Synthesis of Research on New Particle Formation and Growth at the Pittsburgh Air Quality Study

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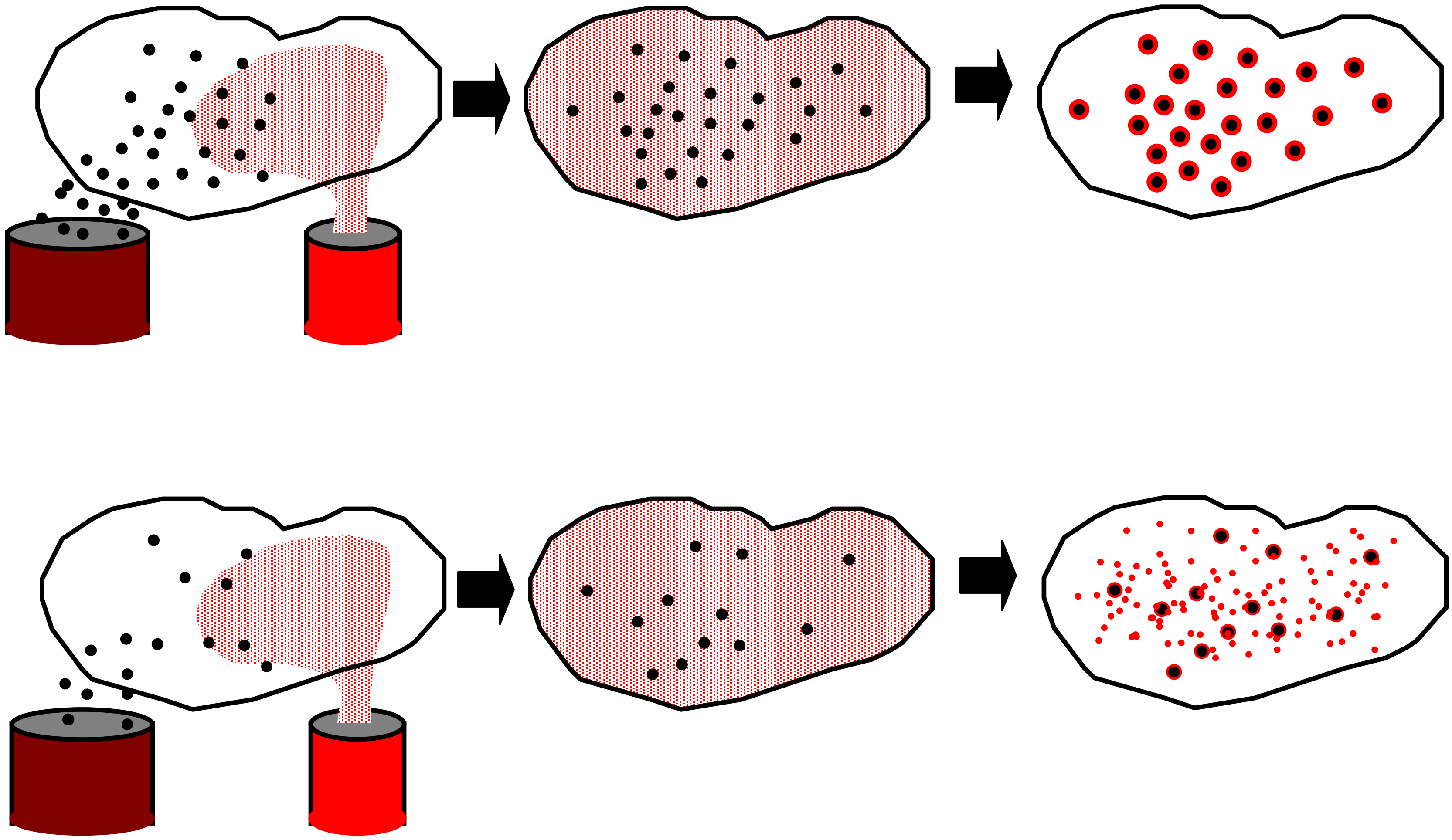
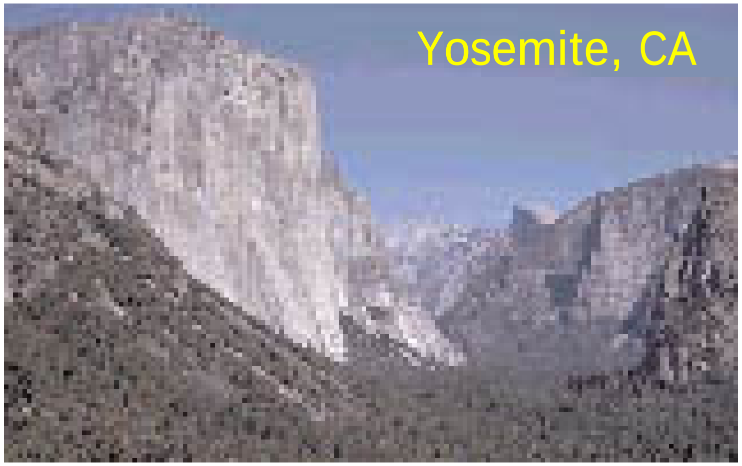
Research Questions

- What are the important characteristics of new the particle formation events?
  - Frequency
  - Correlations with meteorology
  - Correlations with gas & aerosol species
- What is the chemistry of new particle
  - Formation
  - Growth
- Is there a suitable predictive model?
- How will it change under future scenarios?

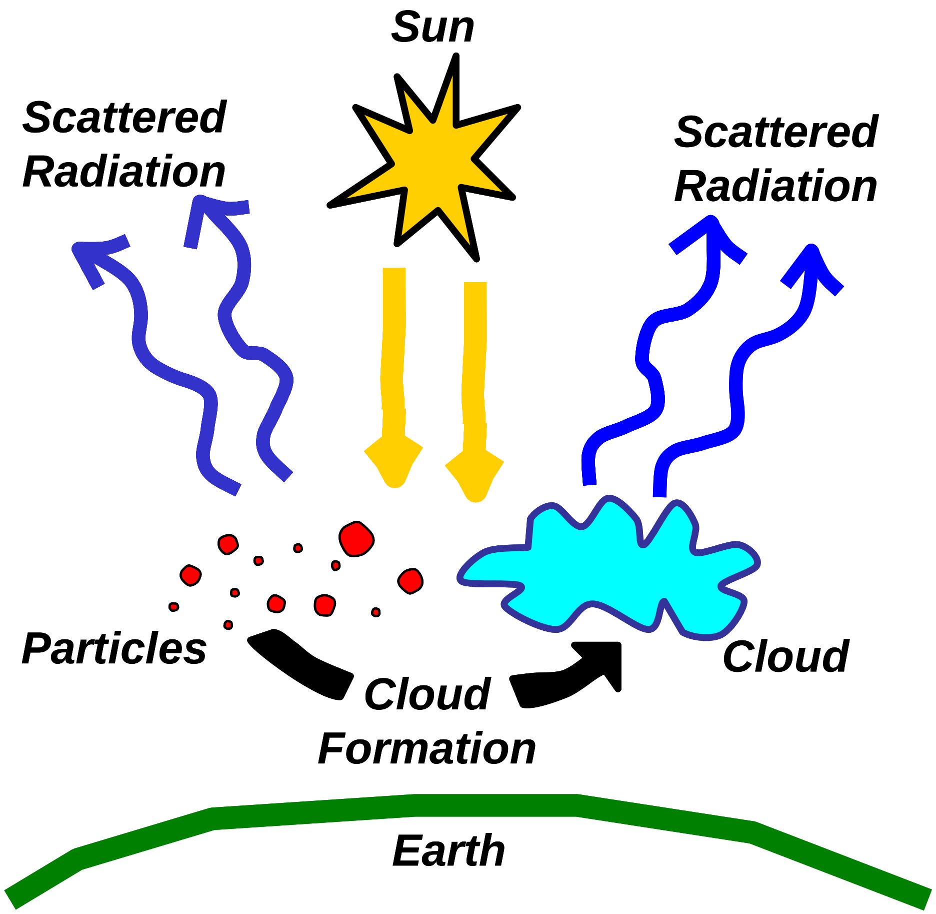
What is Nucleation?



Why is Nucleation Important: Climate



EPA (2001) National Air Quality: Status and Trends

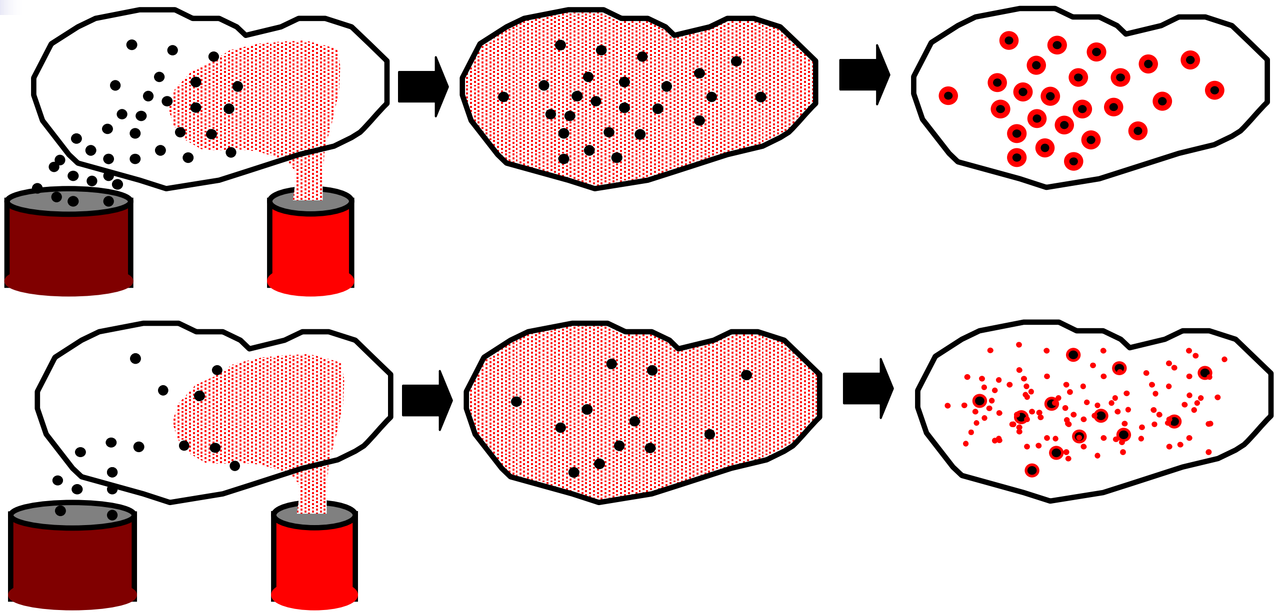


Why Is Nucleation Important: Health

- Health Effects
  - Solid ultrafine particles (C, TiO_2, PTFE, metals) behave differently than larger particles of the same composition
    - Significantly greater inflammatory response in rats than with same mass dosage of larger particles[1,2]
    - Translocation to bloodstream[3], brain[4], and liver[5]
  - Ambient Ultrafine – Picture is More Complex
    - Epidemiology Doesn't Provide Much Guidance
    - Ultrafine Source Attribution Problem

