# Insights into the chemical processes that affect growth rates of freshly nucleated particles

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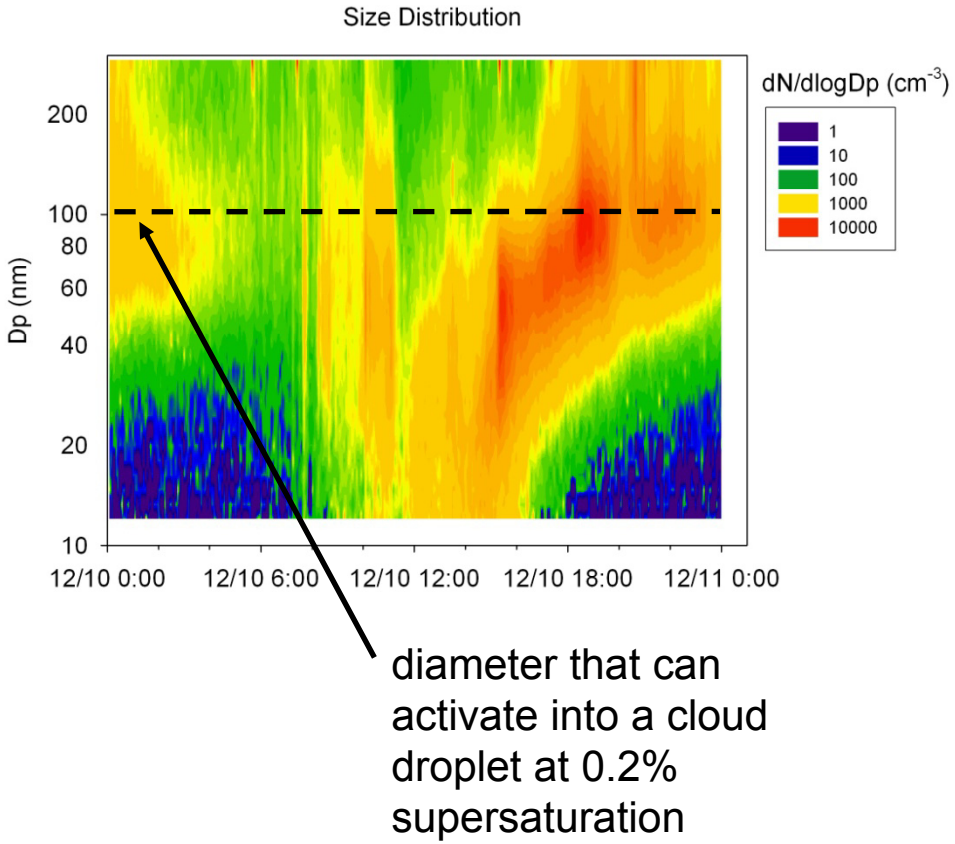
The impacts of *new particle formation* on climate are to modify the amount and properties of cloud condensation nuclei (CCN).

