Nucleation and Growth of Atmospheric Aerosols

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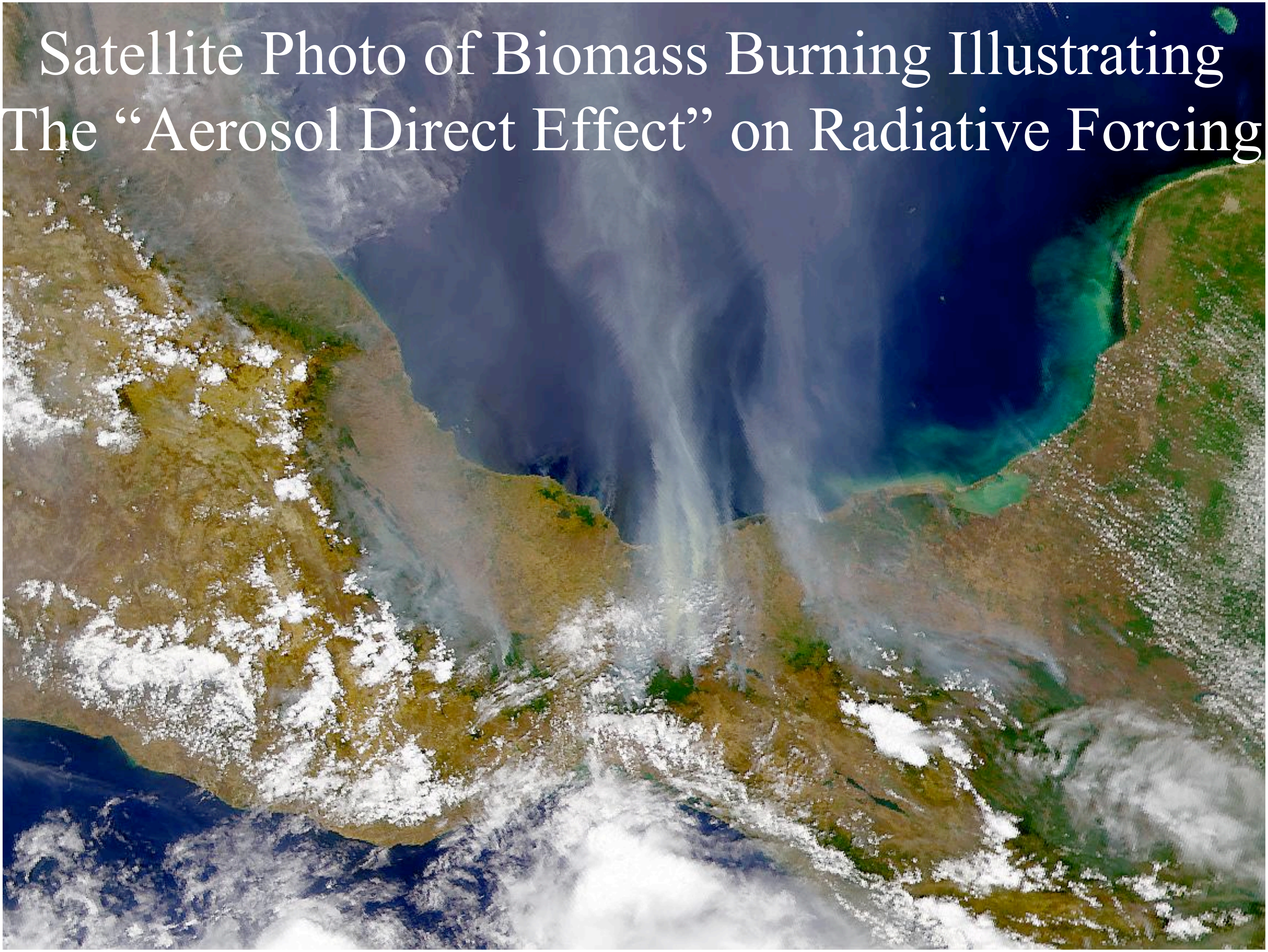
Acknowledgments

Jim Smith, Fred Eisele , Jeff Rathbone, Lee Mauldin, Kelley Barsanti and others (NCAR)
Ken Iida, Chongai Kuang, Mark Emery, Mari Titcombe,
Hiromu Sakurai,Mark Stolzenburg, Jeff Roberts, Alon McCormick(UMN)

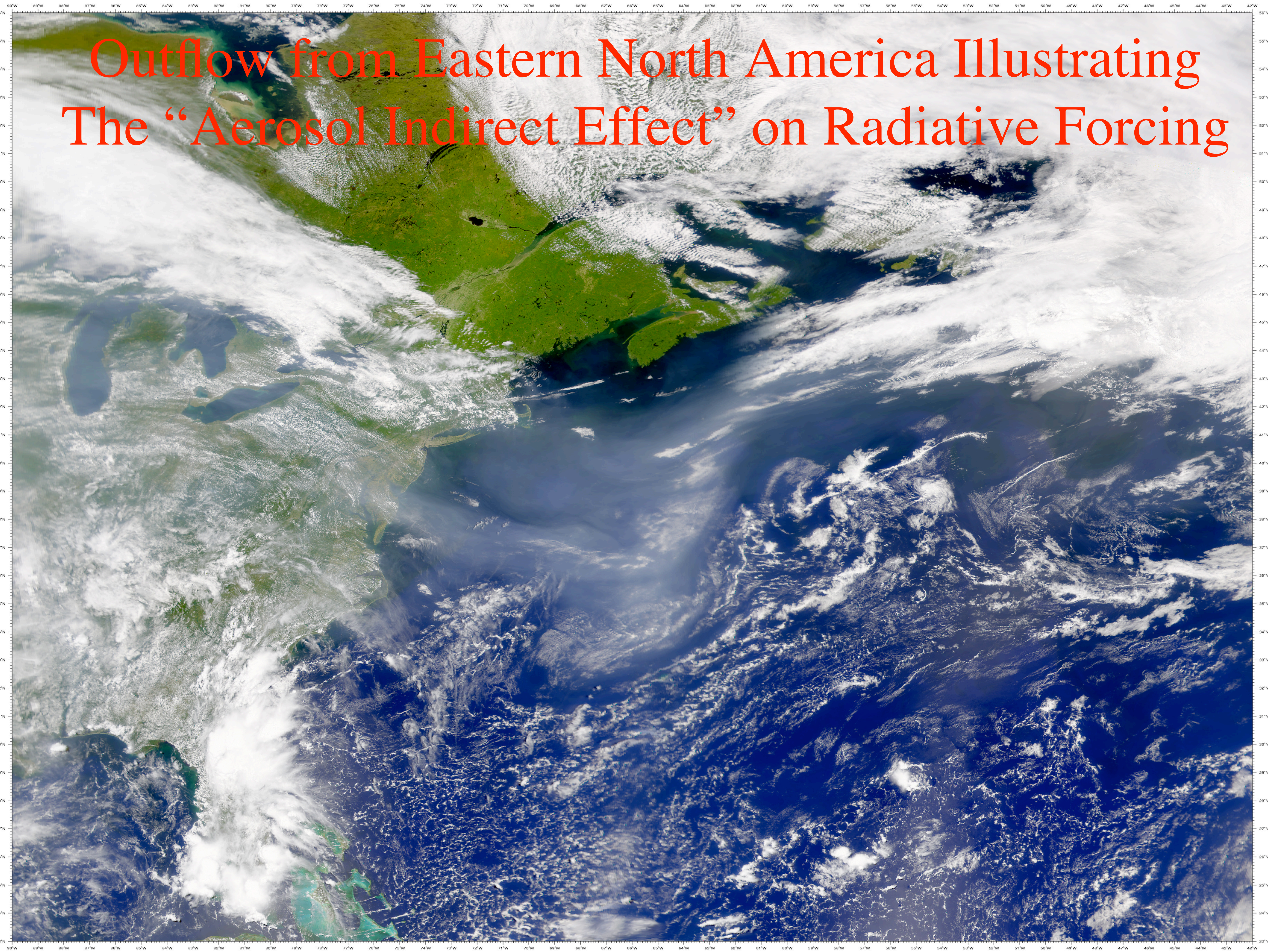
DOE ASP, NSF NIRT

NOSA, 11/8//07

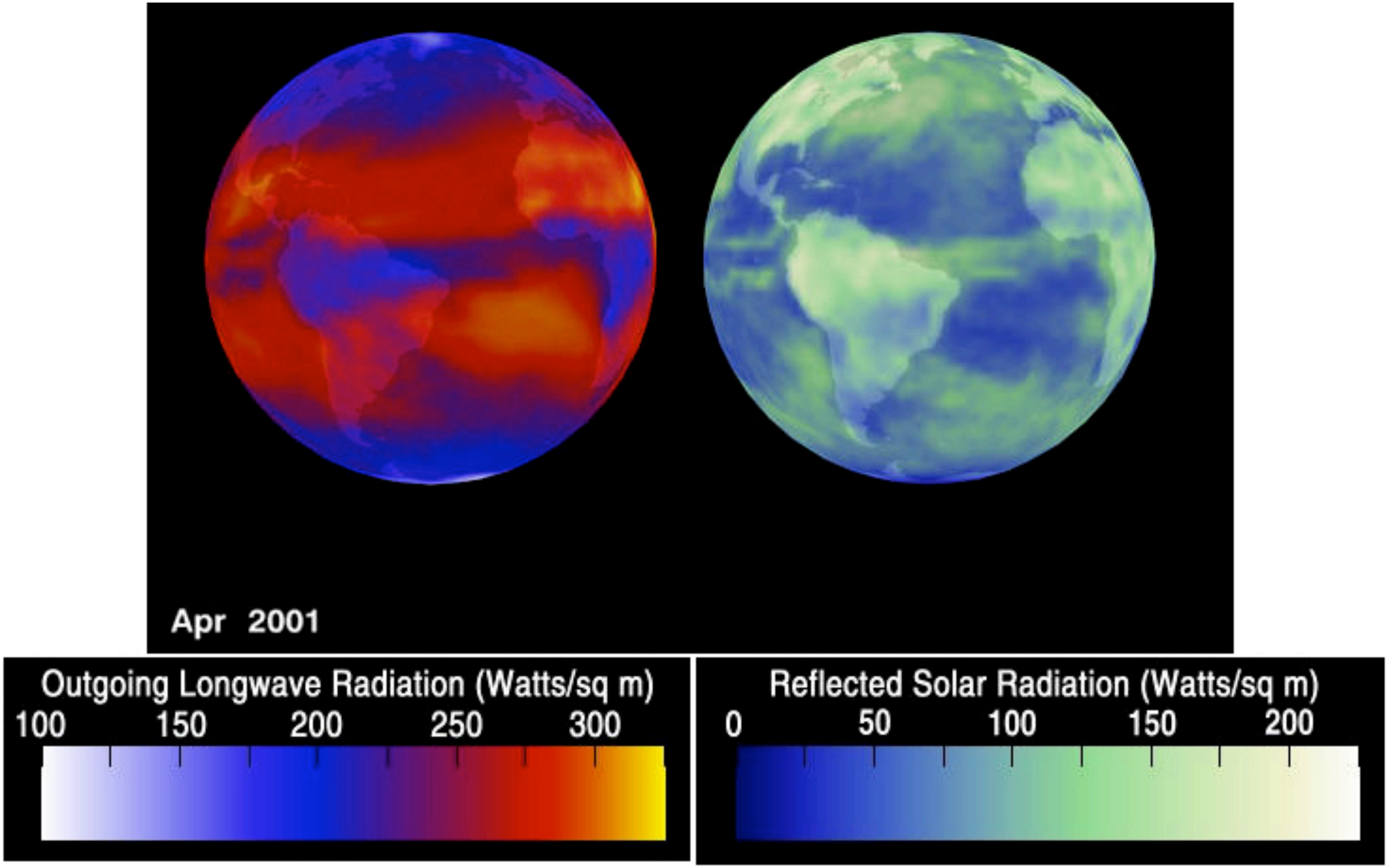
Satellite Photo of Biomass Burning Illustrating The "Aerosol Direct Effect" on Radiative Forcing



