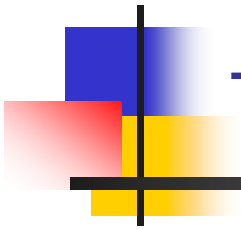


Scanning Mobility Particle Sizer



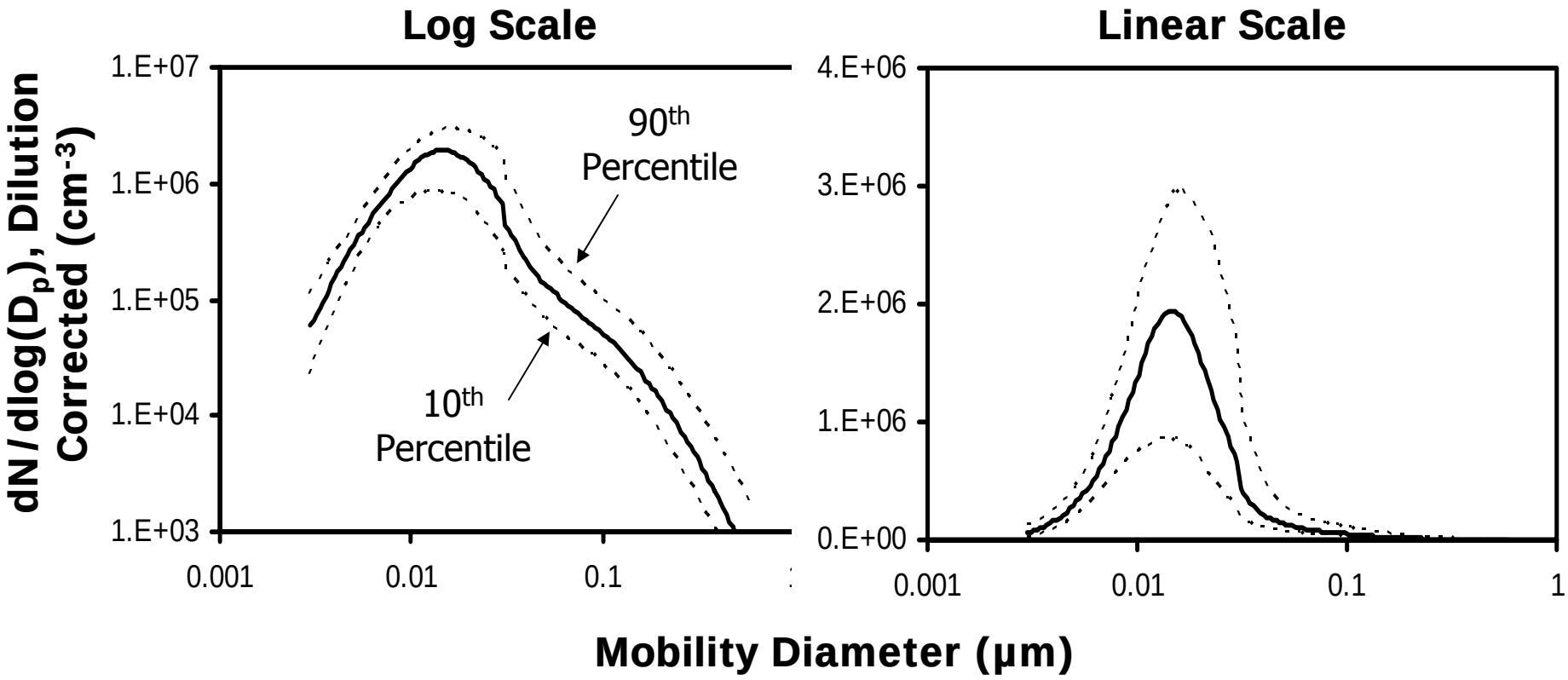