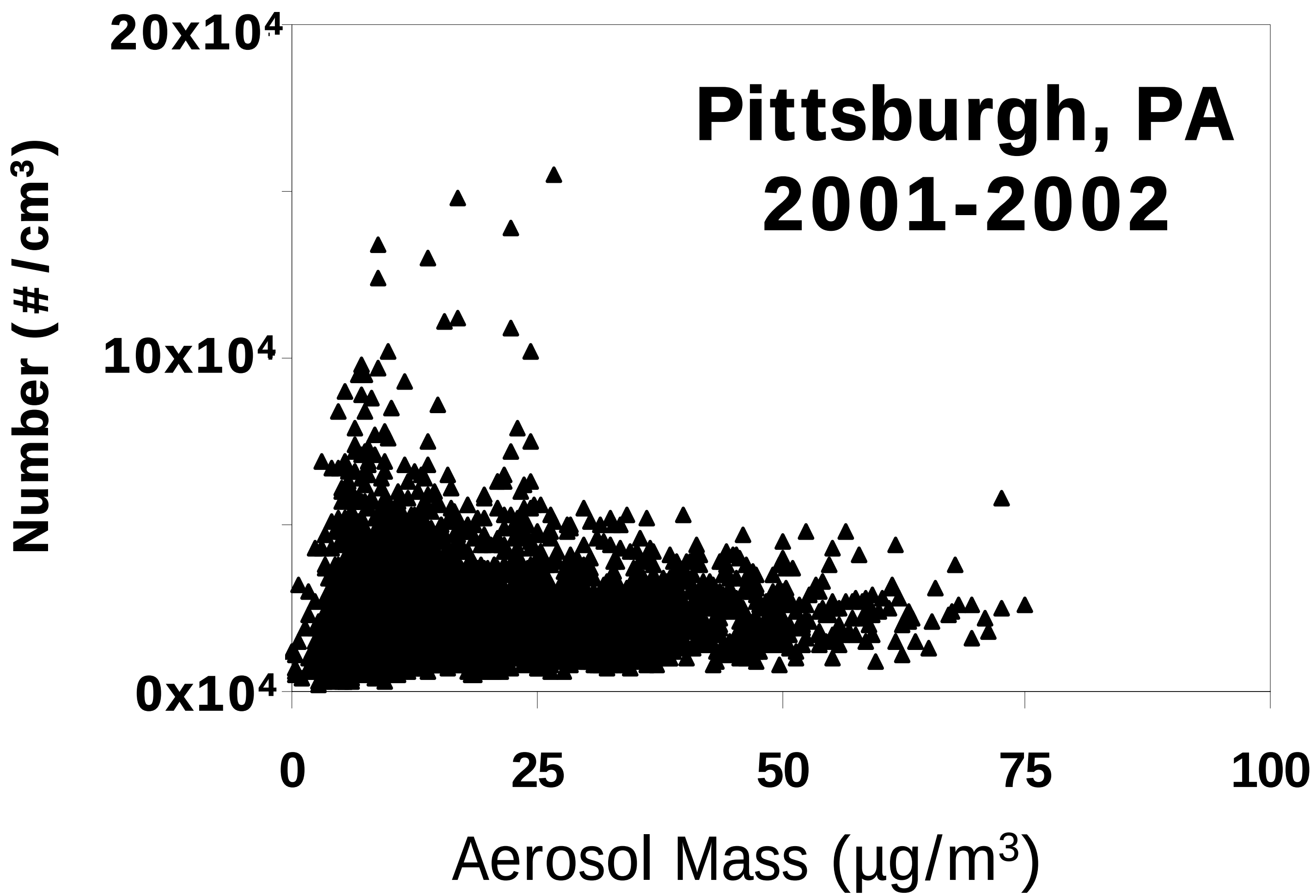
[1]Oberdorster et al. (1992) Environ. Health Perspect. 97: 193-199.
[2]Li et al. (1999) Inhal. Toxicol. 11: 709-731.
[3]Nemmar et al. (2002) Circulation 105: 411-414.
[4]Oberdorster et al. (2003) Am J Resp Crit Care Med, in press.
[5]Oberdorster et al. (2002) Toxicol. Environ. Health A 65 (20): 1531-1543.
[6]Peters et al. (1997) Am. J. Respir. Crit. Care Med. 155: 1276-1383.

Why Is Nucleation Important: Likely to change in the future



- Clear Skies – Reduce SO_2 and NO_3
  - Reduce particle surface area (PROMOTE NPF)
  - Reduce sulfuric acid formation (HINDER NPF)
- Low Sulfur Diesel & Particle Traps
  - Reduce particle surface area (PROMOTE NPF)

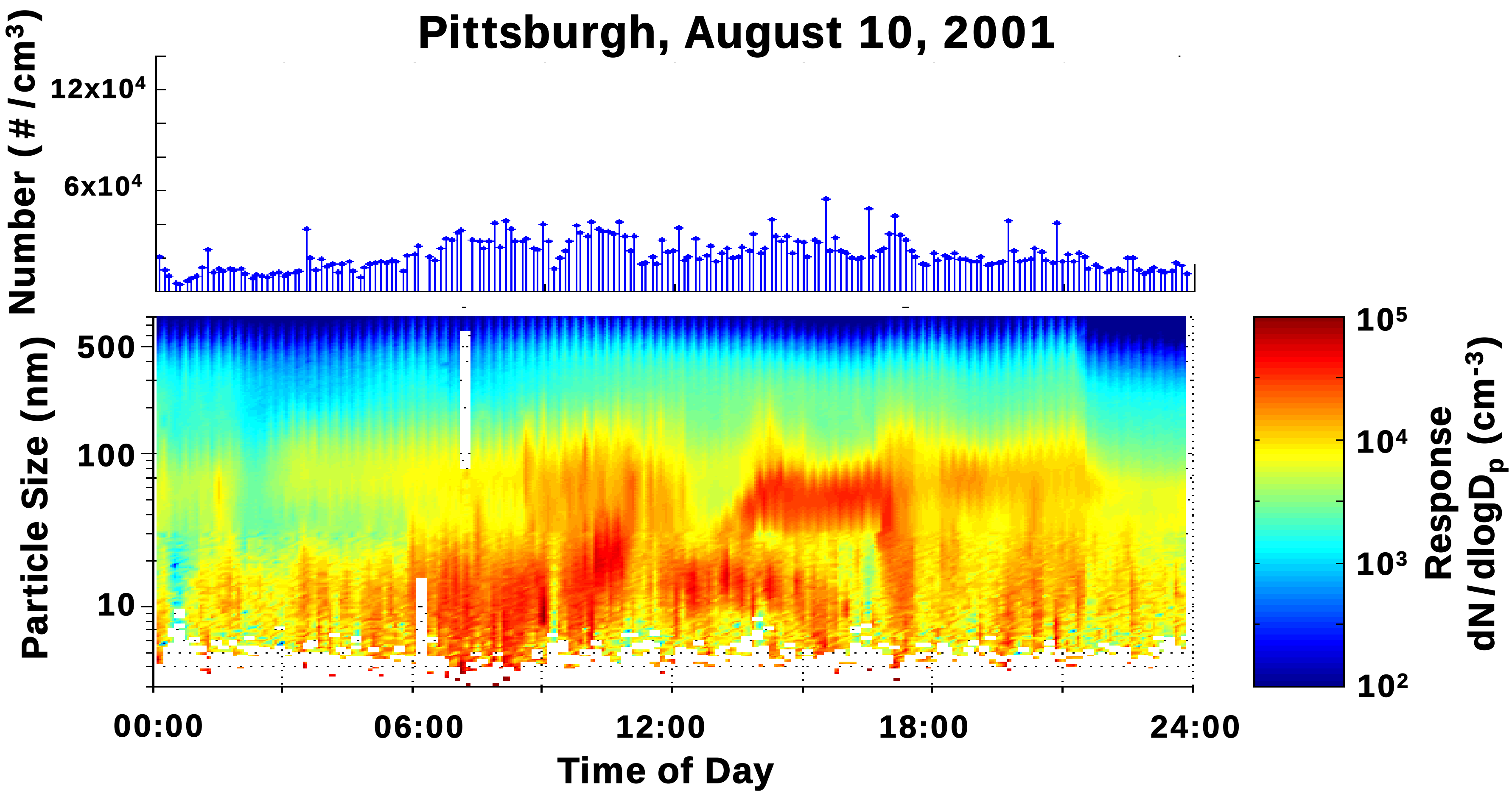
Overall Number vs. Mass Correlation



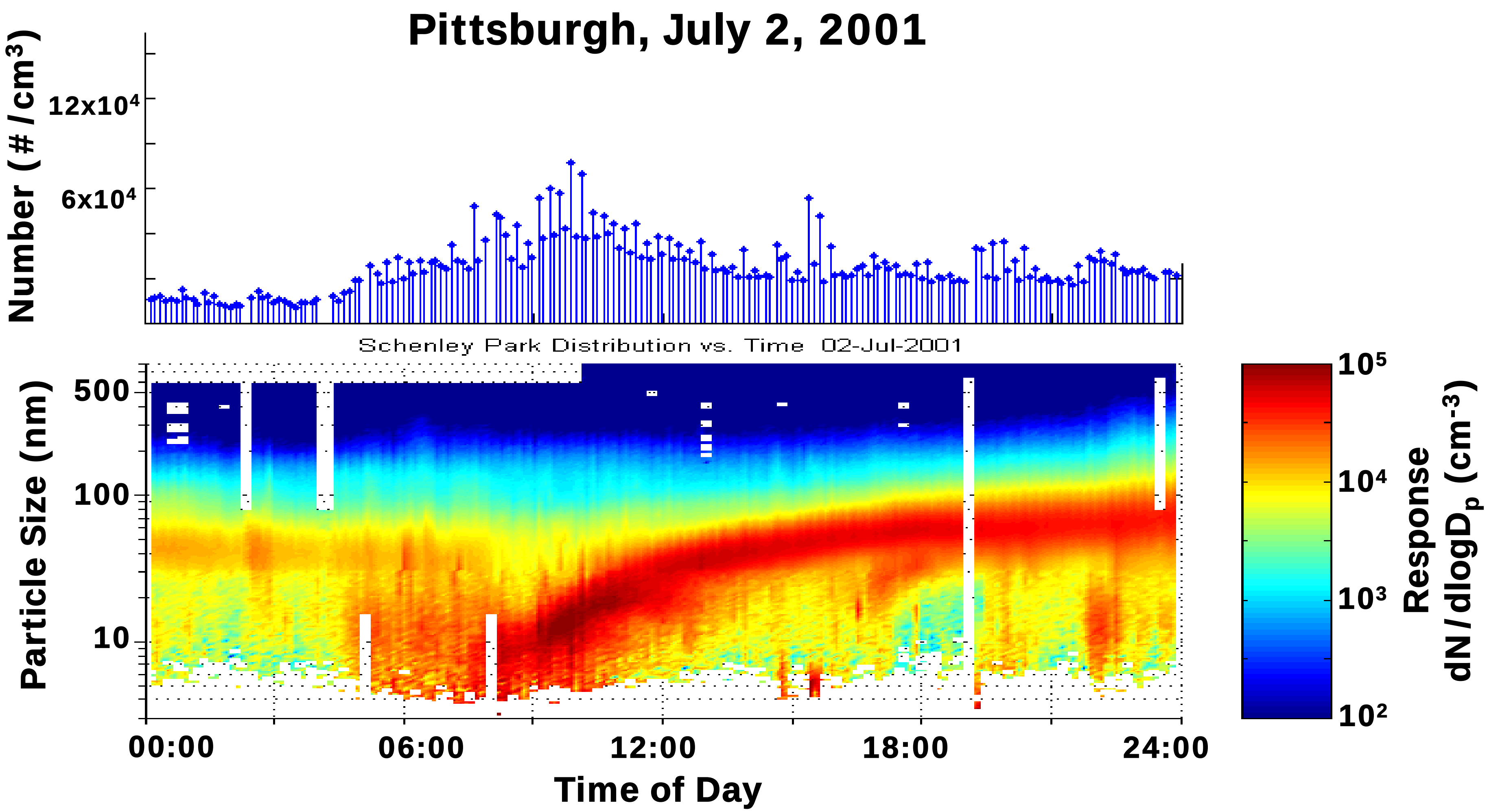
Methods

- Field Sampling Part of the Pittsburgh Air Quality Study
  - Particle size distribution measurements at the central sampling site from 3 nm – 10 µm (14 months)
  - Simultaneous measurement of size distributions at upwind rural site for targeted periods
  - Collocated gas-phase, aerosol-phase, and meteorological data collection
  - Aerosol Mass Spectrometry
- Modeling of Nucleation Events