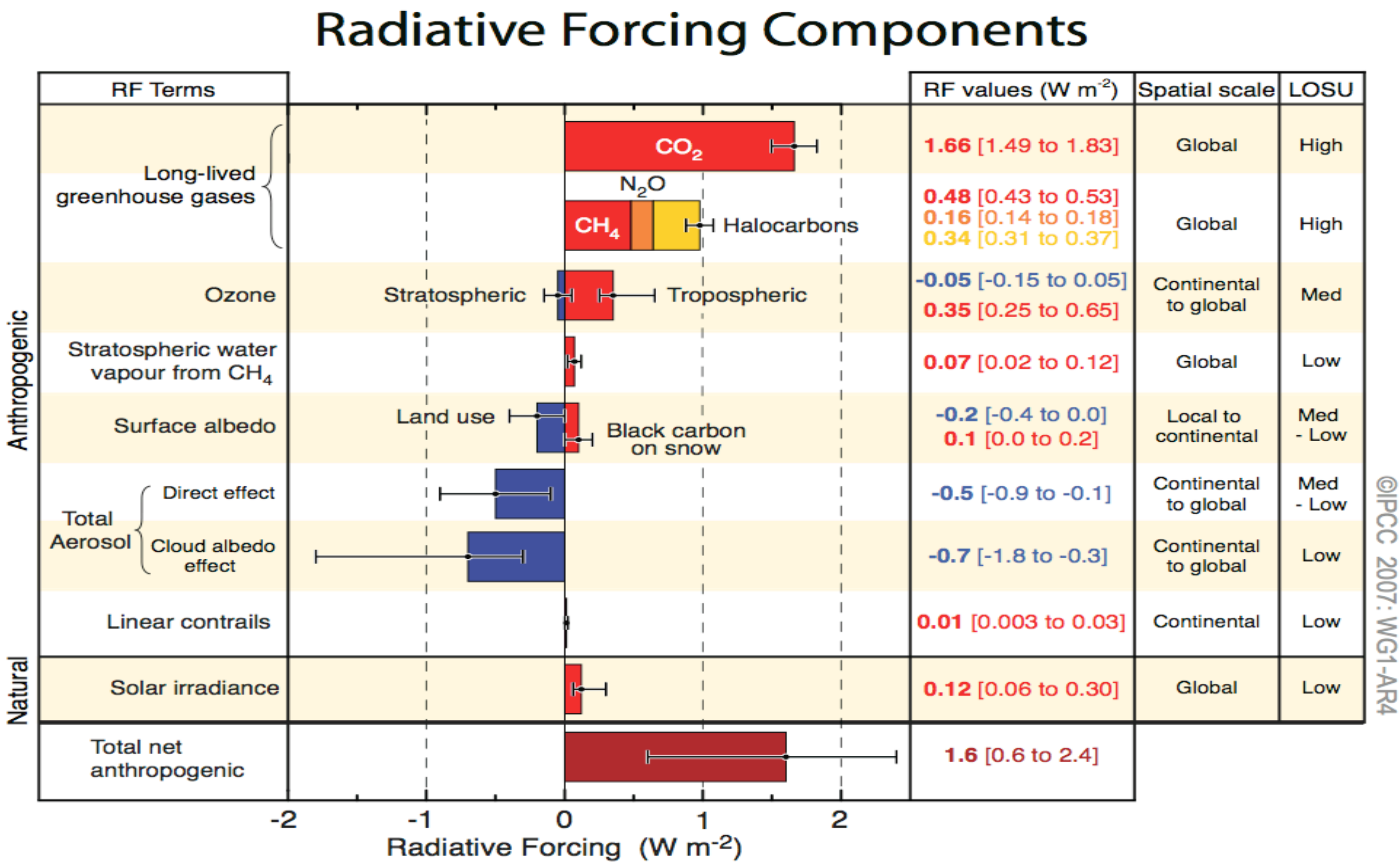
Outflow from Eastern North America Illustrating The "Aerosol Indirect Effect" on Radiative Forcing



IR and Reflected Visible Radiation, April 2001



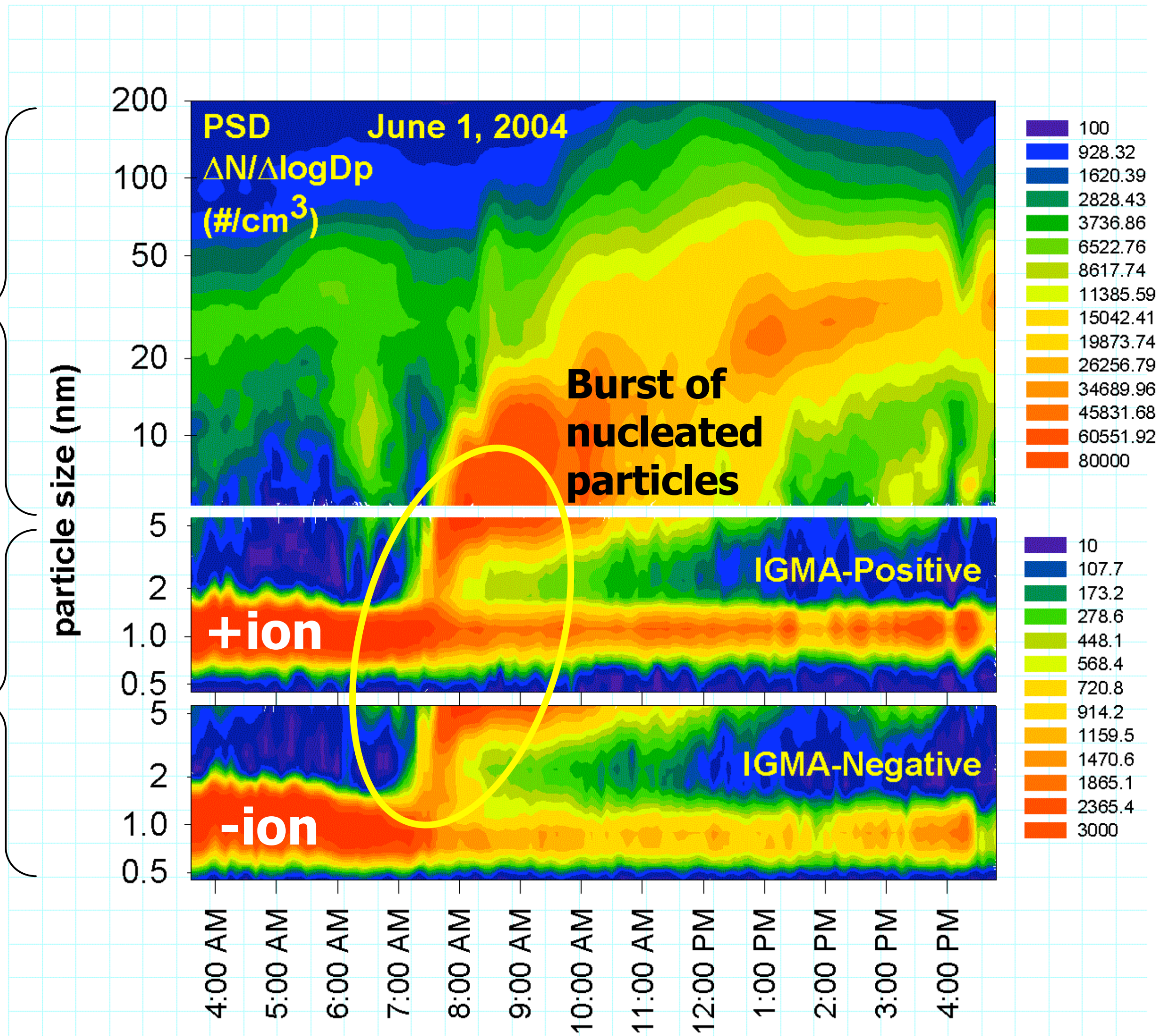
Global-average radiative forcing estimates and ranges (IPCC 2007)



New Particle Formation (NPF) Event Boulder, CO

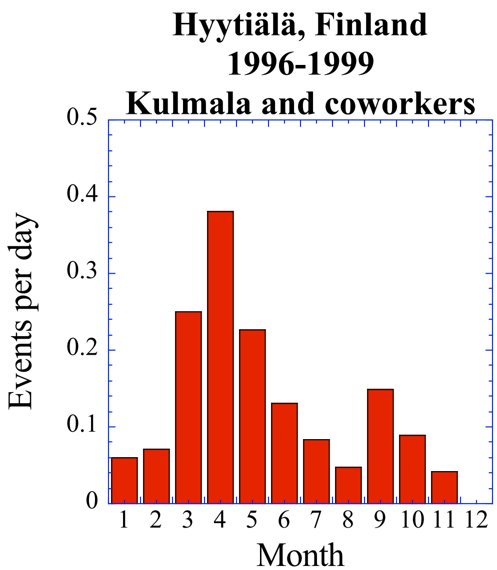
Size Distribution of all charge states

Size Distribution of Charged Particles (Ions)

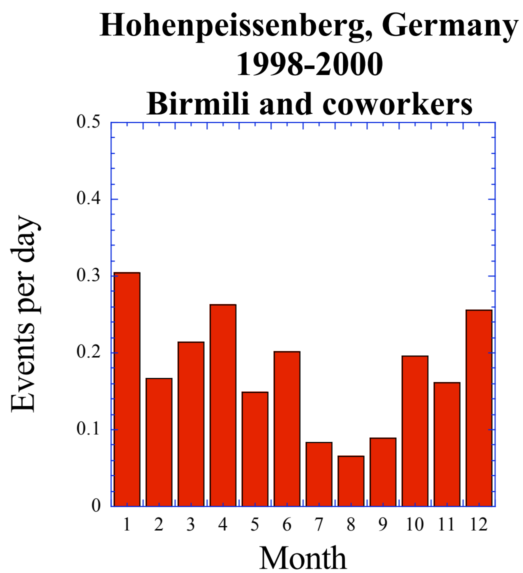


Frequency of Regional NPF Events at Three Locations

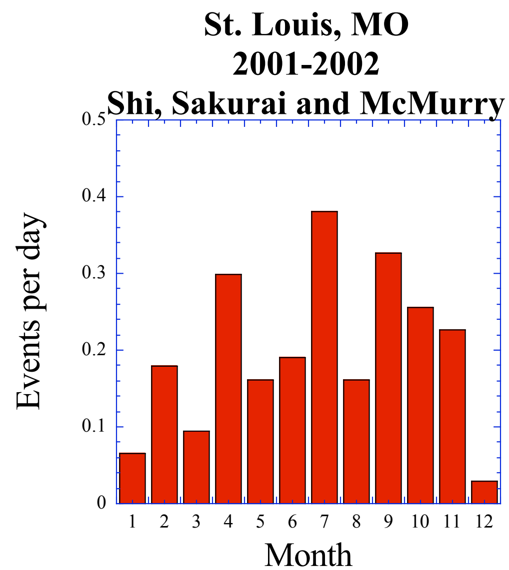
(Kulmala, McMurry et al., JAS, 2004)



Finnish Boreal Forest



Continental Europe



Major U.S. City

John Aitken, 1911-12, "The Sun as a Fog Producer," Proc. Royal Society of Edinburgh **XXXII**.