Scanning Mobility Particle Sizer





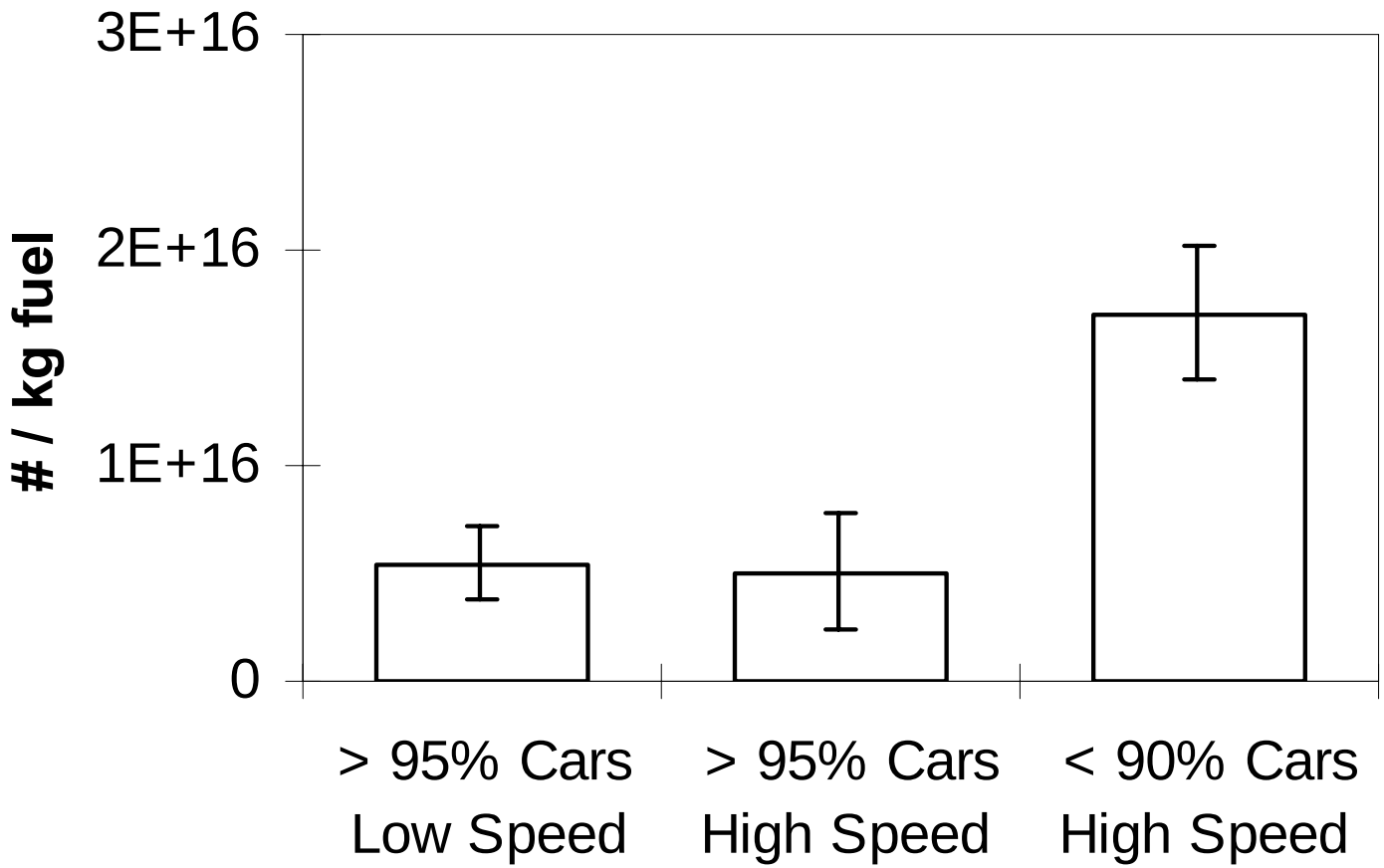
Traffic and modeling

Traffic Emission Sampling