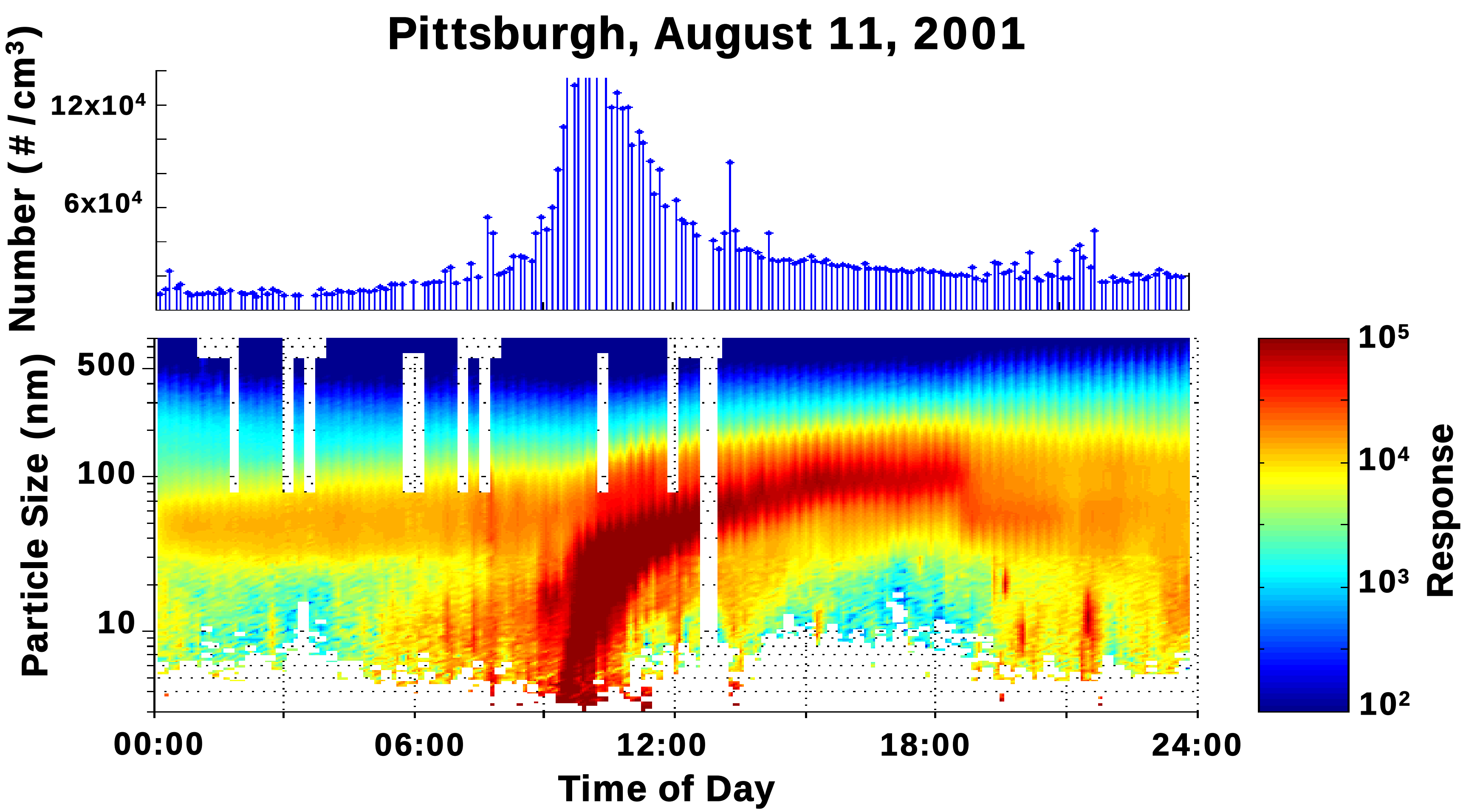
Example: No Nucleation



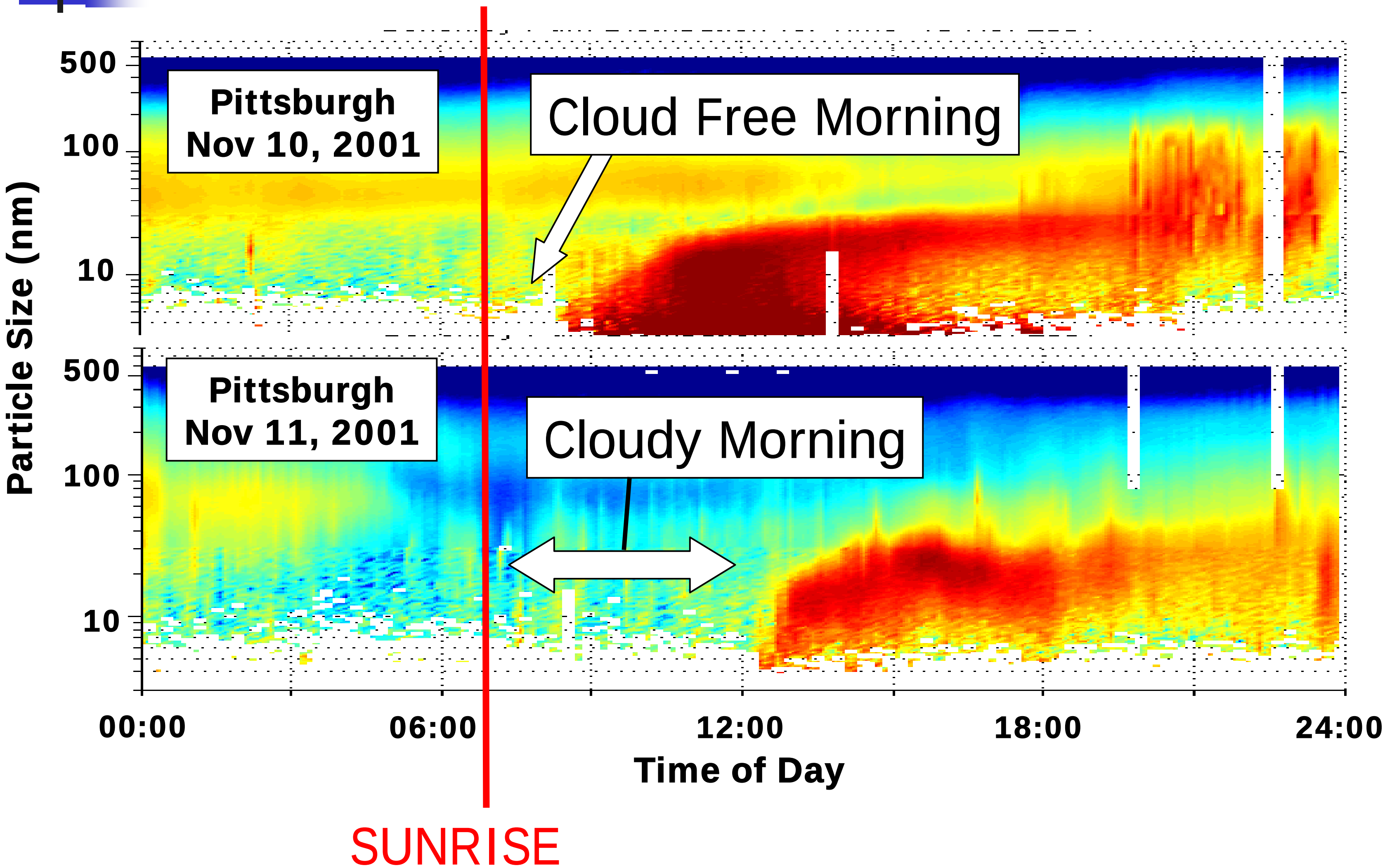
Example: Weak Nucleation



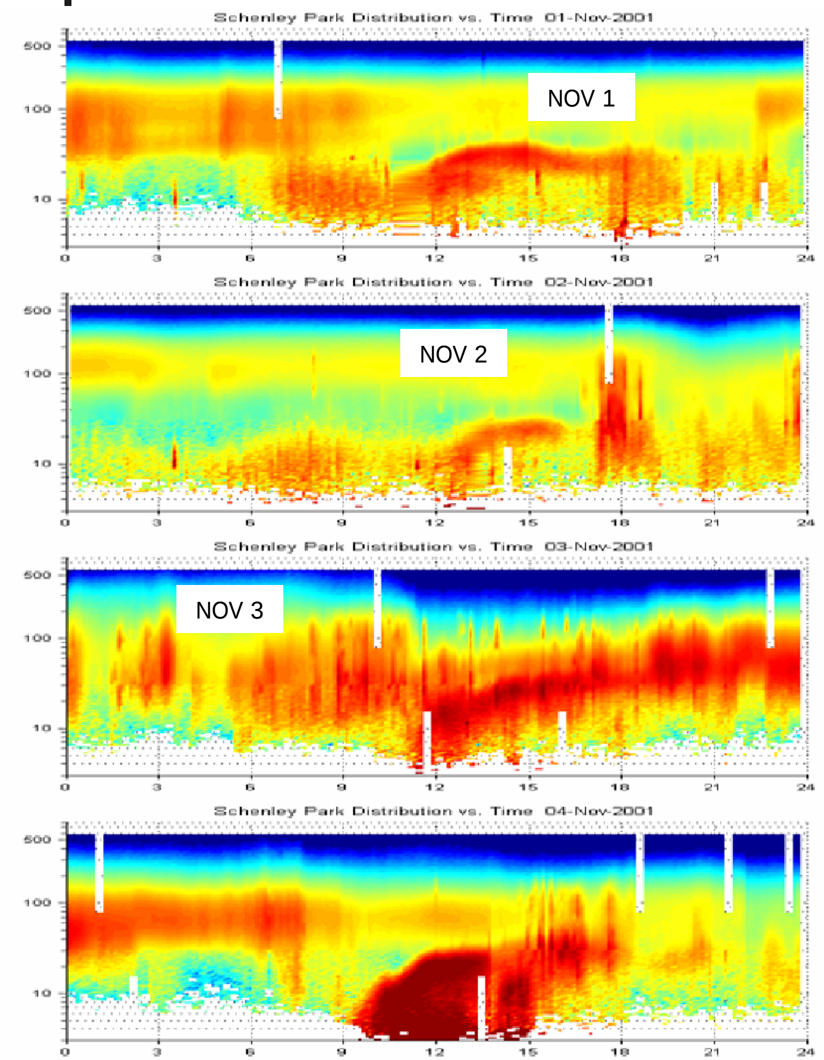
Example: Strong Nucleation

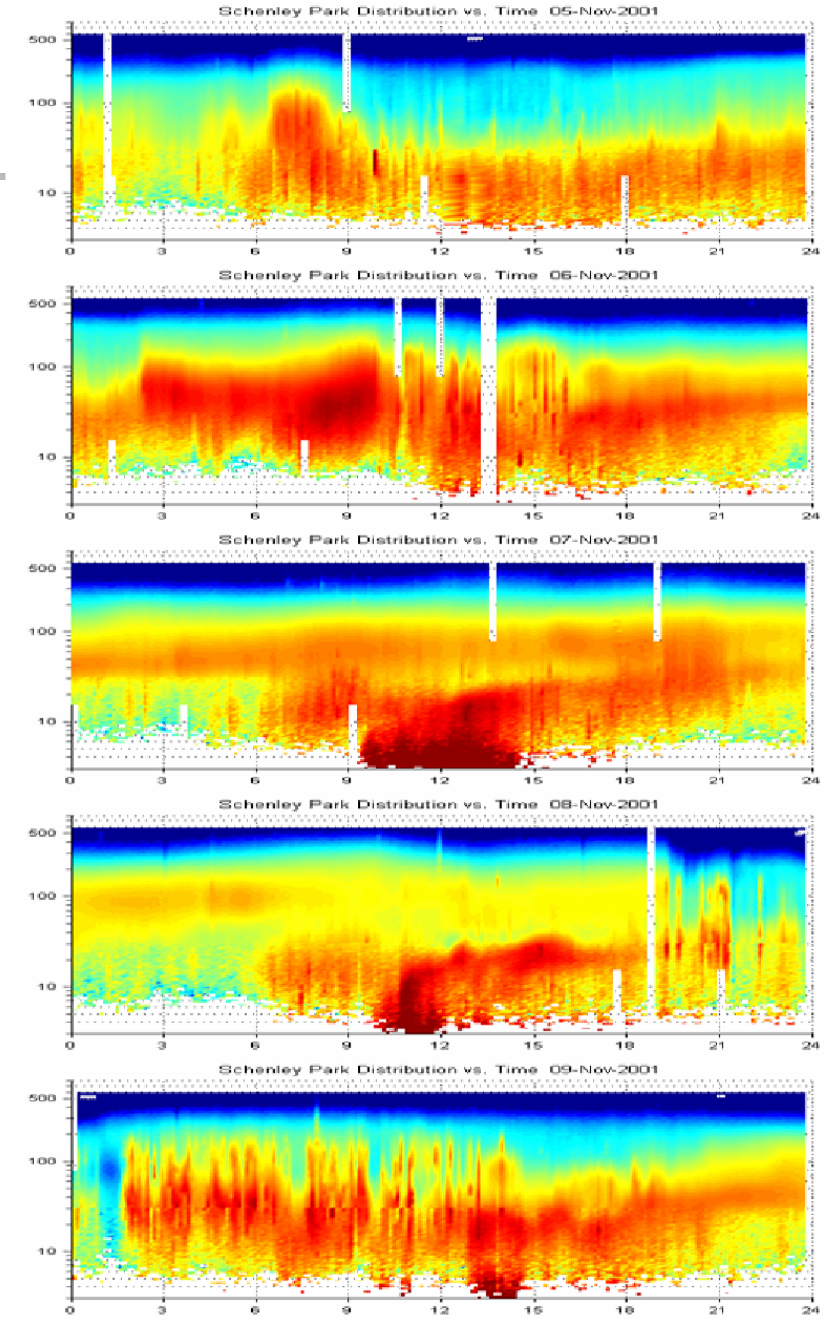


Sunlight and New Particle Formation

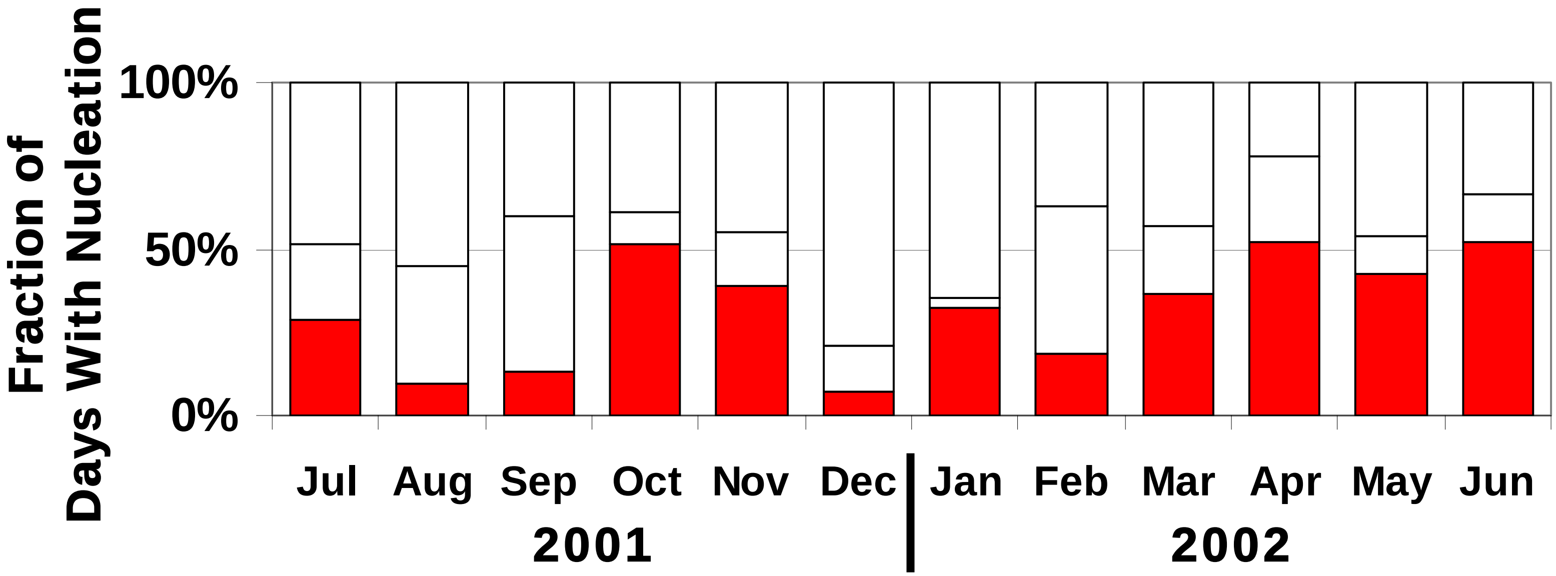


Count them up