- Sunlight on air containing SO_2 produces particles
- Radioactivity has the same effect (ion-induced nucleation)
- NH_3, H_2O_2 & O_3 enhance particle formation by SO_2
- Combustion products produce "very great numbers of nuclei"

"*Though this investigation clearly shows that the sun produces certain kinds of fogs yet is by no means here contended that it is to be censured for their appearance. It would rather appear that it is doing its best to show us the state of pollution into which our modern civilisation has brought our atmosphere…*"

Why is *New Particle Formation* Important?

- It occurs frequently throughout the troposphere
- It appears to be an important source of Cloud Condensation Nuclei (CCN)

  -*Aerosol Indirect Effect* on Radiative Forcing

Key Scientific Questions Regarding NPF

- *What are the physical/chemical processes that control the rates at which new particles (stable molecular clusters) are produced (i.e., the nucleation rates, J)?*

- *What are the physical/chemical processes that control the rates at which freshly nucleated particles grow?*

What do we understand about factors that influence new particle formation rates, J?

-Dependence on "L" (scavenging parameter)

-Dependence on [H_2SO_4]

Scavenging Parameter "L"

$$L = \frac{\text{Loss Rate to Preexisting Particles}}{\text{Loss Rate to Larger Clusters}}$$

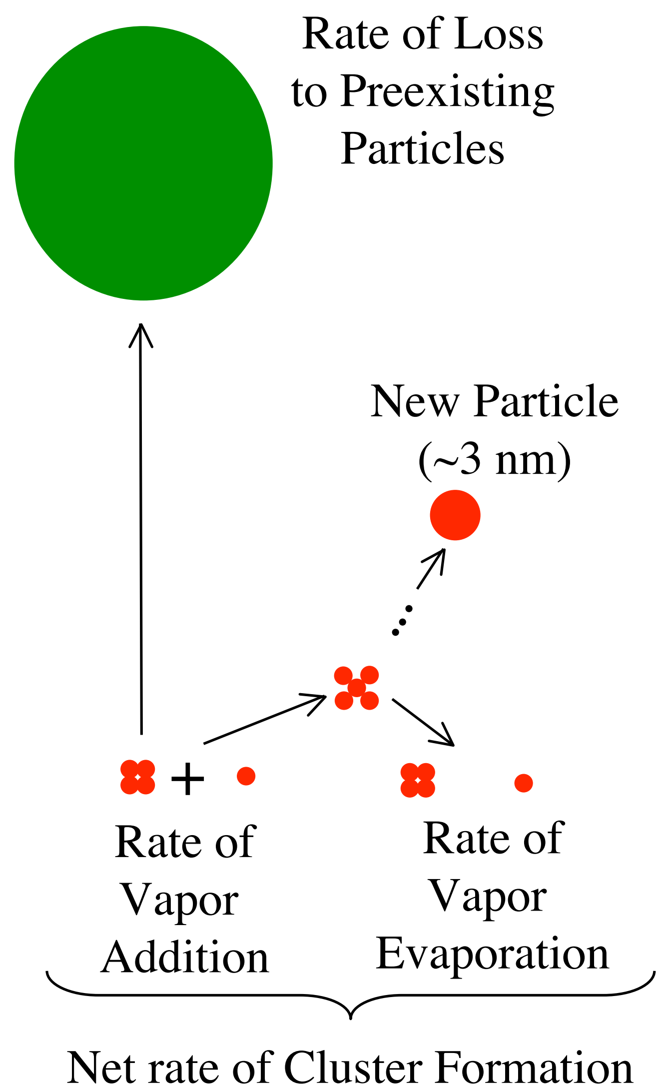
$$= \frac{\bar{c}_1}{4\beta_{11}} \frac{A_{Fuchs}}{[H_2SO_4]}$$

(if H_2SO_4 is the condensing vapor)

A_{Fuchs} = Aerosol "surface area"

c_1 = Mean Thermal Speed of Vapor

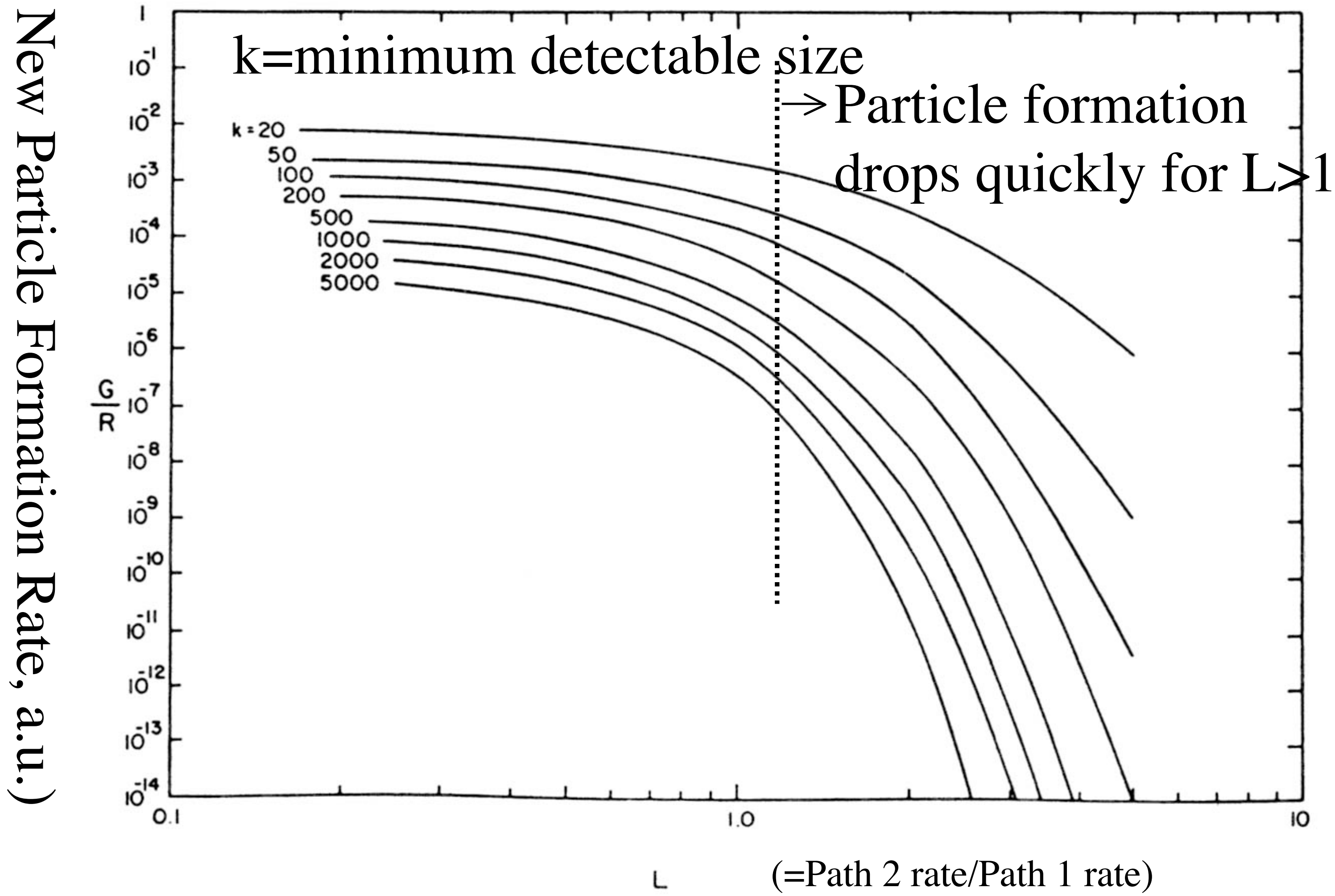
β_{11} = Forward rate constant



McMurry et al., JGR doi:10.1029/2005JD005901

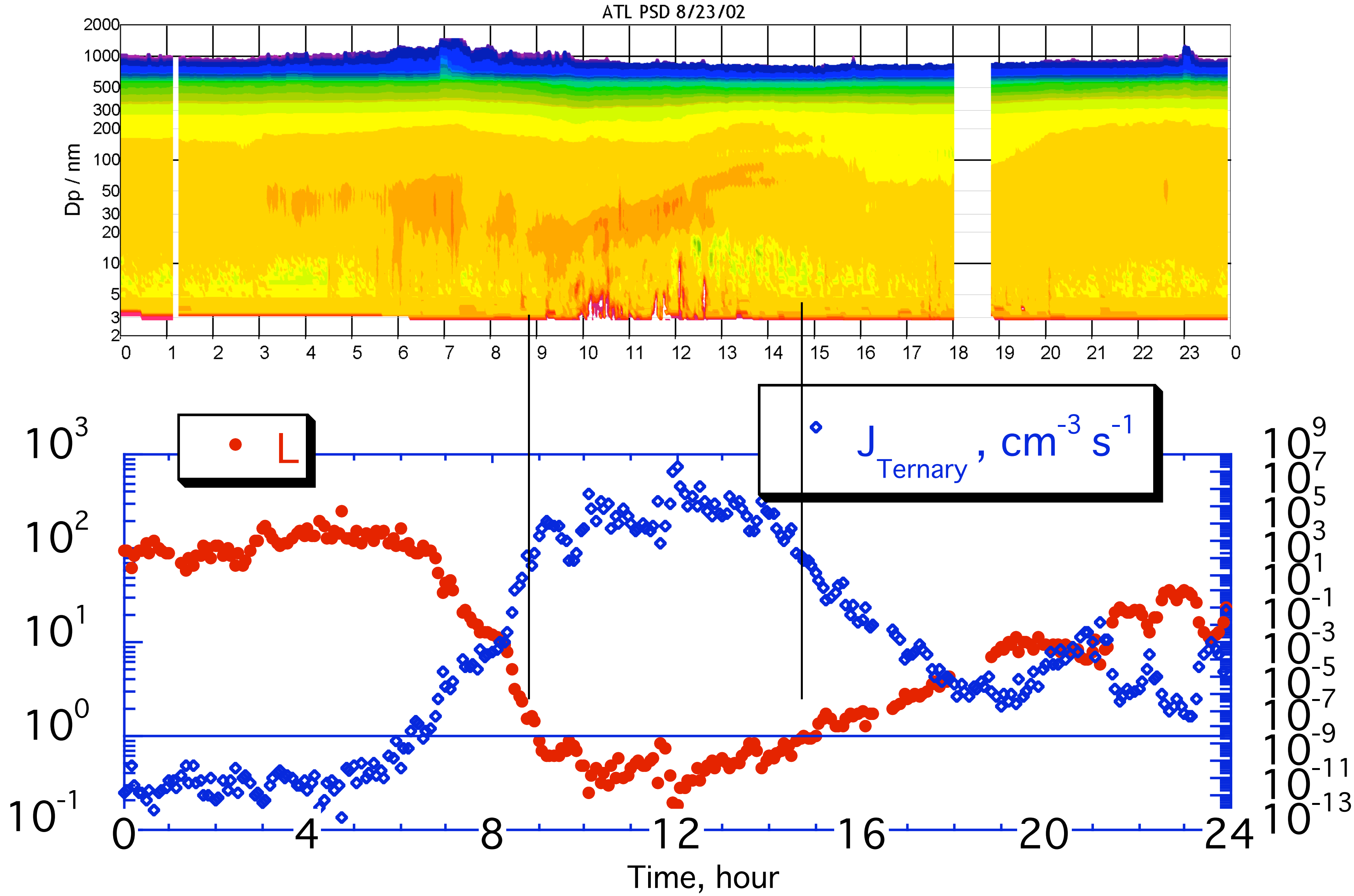
Dependence of New Particle Formation Rates on "L" for Collision-Controlled Nucleation