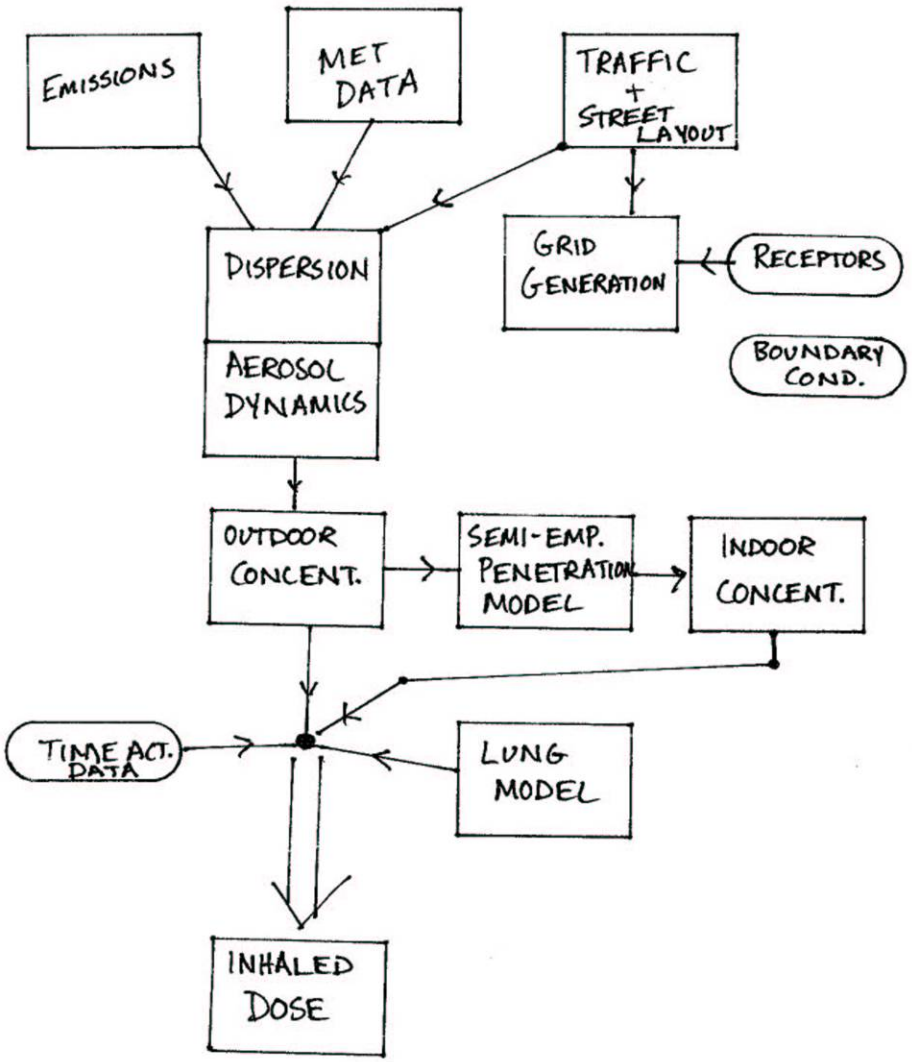


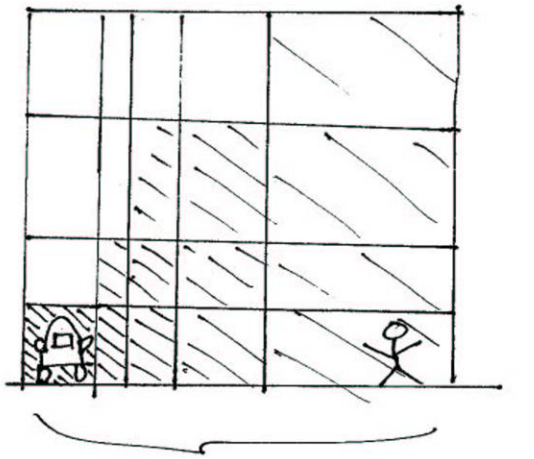
Note: 10th and 90th percentiles on 30-min average size distributions