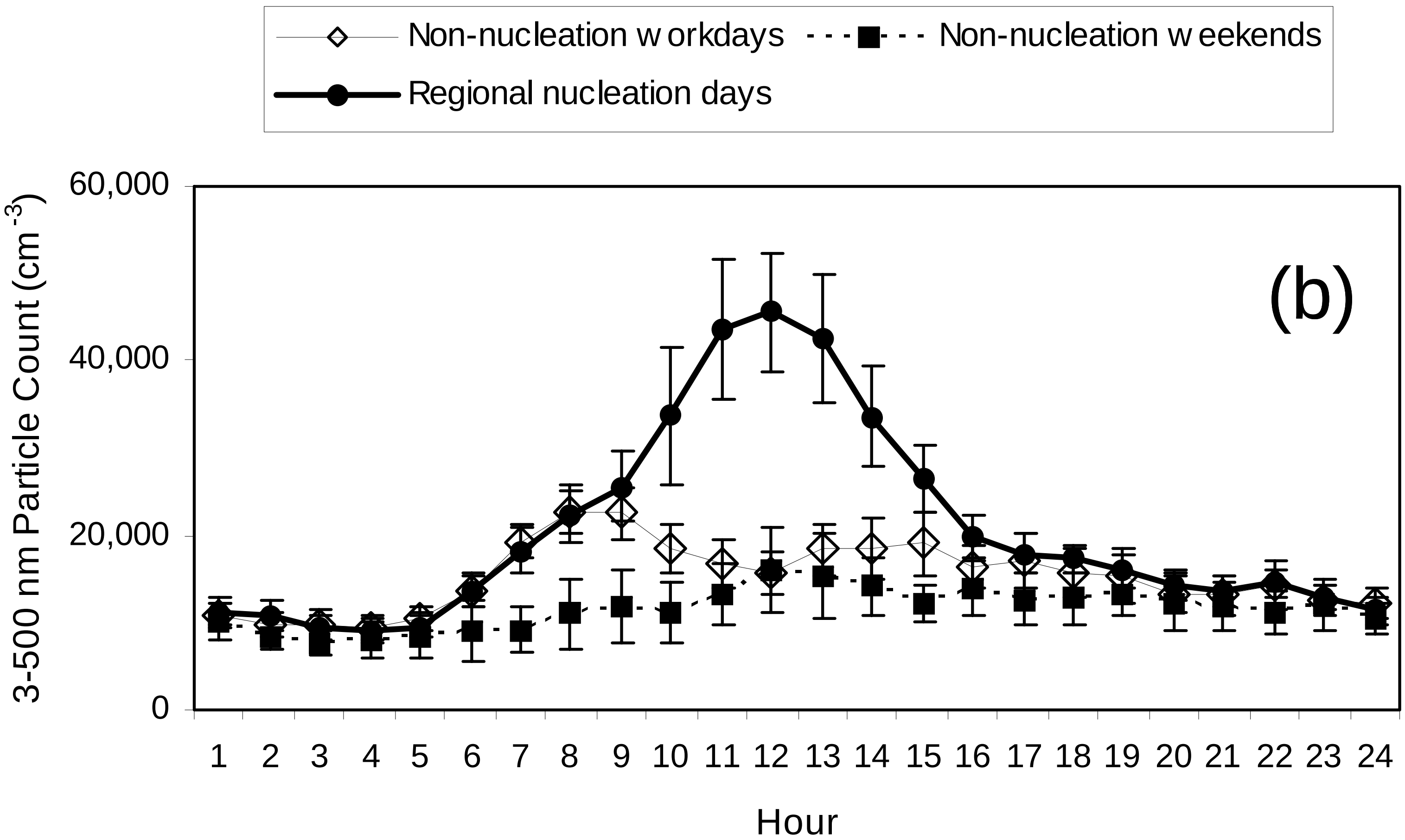
Nucleation Frequency by Month



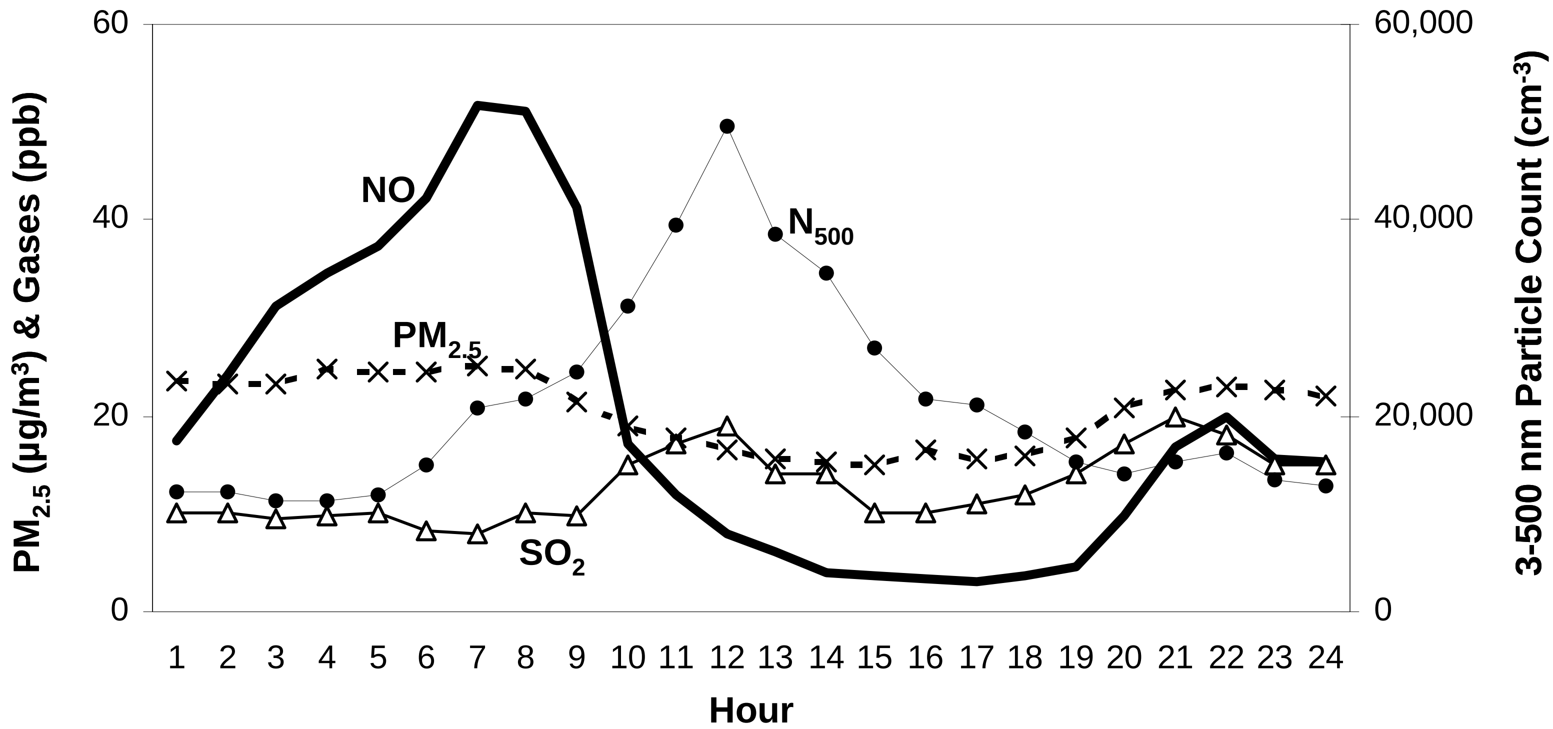
- Significant fraction of days (30%+)
- Most prevalent in spring, fall

Stanier et al. Nucleation Events During the Pittsburgh Air Quality Study: Description and Relation to Key Meteorological, Gas Phase, and Aerosol Parameters. *Aerosol Science & Technology (*2004).