McMurry, JCIS, ***95****, 72, 1983*



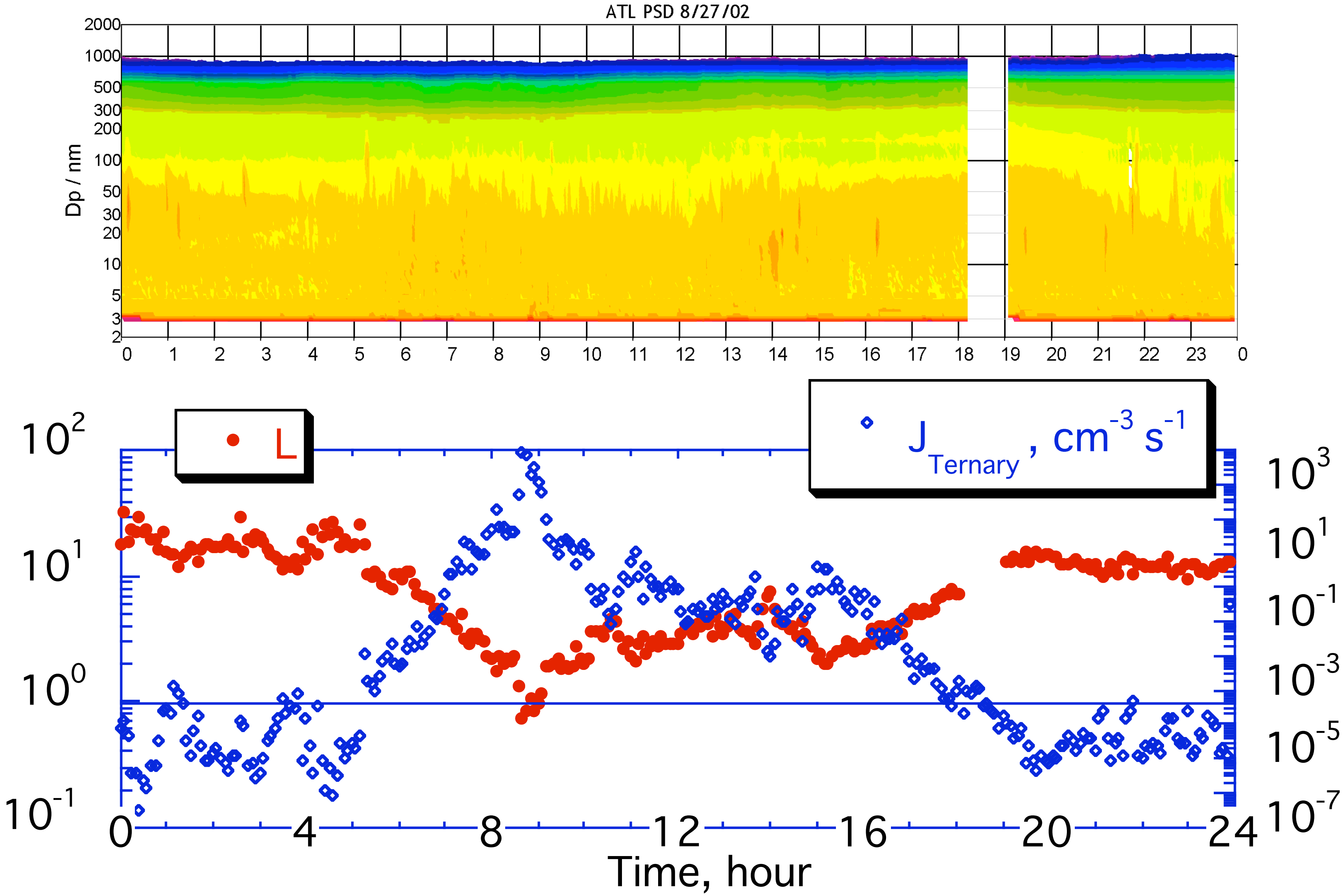
Nucleation & Growth Event
Atlanta, GA, Aug 23, 2002

(McMurry et al, JGR, doi:10.1029/2005JD005901, ***2005****)*

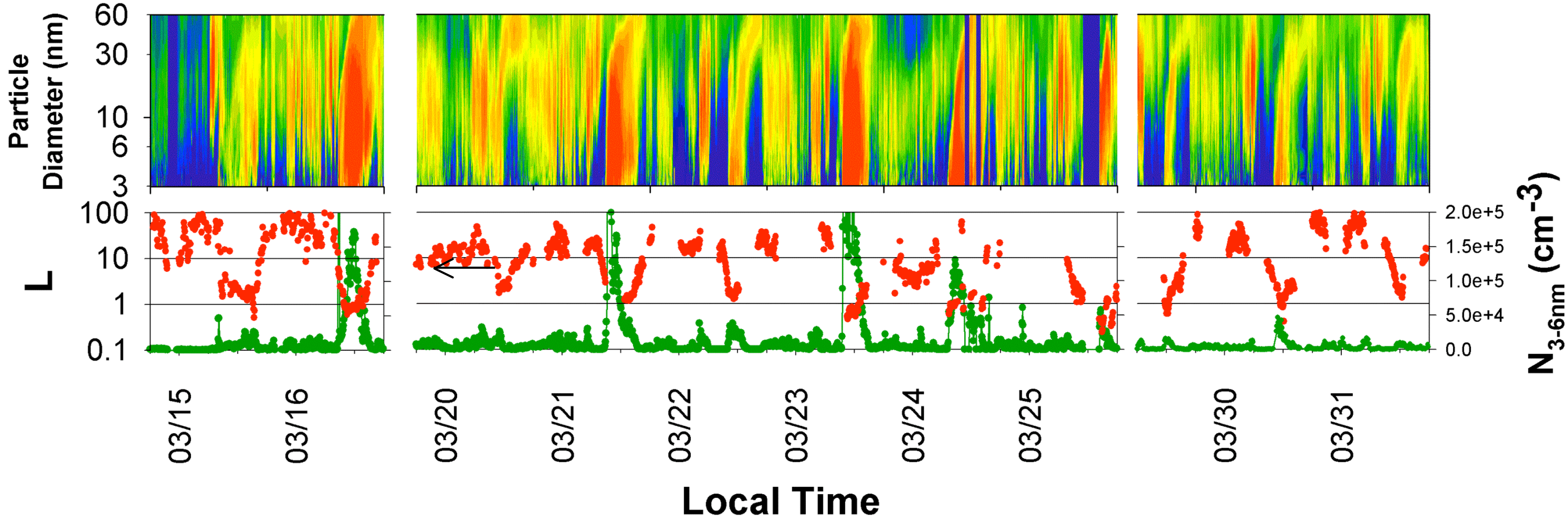


Day with No Nucleation & Growth
Atlanta, GA, Aug 27, 2002

(McMurry et al, JGR, doi:10.1029/2005JD005901, ***2005****)*

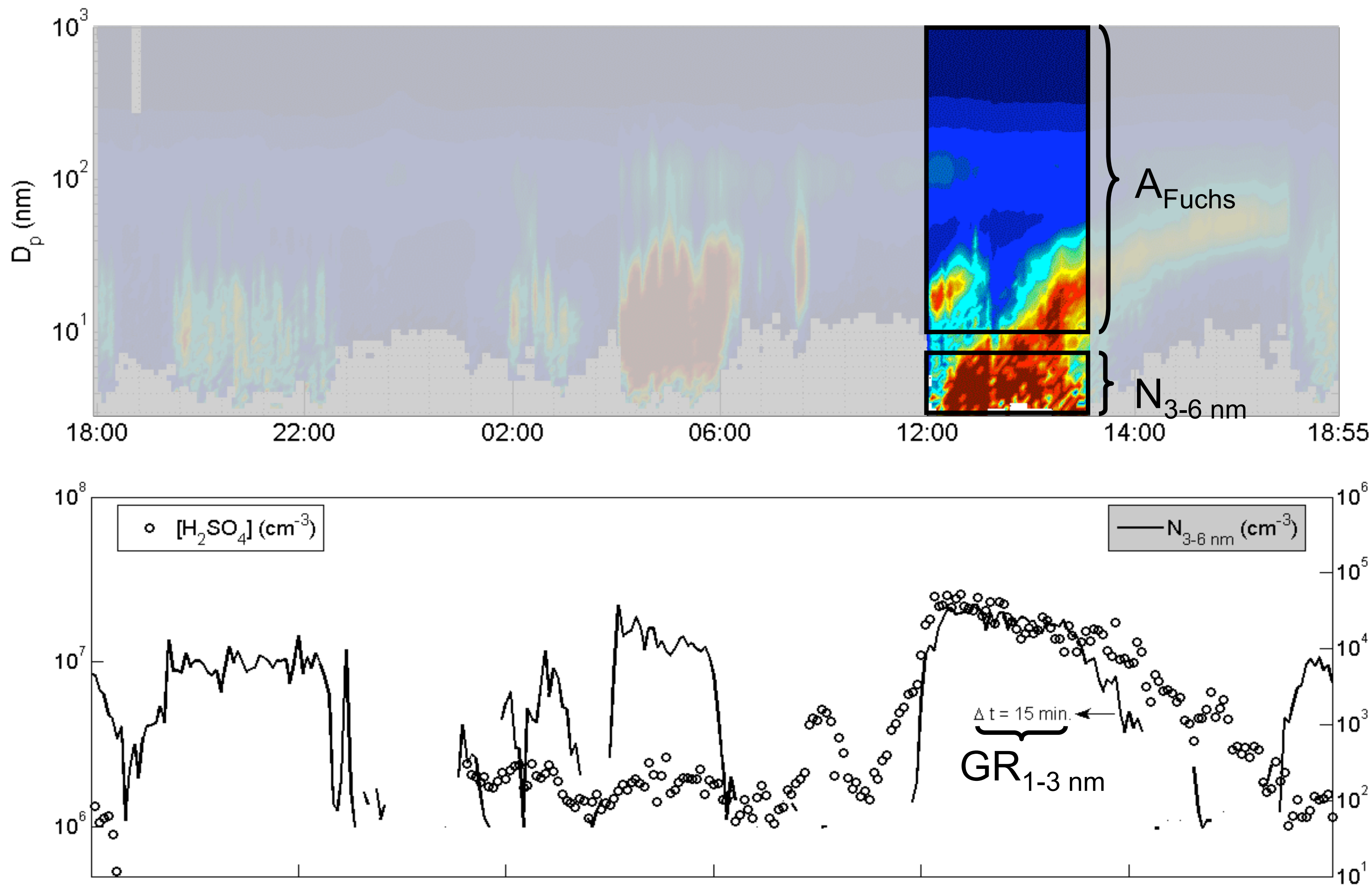


NPF Occurred Frequently in Mexico City, and was observed when “L” Dropped Below 1