Total # Emission Factors for Vehicles

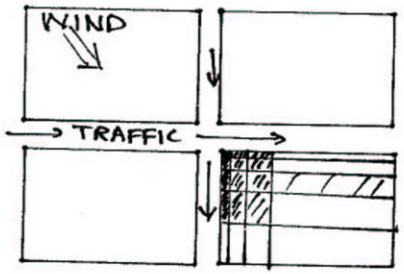


"Spin-Off" of Modeling Techniques



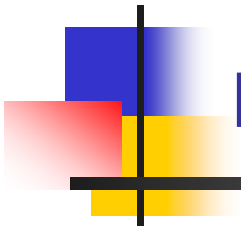


Coupled aerosol dynamics + dispersion



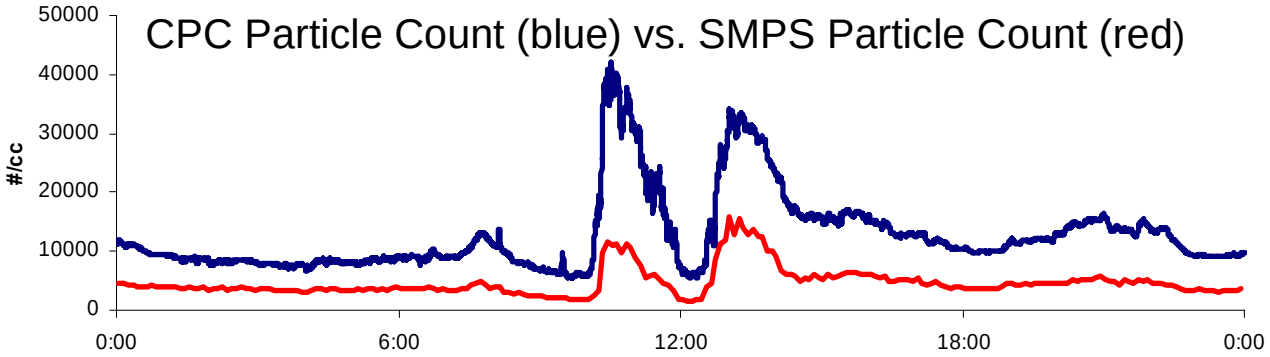
Calculation of gas-phase ammonia

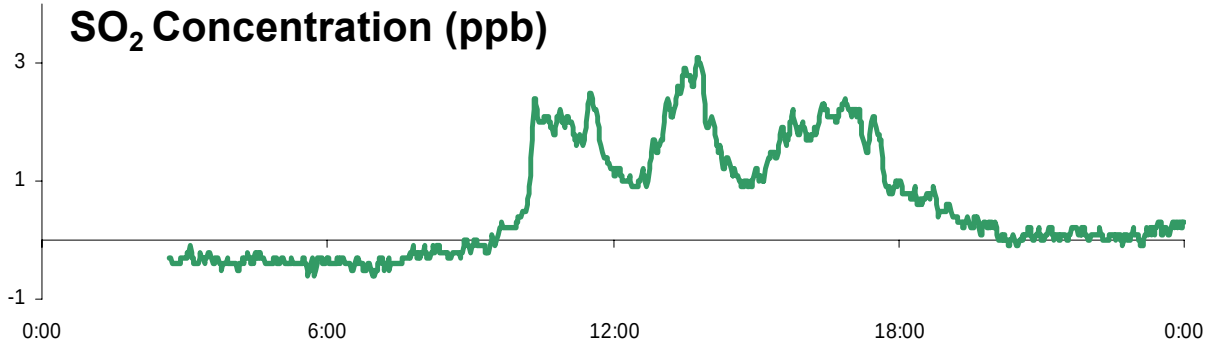
- Estimated from comparison of measured total NH_3 with $PM_{2.5}$ SO_4, NO_3
  - When sufficient ammonia is available to neutralize these species, excess ammonia assumed to be in gas-phase
  - Otherwise, lower limit for parameterization used
- Compared to equilibrium calculations using GFEMN for total NH_3, NO_3, and SO_4