Diurnal Pattern

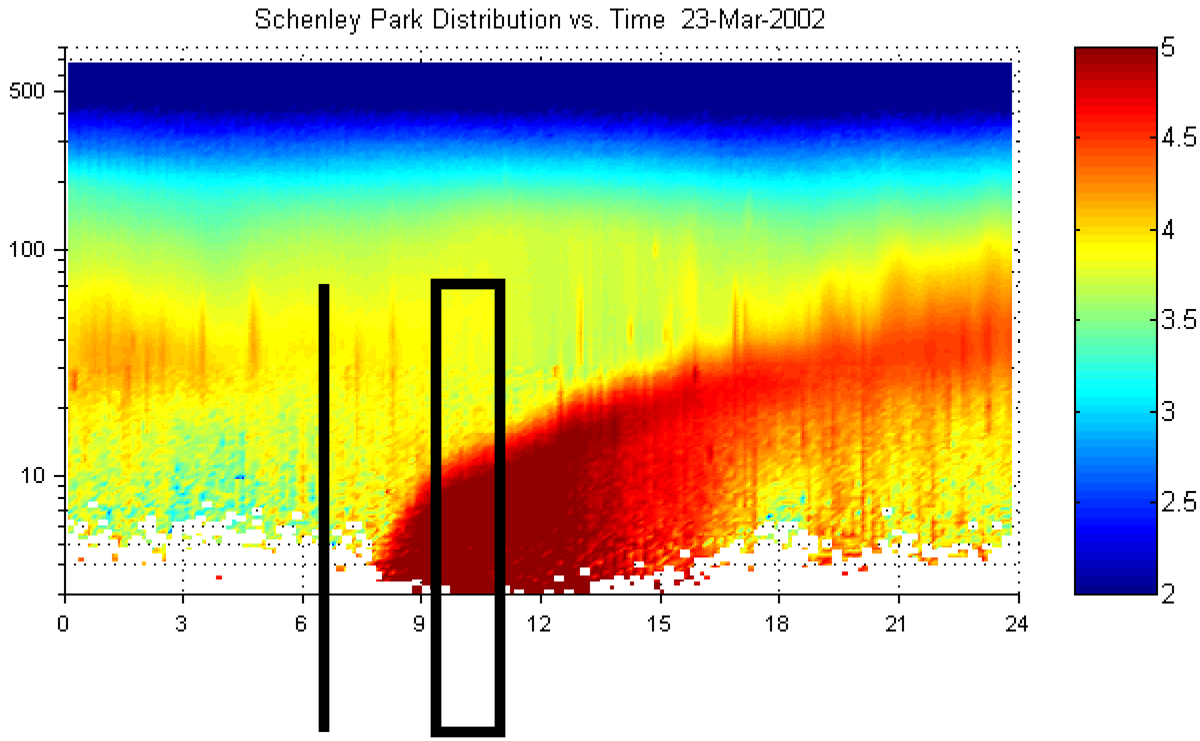


Inversion Related NPF



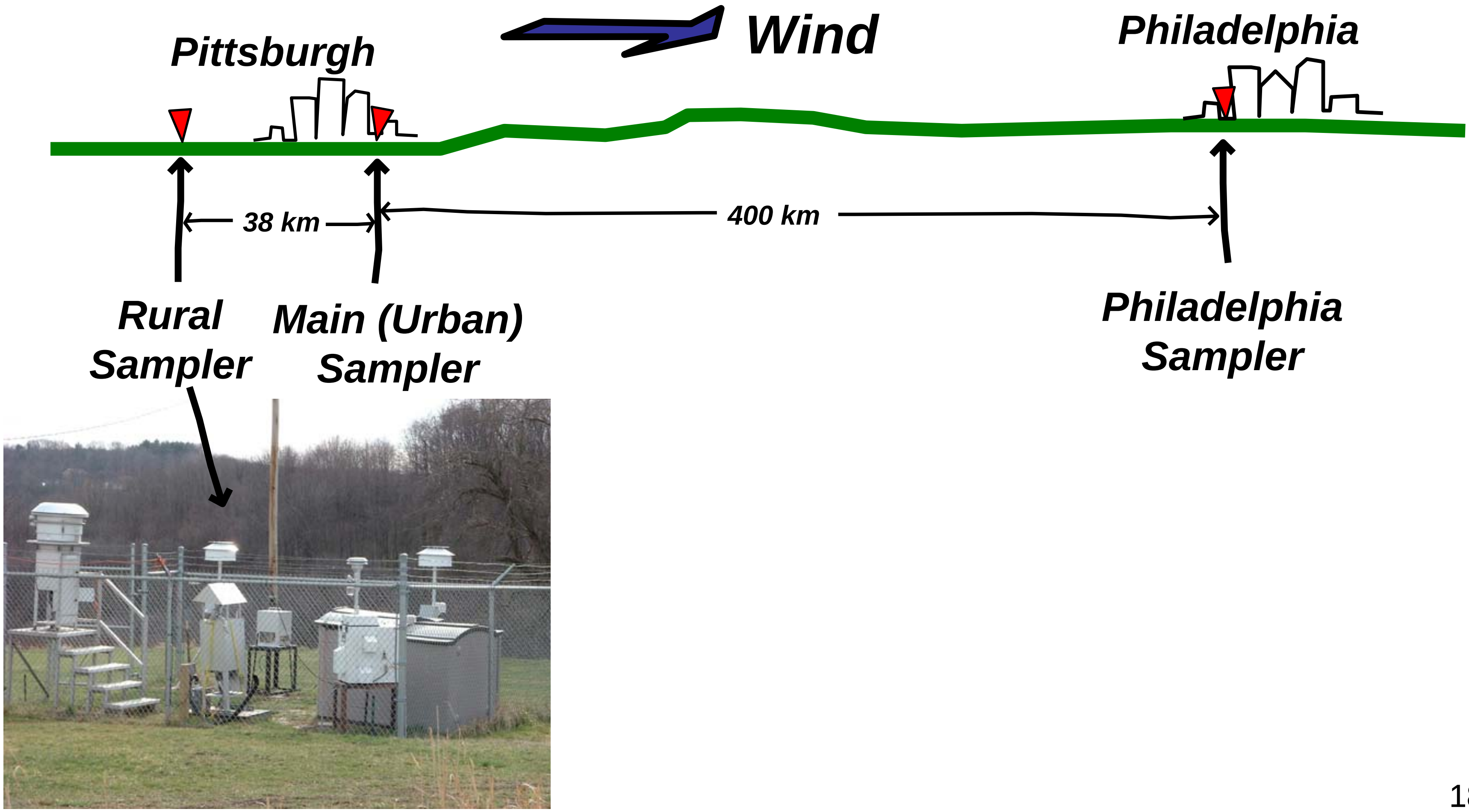
Average of July – November 2001 Inversion-Related Events

Sometimes Coincide with BL Mix

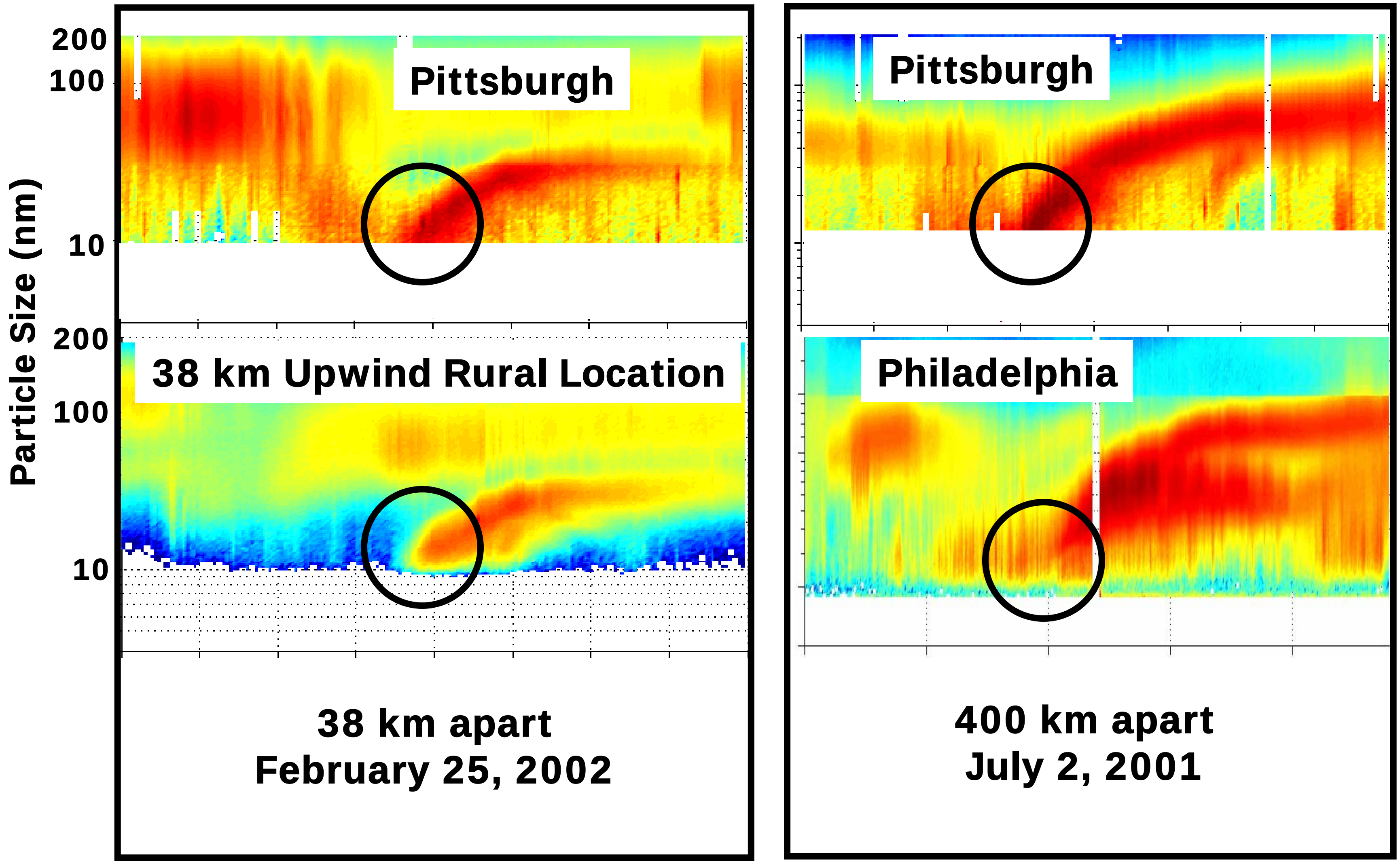


Nucleation's Spatial Coverage

- Method: simultaneous sampling



Spatial Coverage Result



Nucleation and Growth Hypotheses

- Nucleation Chemistry Possibilities (sub nm to ~3 nm)
  - A Sulfuric Acid & Water
  - B Sulfuric Acid, Water & Ammonia
  - C Organic Compounds, alone or with A or B
  - D Any of the above, assisted by atmospheric ions