Iida, McMurry et al., 2007

Dependence of J on H_2SO_4: Mexico City, March 2006

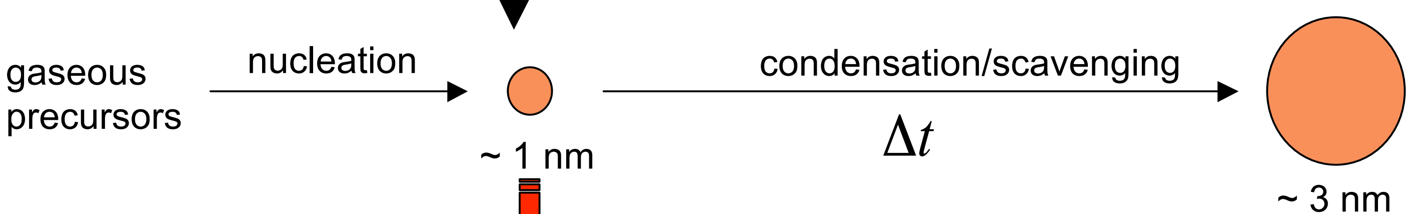


Kuang et al., submitted 2007

Estimating $J_{1\ nm}$ from $J_{3\ nm}$

$$J = K \cdot [\mathrm{H_2SO_4}]^P$$

direct measurement



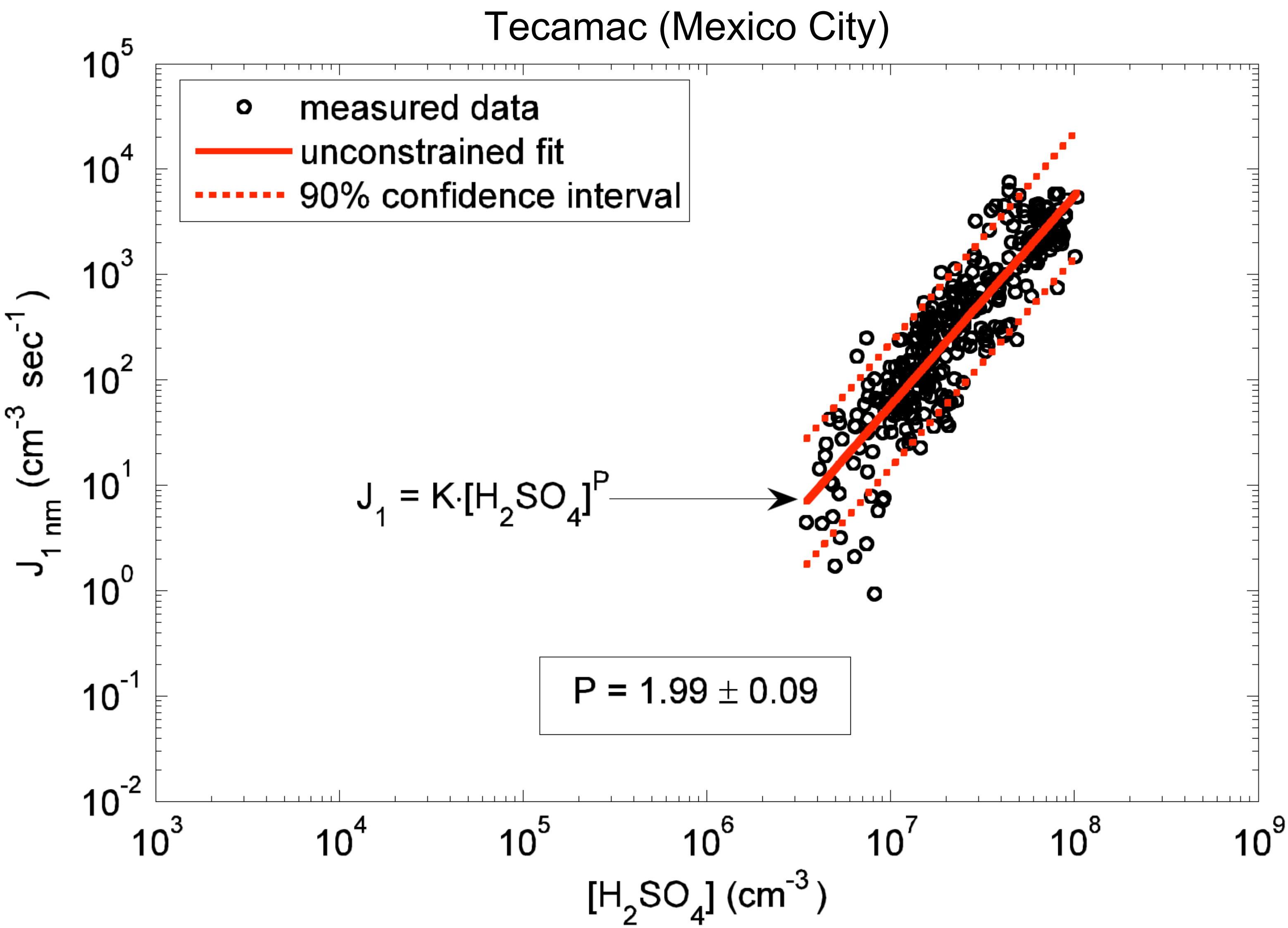
$$J_{1\ nm}(t) = J_{3\ nm}(t+\Delta t)\exp\left[\frac{A_{Fuchs}}{GR_{1-3\ nm}}\psi_{(T,\rho_P,1\ nm,3\ nm)}\right]$$

Accounts for growth probability from 1 ➔ 3 nm

$$J_{3\ nm} \approx \frac{N_{3-6\ nm}}{\Delta D_p} \cdot GR_{1-3\ nm}$$

McMurry et al., JGR 2005

$J_{1\ nm} = K[H_2SO_4]^2$
Kuang et al, 2007, submitted



Kuang et al., submitted 2007

Best-Fit Parameters *P* and *K* for all observations

Location	Air Mass Type	P[a]	Log $K_{kinetic}$[a]
Tecamac	City	1.99 ± 0.09	-12.2 ± 0.59
Atlanta	City	2.01 ± 0.35	-13.8 ± 0.98
Boulder	Small City	1.98 ± 0.23	-13.4 ± 0.83
Hyytiälä	Boreal Forest	1.99 ± 0.11	-12.4 ± 0.49
Idaho Hill	Mountain Forest	2.04 ± 0.27	-10.8 ± 1.03
Mauna Loa	Marine/Volcanic	2.00 ± 0.16	-12.3 ± 0.40
Macquarie Island	Marine/Biogenic	2.00 ± 1.94	-14.0 ± 0.90
hard-sphere collision theory – Log $K_{hard\text{-}sphere}$			-9.39

- $P = 2$ ➔ critical cluster contains 2 H_2SO_4 molecules
- Suggests bimolecular nucleation mechanism
- $K_{kinetic}$ several orders of magnitude below hard-sphere collision limit
- $K_{kinetic}$ varies with environment

[a] 90% Confidence Interval

Kuang et al., submitted 2007

What *do we understand about Nucleation Rates (J) and New Particle Formation Rates ($J_{3\ nm}$)*?

•*Nucleation* might occur every day.

•*New Particle Formation*, however, only occurs when L<1.

•$J=K[H_2SO_4]^2$; K Varies with Location

•*Ion-Induced Nucleation* only contributes a small fraction (<10%) of NPF in Boulder and Mexico City.

Current work aimed at understanding reasons for p=2 and variability in K

-Cluster-CIMS*: Measurement of neutral molecular clusters (Fred Eisele, Lee Mauldin, Jeff Rathbone, NCAR)

-Bridging the gap: Molecular clusters to nanoparticles

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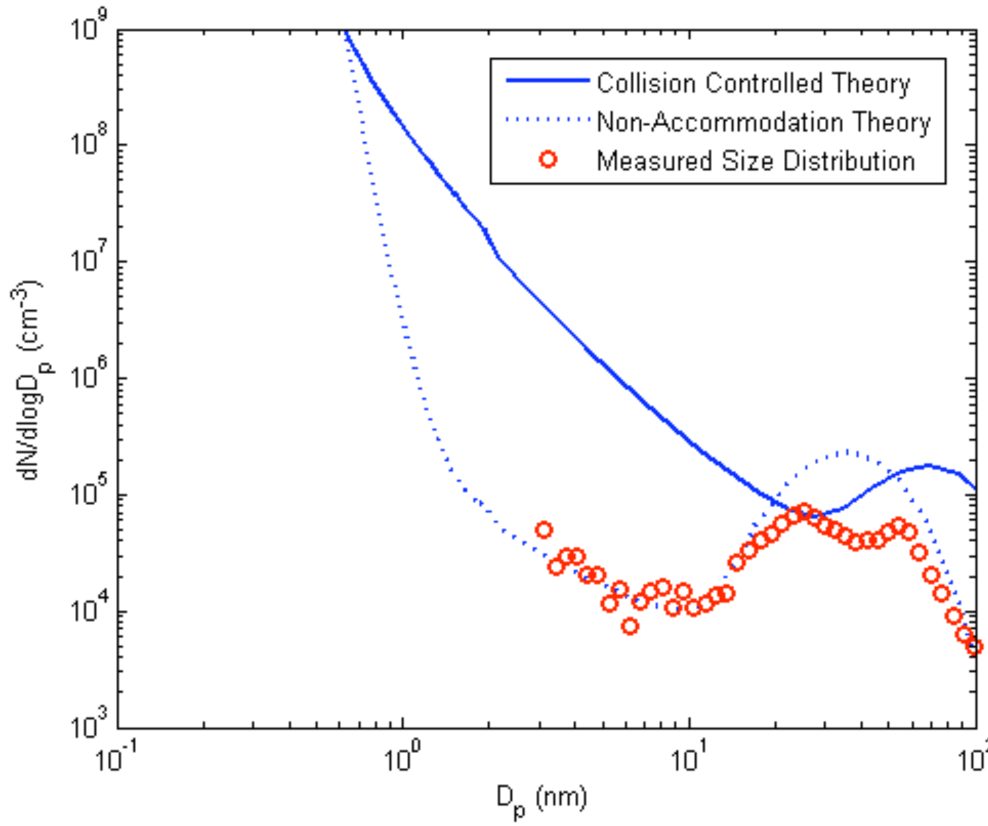
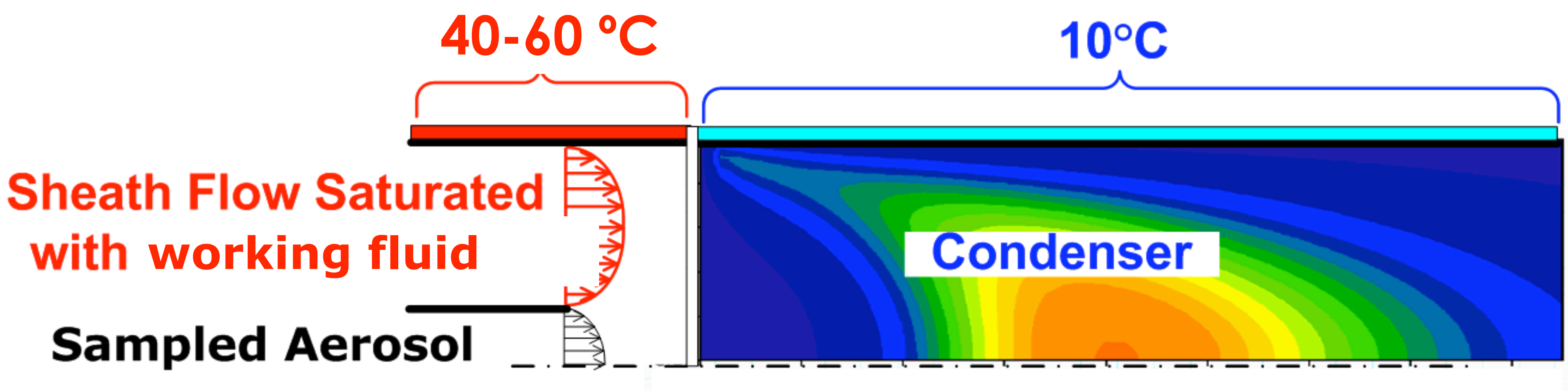
*Cluster Chemical Ionization Mass Spectrometer