**BEACHON Manitou Forest Observatory**
**New Particle Formation event on Dec 10, 2008**

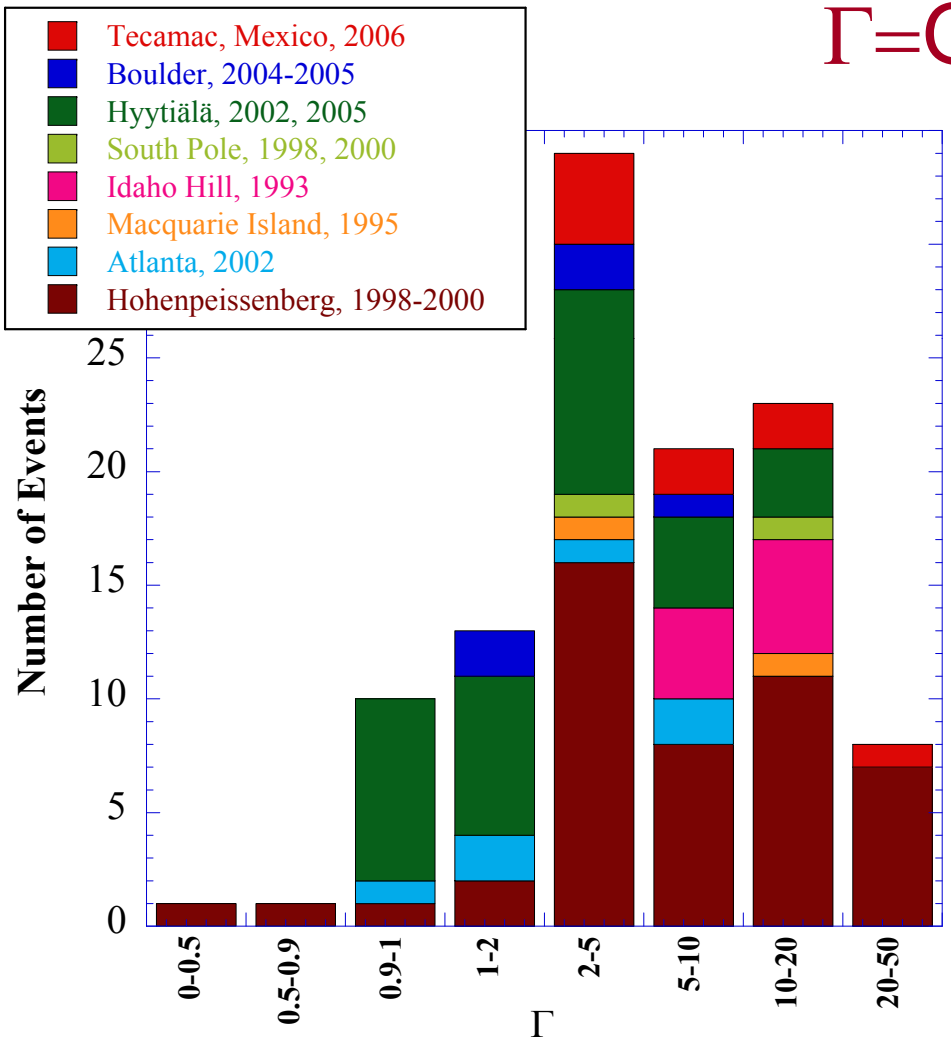



Smith, unpublished

- **Model estimates suggest that new particle formation can contribute up to 40% of the CCN at the boundary layer, and 90% in the remote troposphere (Pierce and Adams, ACP, 2007).**
- **New particle formation is estimated to add as much as a 8 times more particles to the remote southern ocean atmosphere than anthropogenic primary particles (Spracklen et al., ACP, 2006).**

Observed nanoparticle growth rates are typically 2 – 20 times greater than that which can be explained by $H_2SO_4$ condensation