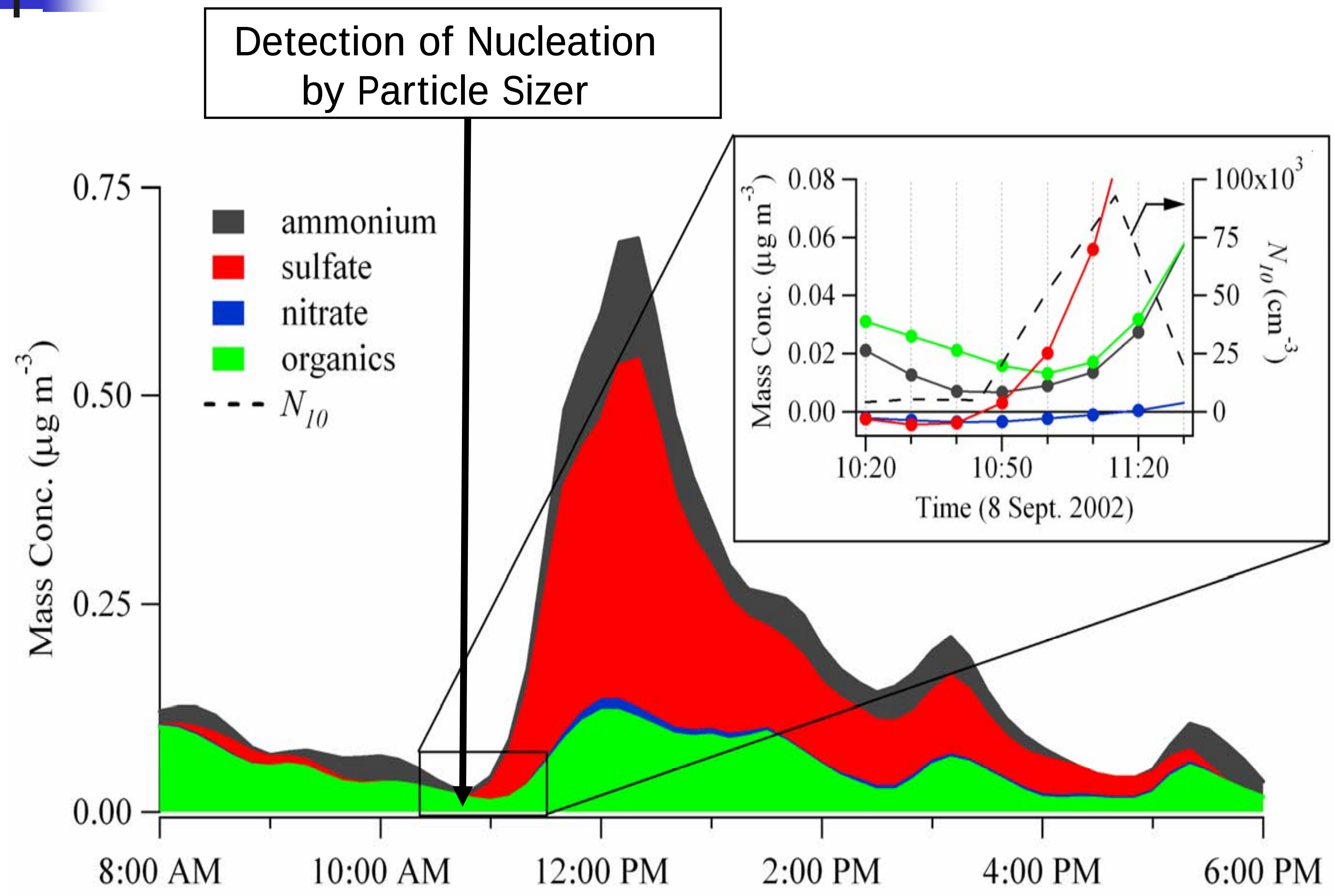
- Particle Growth Possibilities
  - A Sulfuric Acid
  - B Ammonium Sulfate
  - C Organic Compounds – Condensation
  - D Organic Compounds – Heterogeneous Reactions

AMS Nucleation Sampling at Pittsburgh

- Sampled Sept 6 – Sept 21
  - Focused on smallest particles possible to look at chemistry of growth (D_{va} 33-60 nm)
  - Analysis focused on 3 events
    - Sept 8 – very intense, SO_2 high, $N_{3\text{-}10} > 10 \times 10^4$ cm^{-3}
    - Sept 9 – elevated SO_2, $N_{3\text{-}10} > 4 \times 10^4$ cm^{-3}
    - Sept 12 – average SO_2 (<10 ppb), $N_{3\text{-}10} \sim 3 \times 10^4$ cm^{-3}

PC70

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



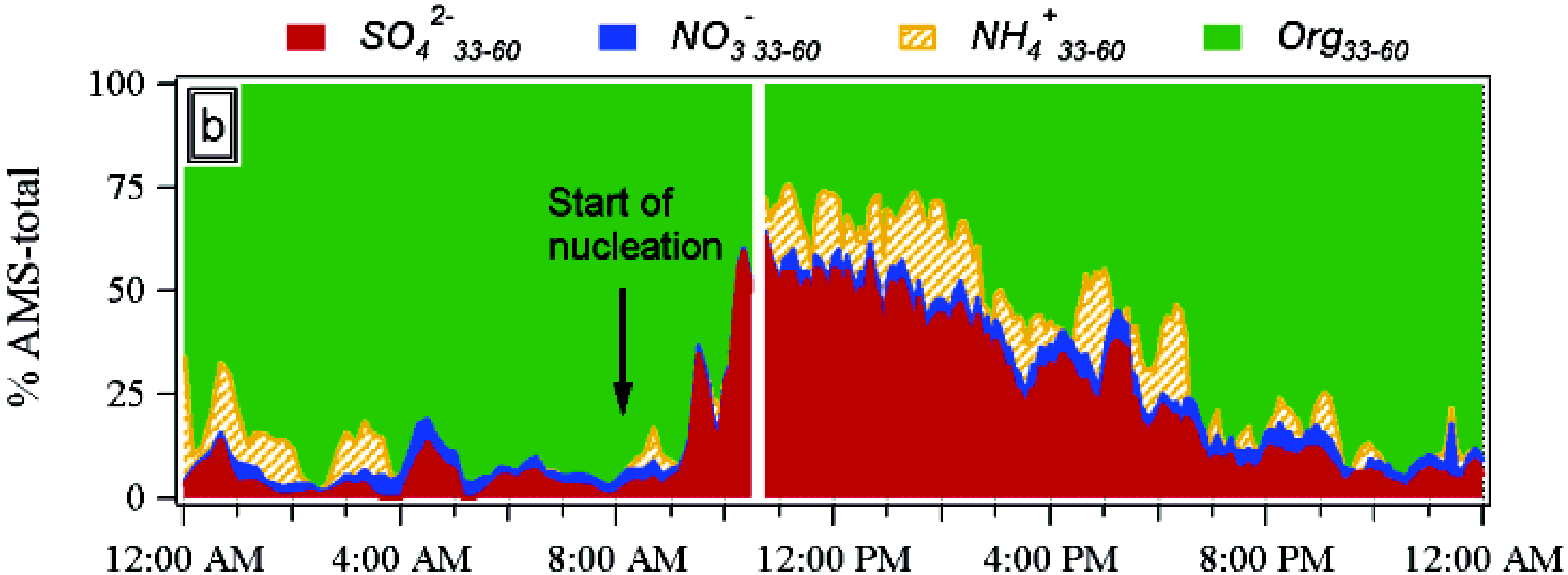
Zhang, et. al. Insights into the Chemistry of Nucleation Bursts and New Particle Growth Events in Pittsburgh based on Aerosol Mass Spectrometry. Environ. Sci. Technol., in press.

Slide 22

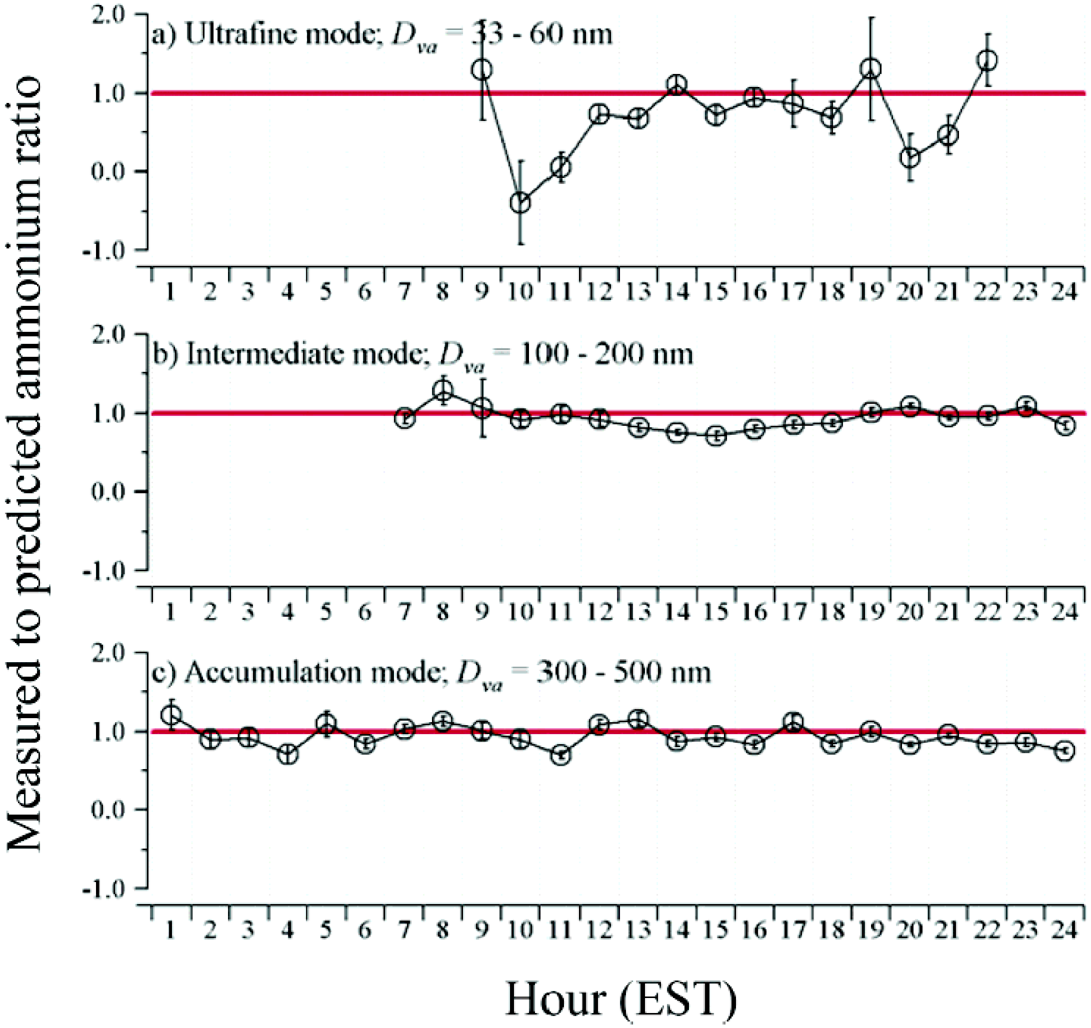
PC70 Redraw without inset

Preferred Customer, 1/19/2004

AMS Time Series – Sept 12



Acidity measured in ultrafines, Sept 8



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)