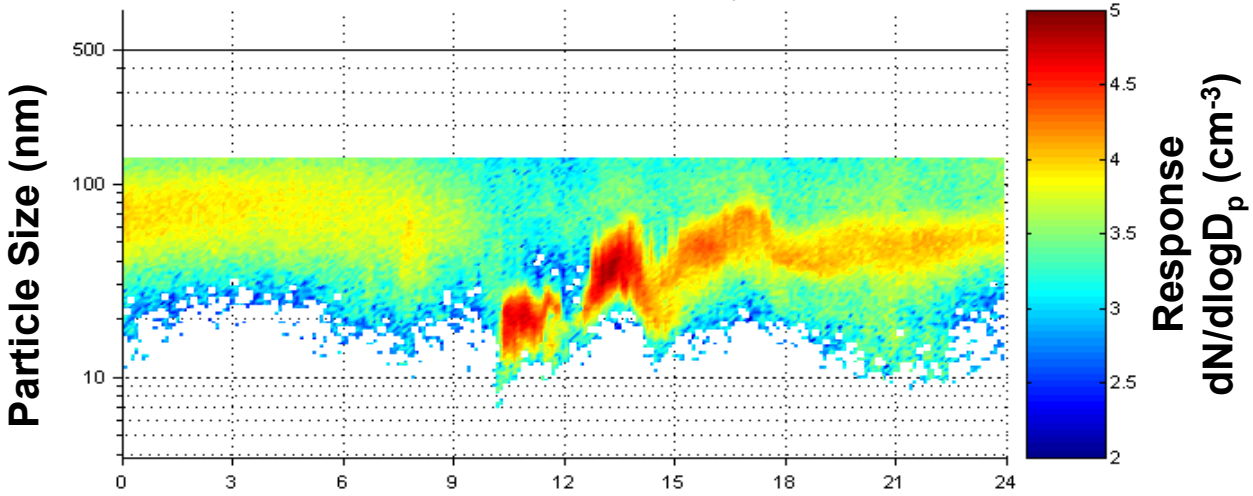


Bondville

September 18, 2005

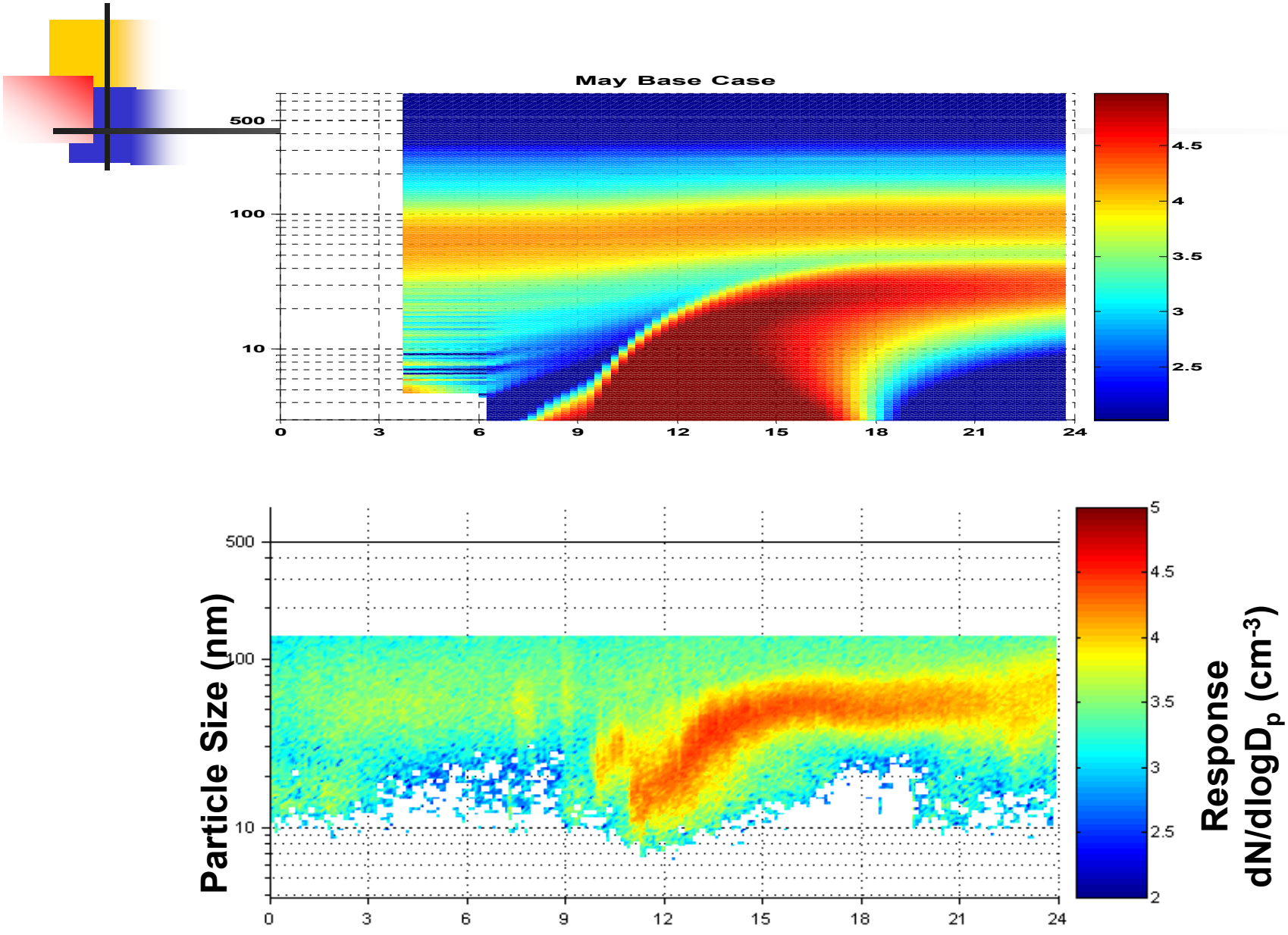


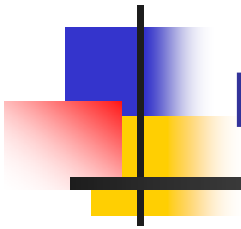




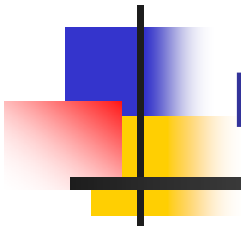
Nucleation Box Model with May 2003 SWS Data

- Constant NH_3 of 1.5 µg m^{-3} (2200 ppt)
- Constant SO_2 of 4 µg m^{-3} (1.54 ppb)
- Actual median RH and T from May dataset
- Bright sun used for UV / OH calculation


May Base Case
500
100
10
0
3
6
9
12
15
18
21
24
4.5
4
3.5
3
2.5
Particle Size (nm)
5
4.5
4
3.5
3
2.5
2
Response
dN/dlogD$_p$ (cm^{-3})



Mexico



PM Background Info

Typical Chemical Makeup