Comparison of Measured and Collision-Controlled Size Distributions

Atlanta, August 19, 2002, 12:37



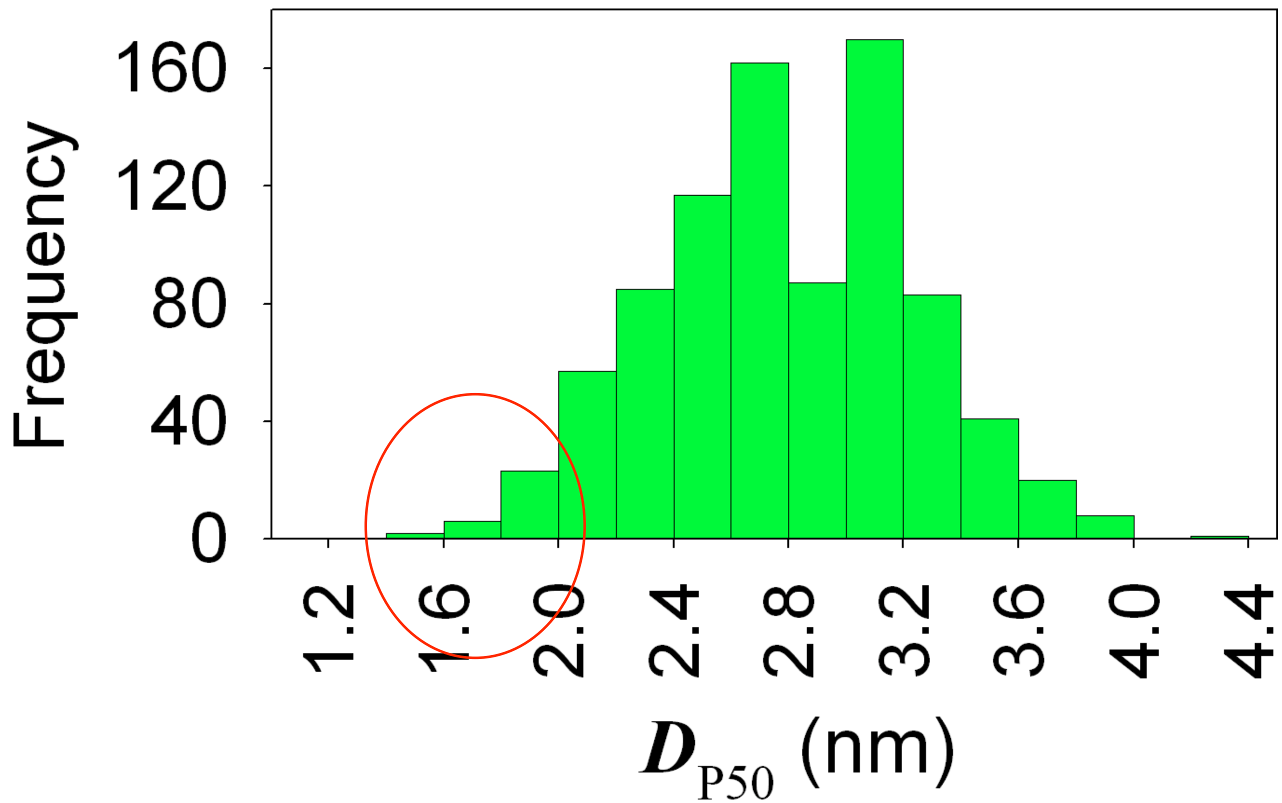
Design of Laminar Flow
1 nm Condensation Particle Counter (Kenjiro Iida)



- Set Condenser T at 10 °C
- Increase saturator temperature until Homogeneous nucleation rate = 1 $cm^{-3}s^{-1}$
- Choose working fluid to optimize detection of very small (~1 nm) particles

Iida., PhD Thesis, 2007

Frequency Distribution of D_{P50} for 861 Organic Liquids (Kenjiro Iida)



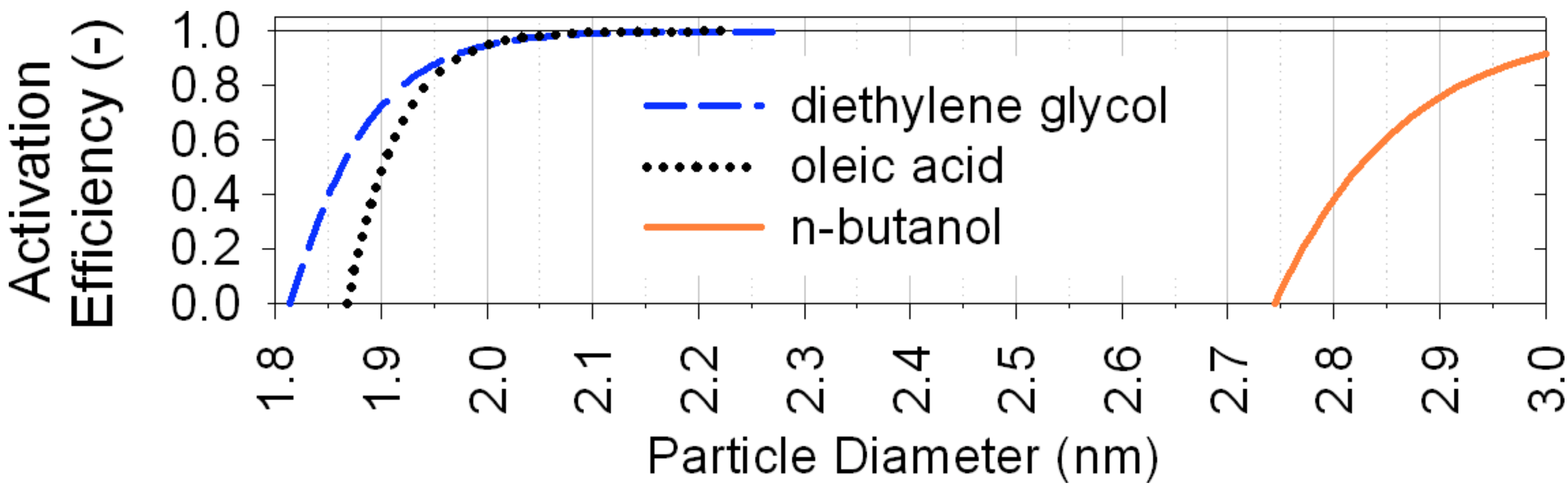
- Our model predicts that several of these liquid organic working fluids activate particles smaller than 2 nm.

Iida., PhD Thesis, 2007

Two Groups of Working Fluids
(Kenjiro Iida)

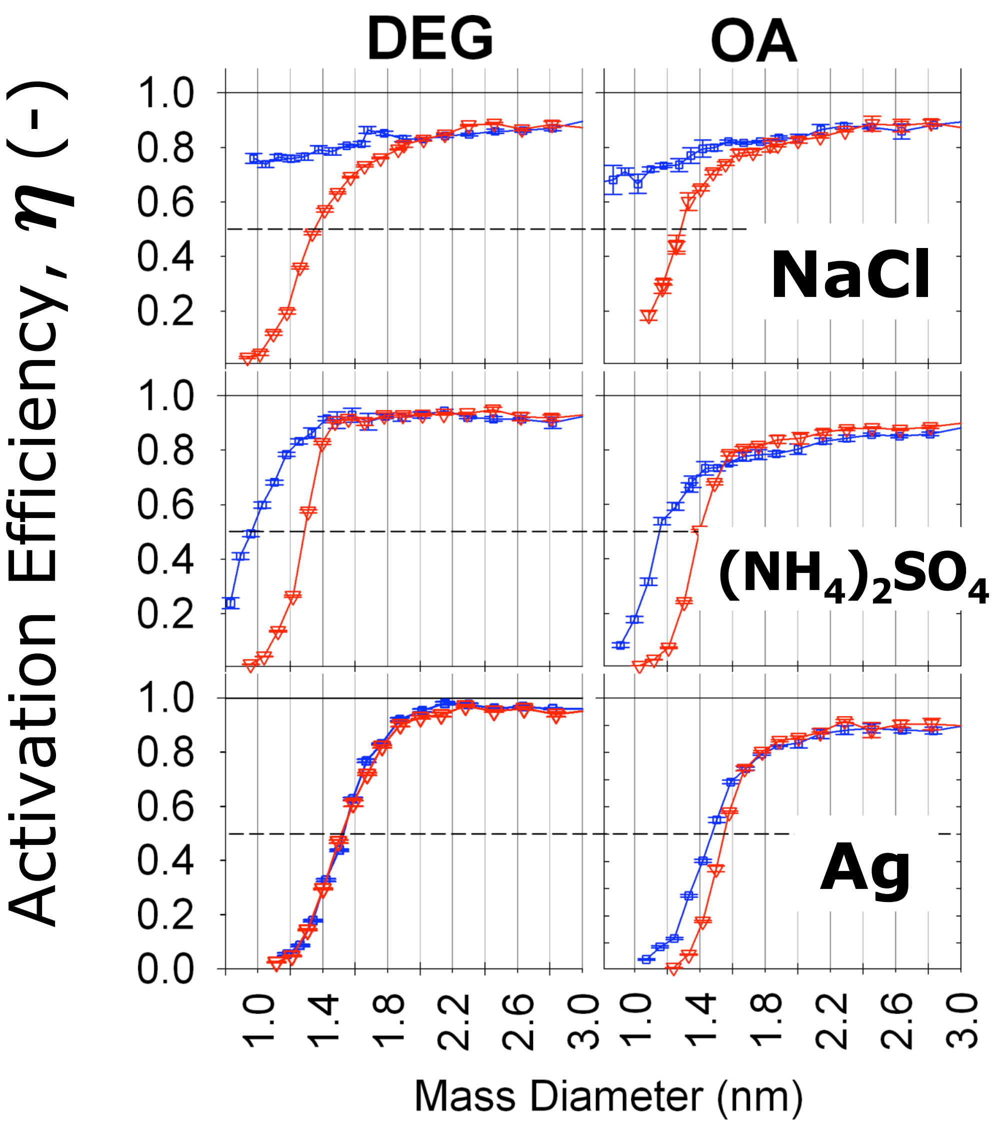
High Surface Tension → Diethylene Glycol

Low Vapor Pressure → Oleic Acid



Iida., PhD Thesis, 2007

Experimental Results (Kenjiro Iida)