Ternary nucleation theory

- 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

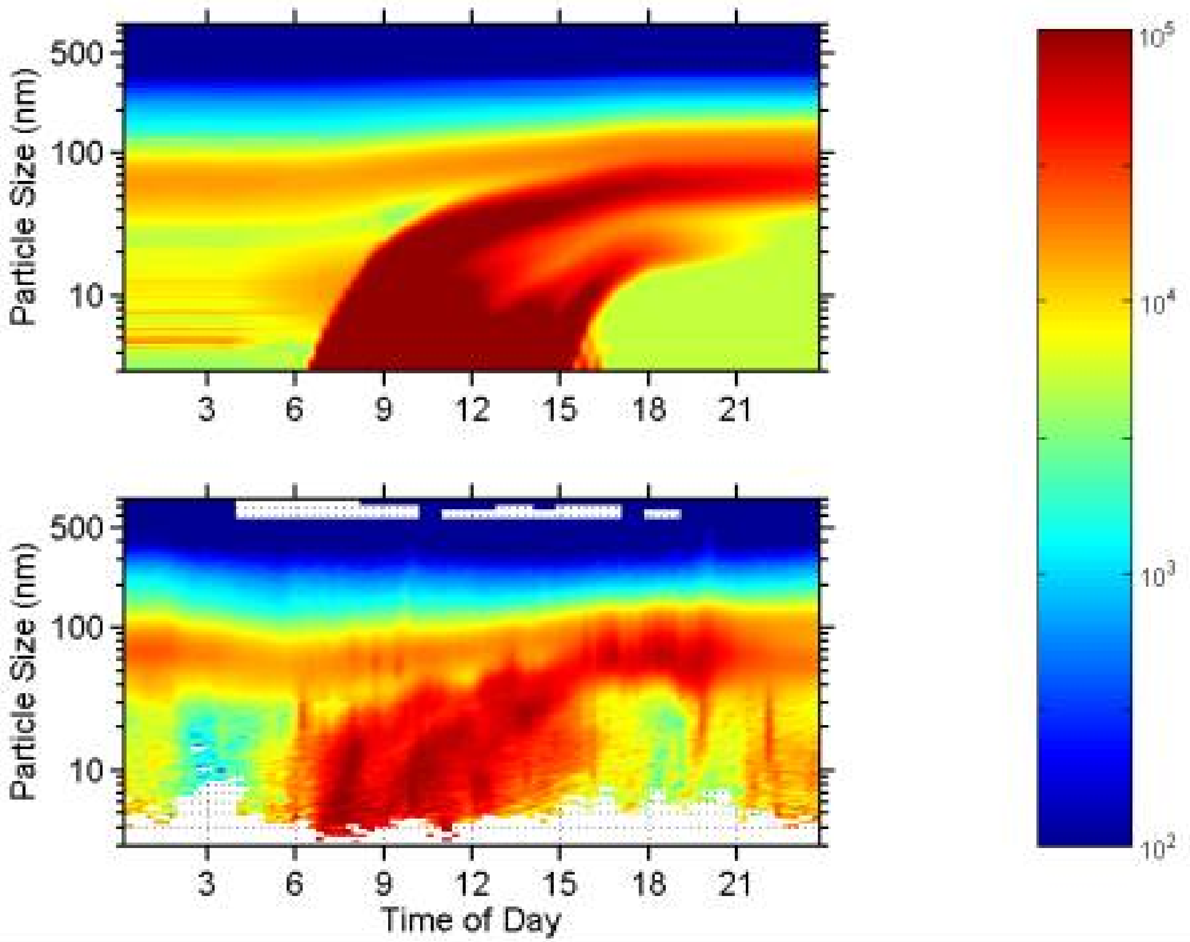
- Approximation for composition of initial nuclei, also dependent on nucleation rate and T
  - Approximately 4 molecules of sulfuric acid, 4 of ammonium in July
  - 2 molecules of sulfuric acid, 2 of ammonium in January

Summary of observations

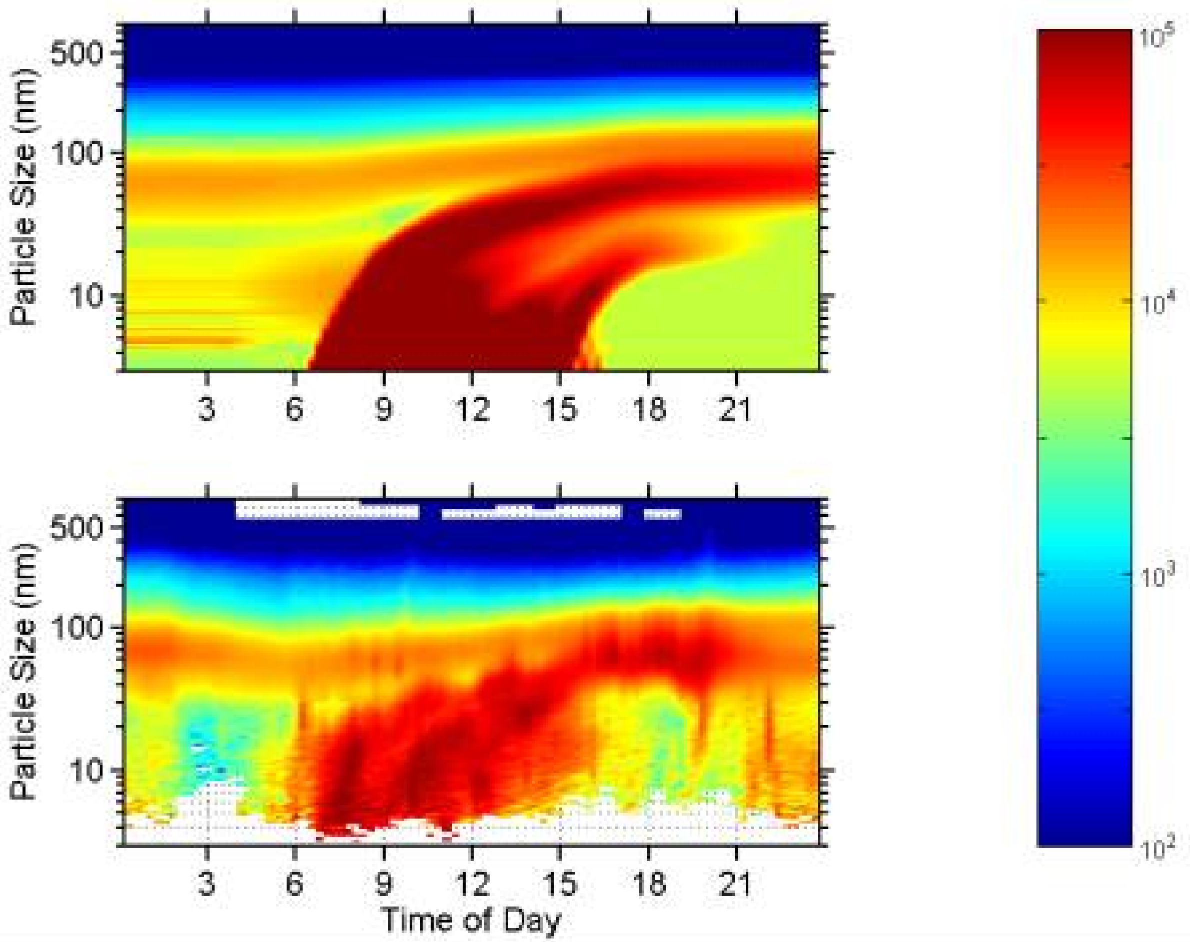
- July: Seventeen days with nucleation
  - Twelve days couldn't be modeled due to missing data, local sources dominating, or unusual meteorology
  - Nineteen days modeled, thirteen exhibiting nucleation
  - Nucleation begins around 9:00 on most days
  - Average growth to about 70 nm
- January: Twelve days with nucleation
  - First two days missing data
  - Nucleation begins around noon on most days
  - Significantly less growth than in July, usually to only about 20 nm

Gaydos et al. Modeling of In-situ Ultrafine Atmospheric Particle Formation in the Eastern United States. *J. Geophys. Res.*, submitted.

Comparison on July 27, 2001

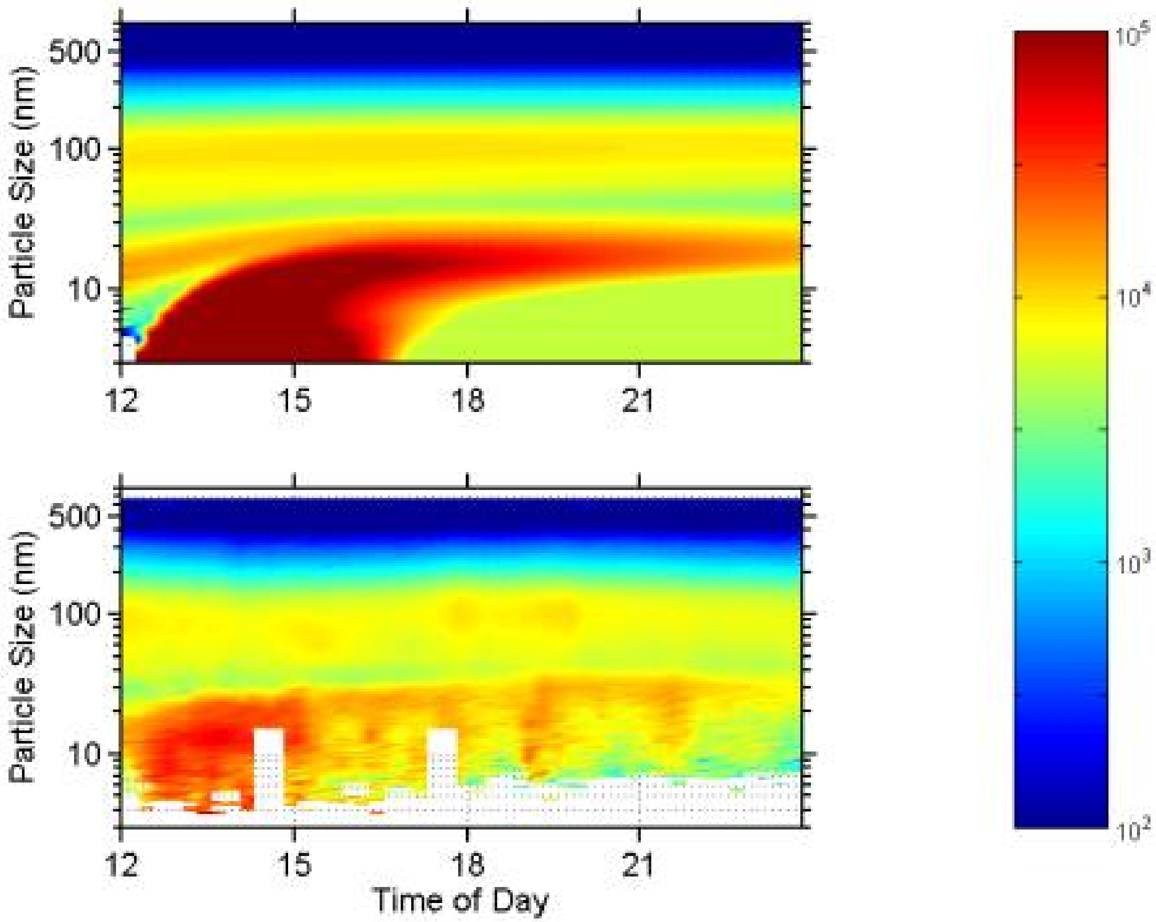


Comparison on July 27, 2001

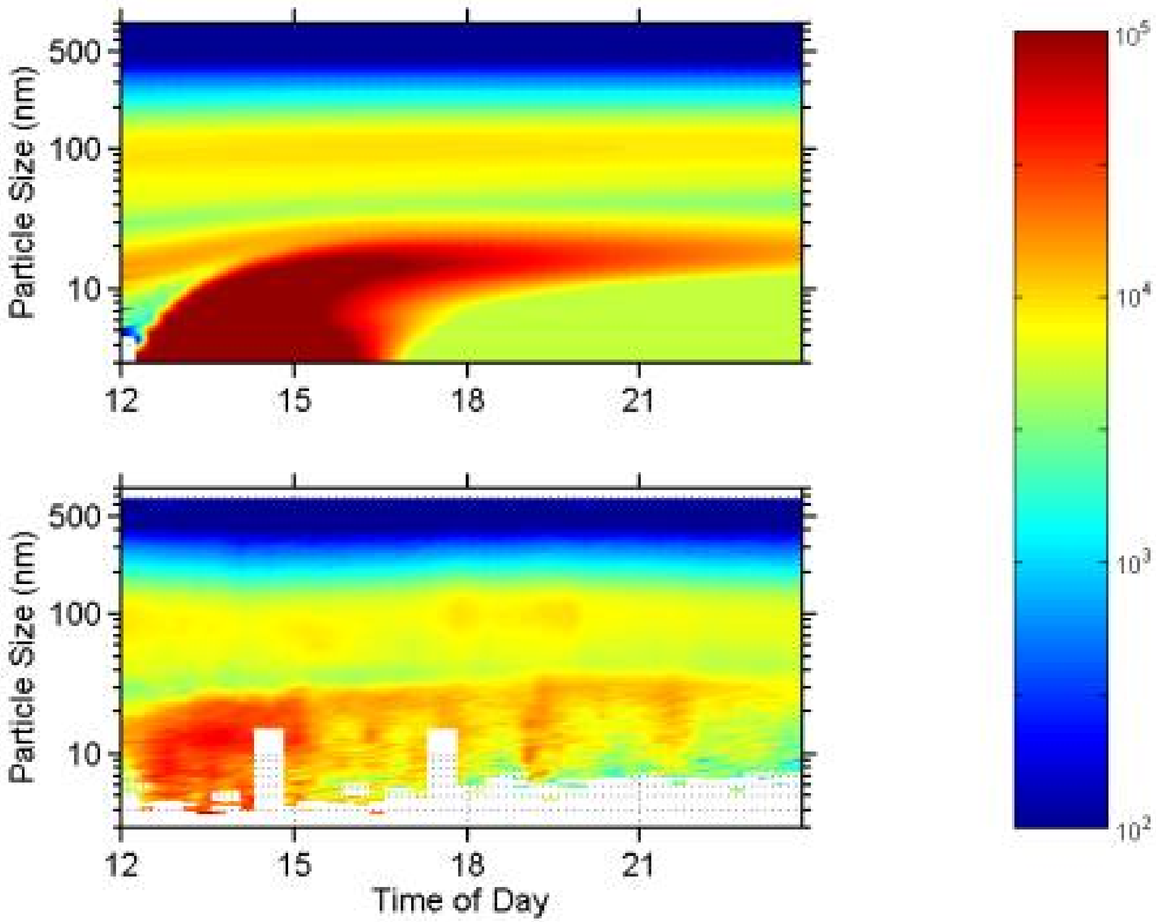


- Model predicted presence or lack of nucleation on all 19 days
- Timing of onset of nucleation within one hour of observations for all 13 events
- Size and shape of growth curve consistent with observations
- High number concentrations predicted

Comparison on January 28, 2002



Comparison on January 28, 2002

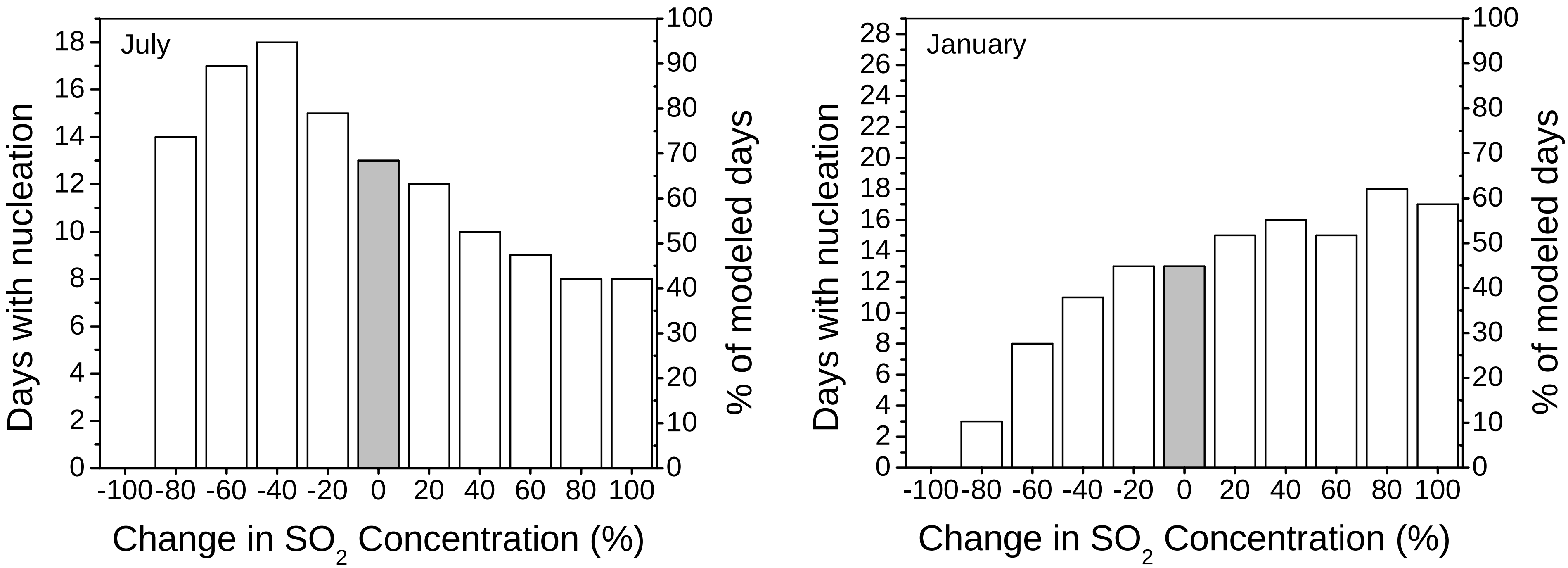


- 25 out of 29 days predicted correctly
- Timing of onset of nucleation not as good (6 of 12 within one hour)
- Growth generally underpredicted with two exceptions
- High number concentrations predicted

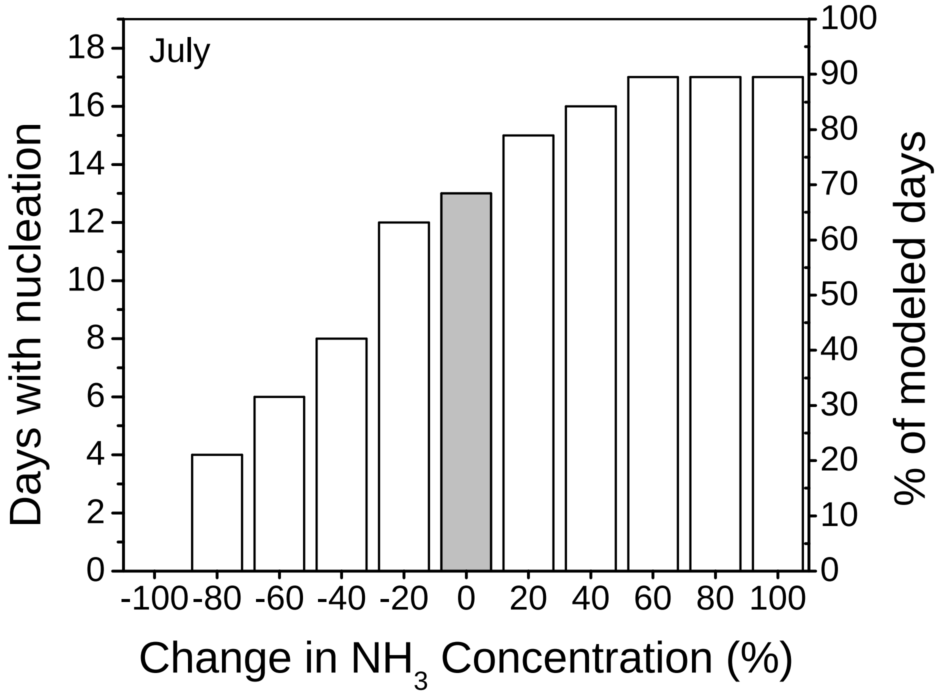
Summary of OH sensitivity

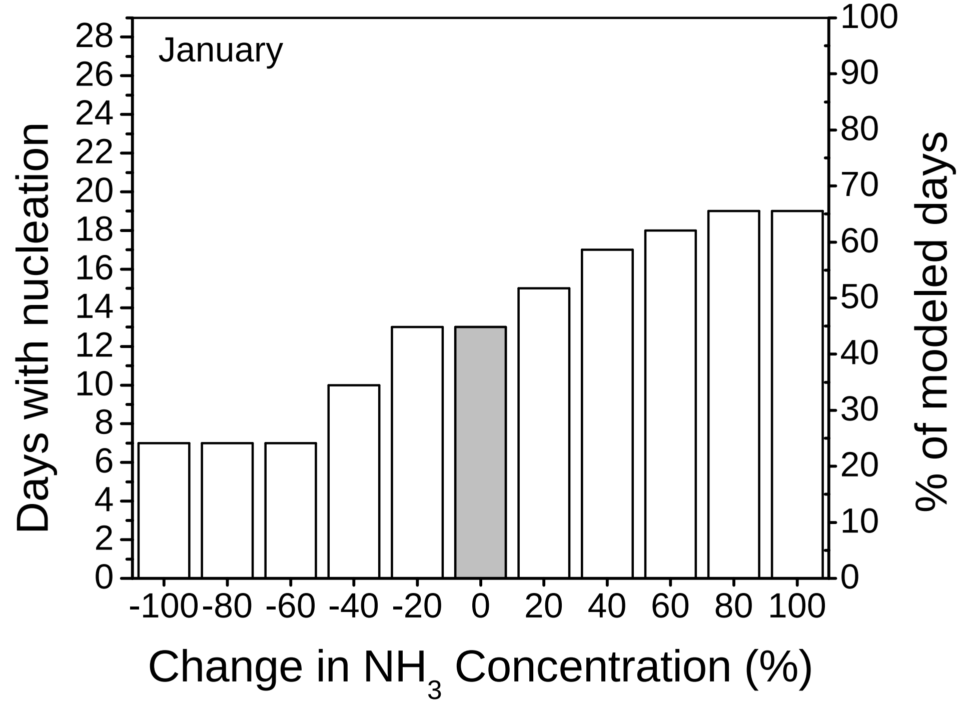
- In July, number of events remains constant for all OH values
- Growth is affected:
  - For double OH, nine events reach 100 nm
  - Growth 20% less with half the OH
- In January, number of events ranges from 8 to 21 depending on OH value
  - Sixteen events grow to at least 20 nm with OH x 2
  - Only two grow above 10 nm with half OH

Sensitivity to SO_2 Emissions



Sensitivity to NH_3 Emissions





Research Questions

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- What is the chemistry of new particle
- Is there a suitable predictive model?
- How will it change under future scenarios?
  - SO_2 and NH_3 controls

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- What are the important characteristics of new the particle formation events?
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  - SO_2 and NH_3 controls
  - Further Control of Vehicular Primary Emissions
- How representative is Pittsburgh?
- What is the vertical profile?