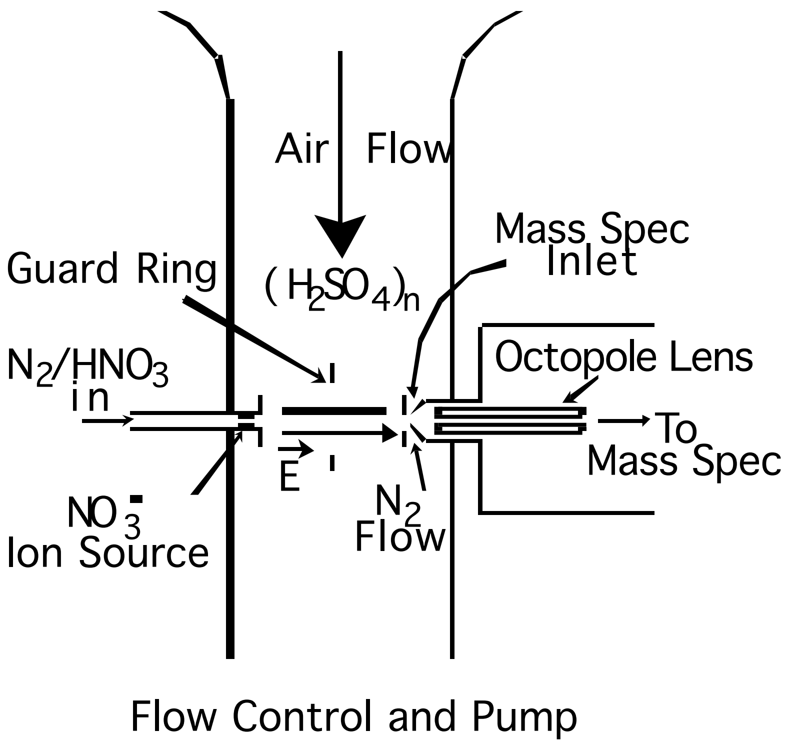


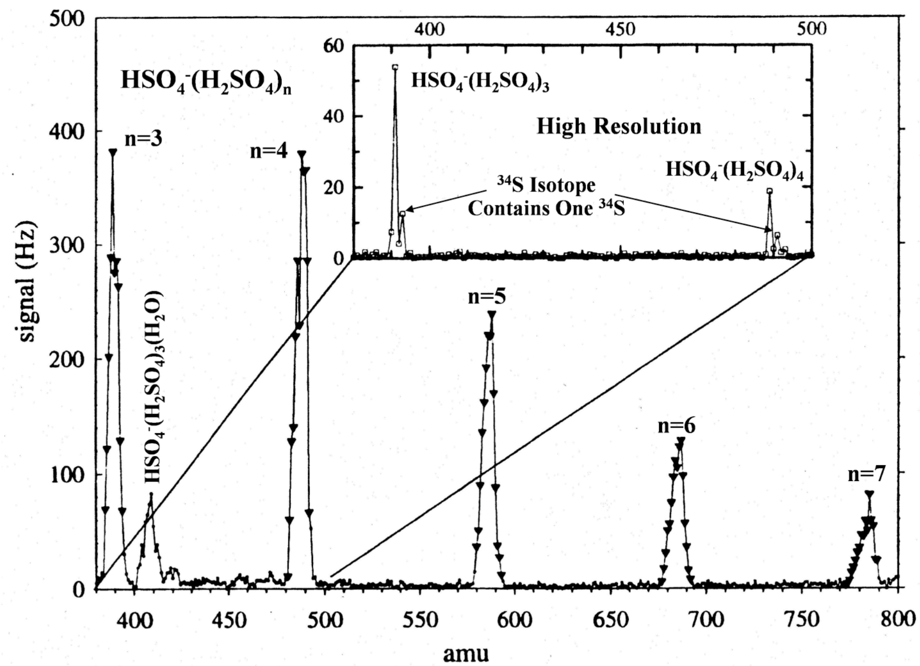
Qualitative Trends

- Negatively charged particles are more easily activated
- Minimum detectable size is sensitive to particle composition

Iida., PhD Thesis, 2007

Cluster-CIMS: Neutral Molecular Clusters (Cluster-Chemical Ionization Mass Spectrometer):





Data from laboratory studies of Eisele and Hanson, 2000

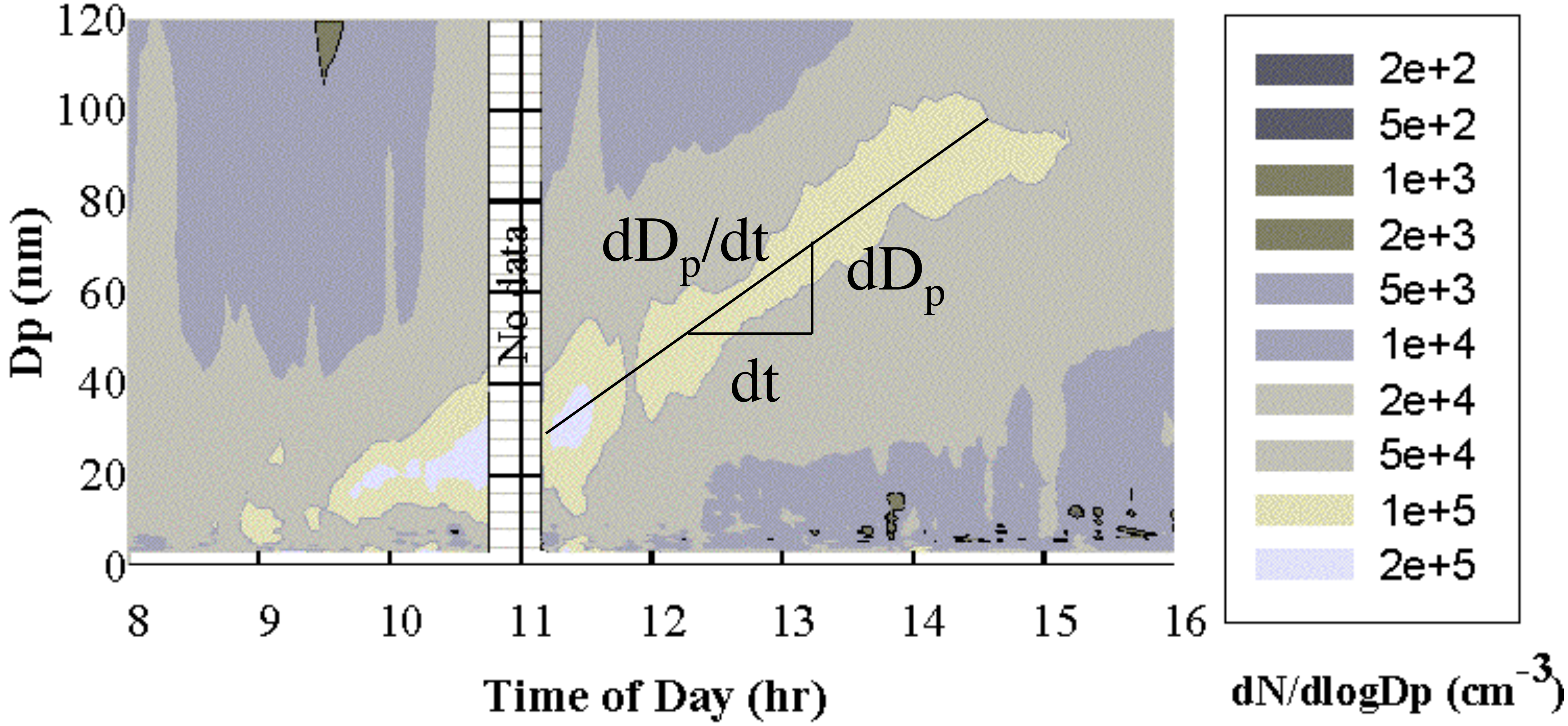
What do we understand about growth rates of freshly nucleated particles?

- Overview of observations
- Dependence on $[H_2SO_4]$

Growth Rates of Freshly Nucleated Particles

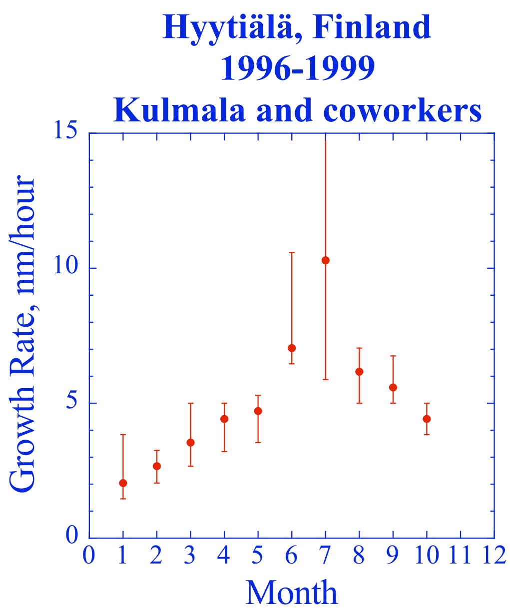
(Stolzenburg, McMurry et al, JGR 110, DOI:10.1029/2005JD005935, 2005)

August 5, 2002, Atlanta, GA

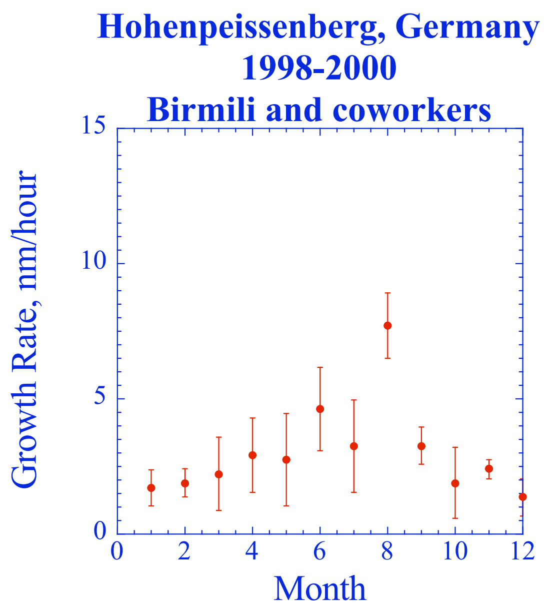


Stolzenburg et al., JGR, 2005

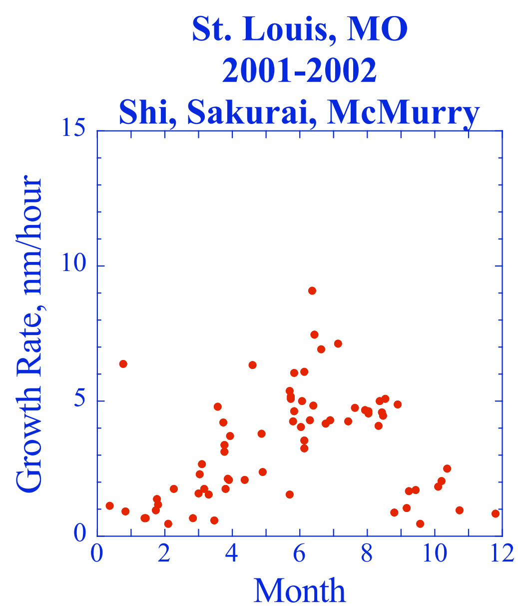
Measured Diameter Growth Rates During Regional NPF Events at Three Locations



Finnish Boreal Forest



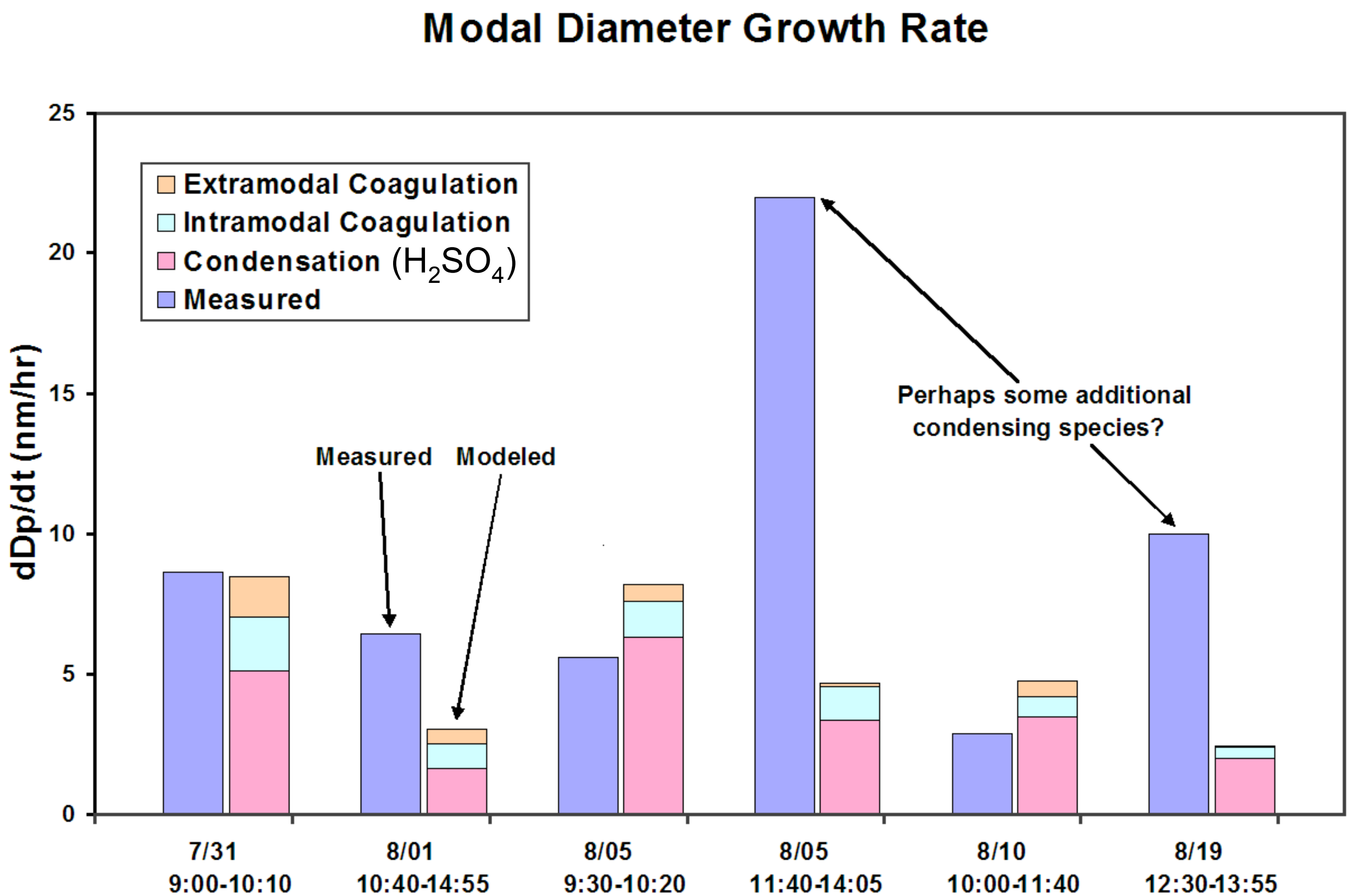
Continental Europe



Major U.S. City

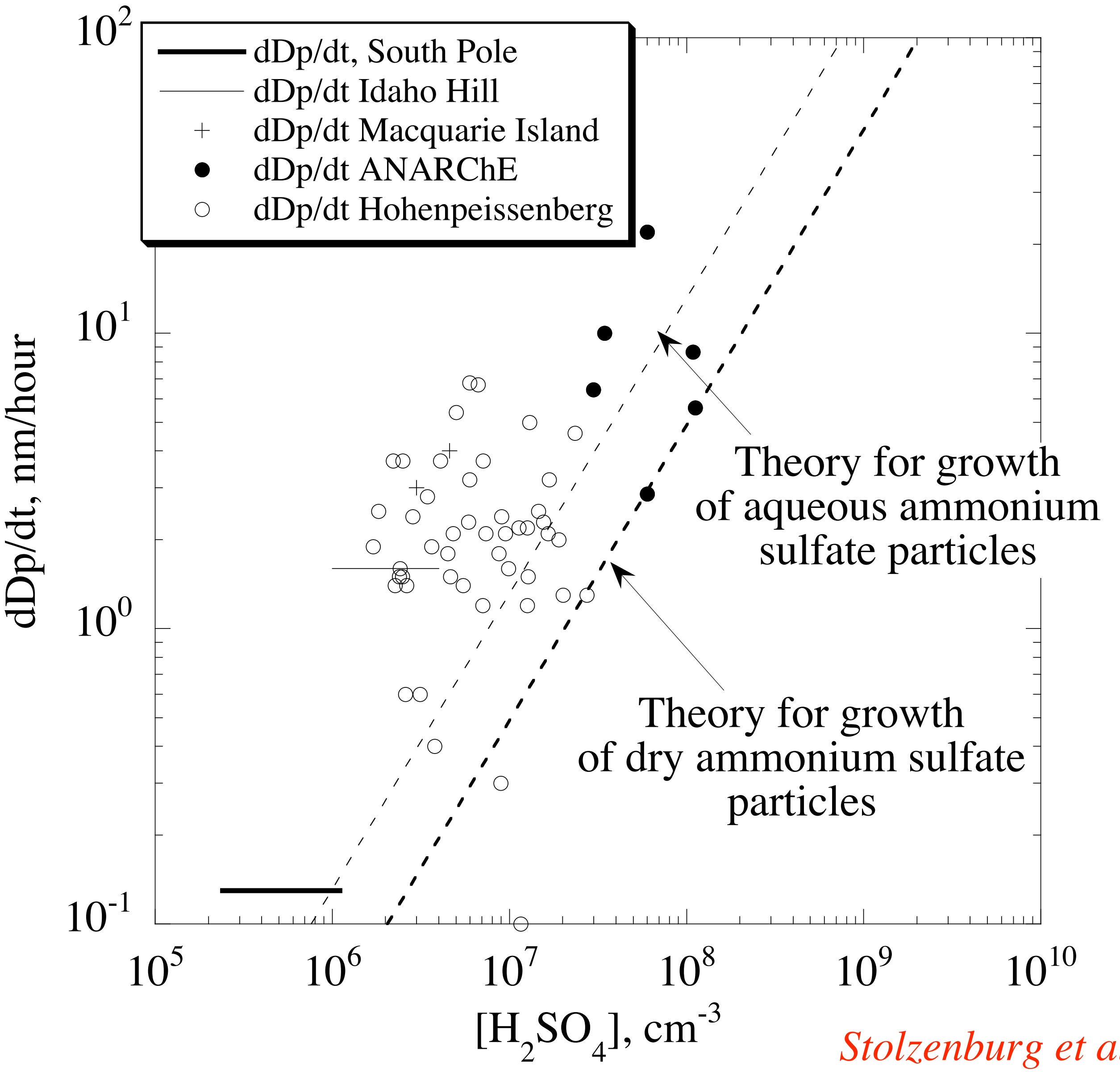
Kulmala, McMurry et al., JAS, 2004

Comparison of Measured and Calculated Growth Rates (Atlanta 2002)



Stolzenburg et al, JGR 110, DOI:10.1029/2005JD005935, 2005

Summary of Diameter Growth Rates vs $[H_2SO_4]$



Stolzenburg et al, JGR, 2005

Current work aimed at understanding why growth rates are so high.

-TDCIMS* measurements of composition:
Reconcile measured growth rates with chemical processes (Jim Smith & Kelley Barsanti NCAR)

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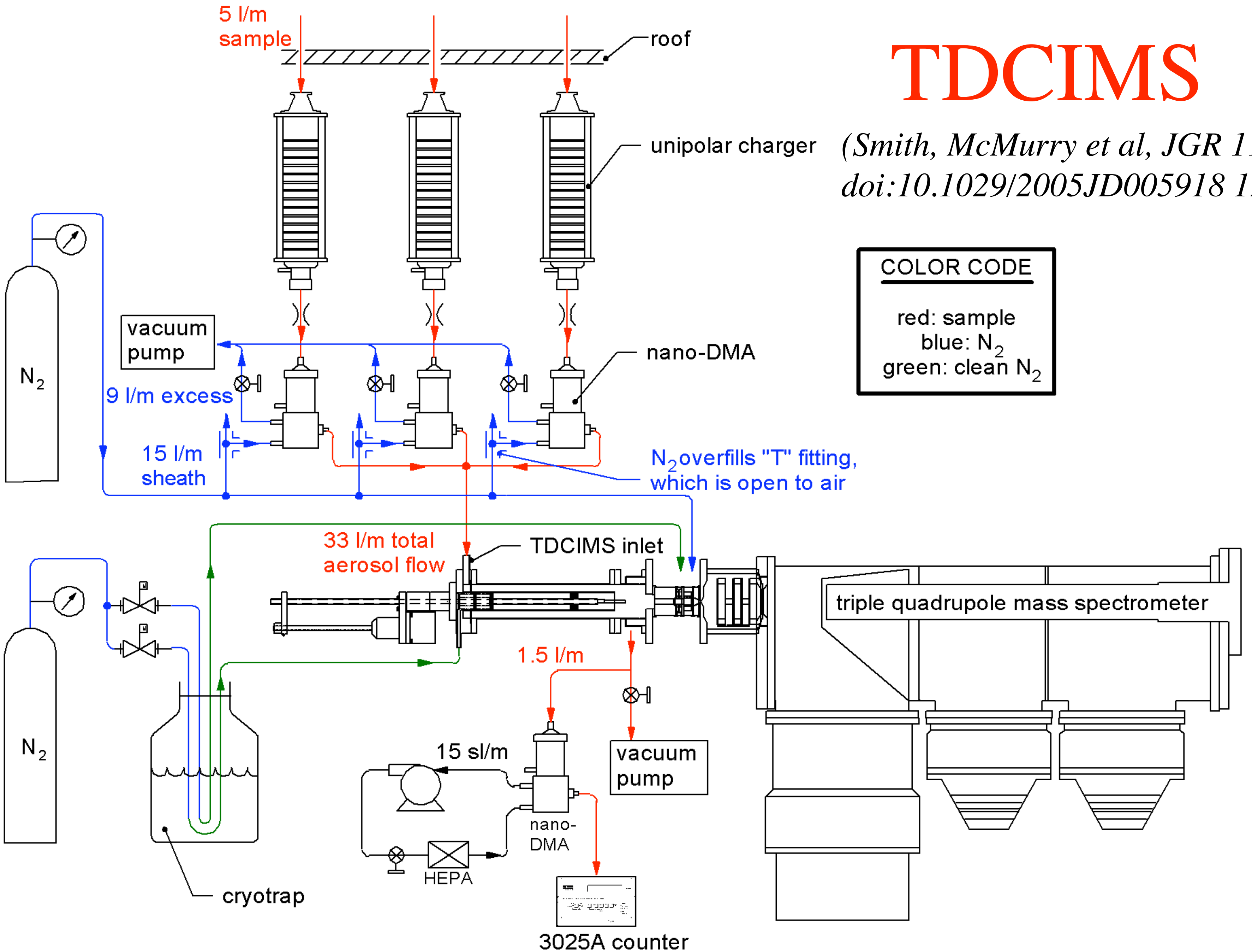
*Thermal Desorption Chemical Ionization Mass Spectrometer

TDCIMS

(Smith, McMurry et al, JGR 110, doi:10.1029/2005JD005918 1200)



Conclusions

- Nucleation is likely to affect climate: Concentrations of Cloud Condensation Nuclei
  - Nucleation occurs on 5 to 40% of the days throughout the year
  - Particle Growth rates are fast: 20 to 100 nm in a day.
- Factors that determine occurrence and extent of NPF
  - "L"
  - J~K[H2SO4]^2, (K's vary with location, however)
  - Cluster-CIMS and 1 nm SMPS show promise for understanding K.
  - Ion Induced Nucleation on some days
  - Participating species are not all yet known
- TDCIMS is providing new information on nanoparticle composition
  - In Atlanta, nucleated particles were mostly $(NH_4)_2SO_4$
  - In Mexico City, nucleated particles were mostly organics and nitrates (5-10% sulfates)
    - » consistent with H_2SO_4 contributions to growth

Thank You