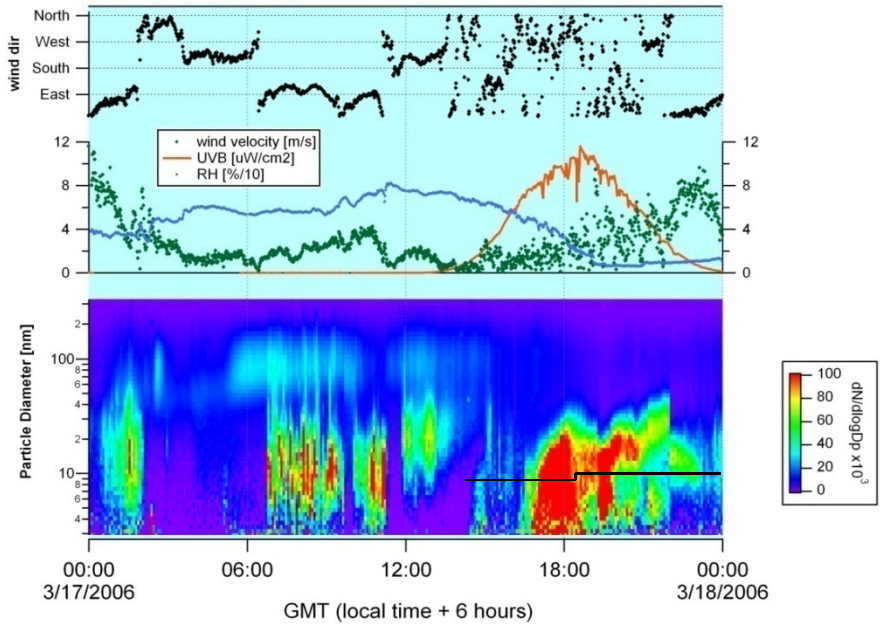
$\Gamma = GR/GR_{H_2SO_4}$



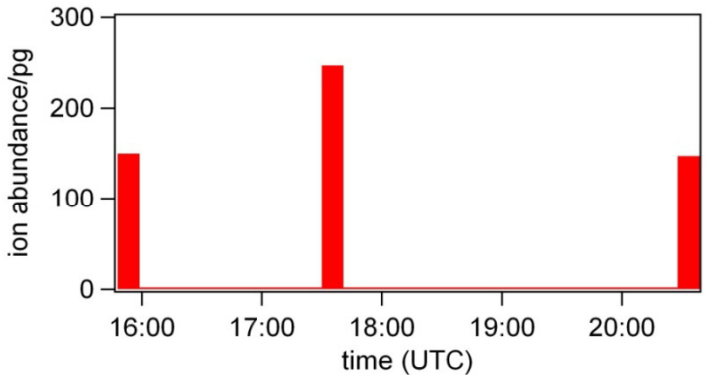

Stolzenburg et al., 2005; Wehner et al, 2005; unpublished, 2009

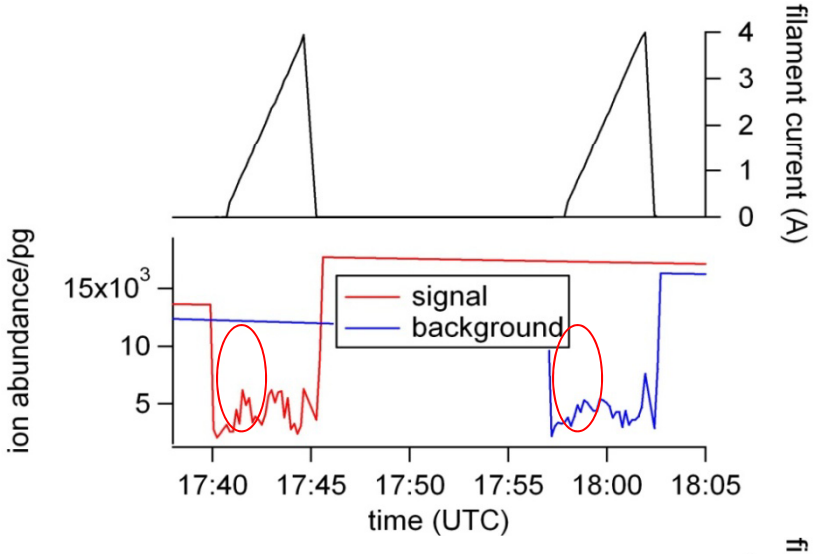
# TDCIMS observations of amines in particles formed from nucleation during MILAGRO

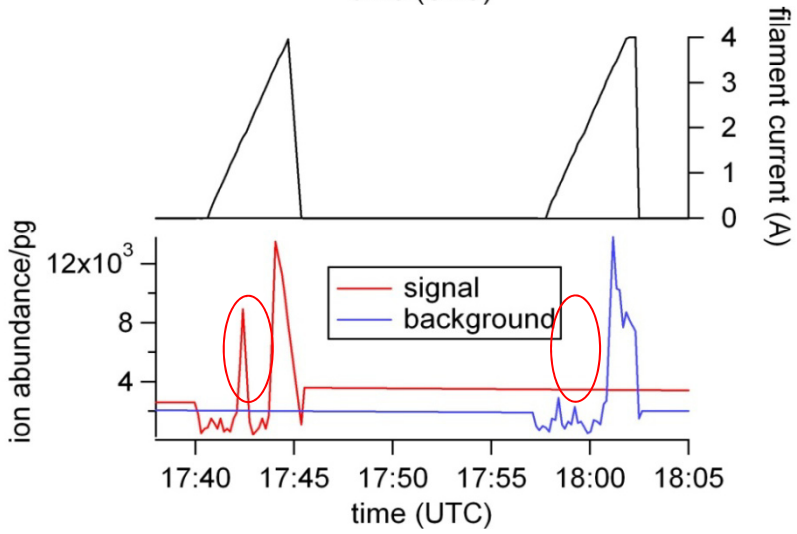
TDCIMS measurements of **8-10 nm** particles during March 17, 2006




m/z 46: dimethylammonium



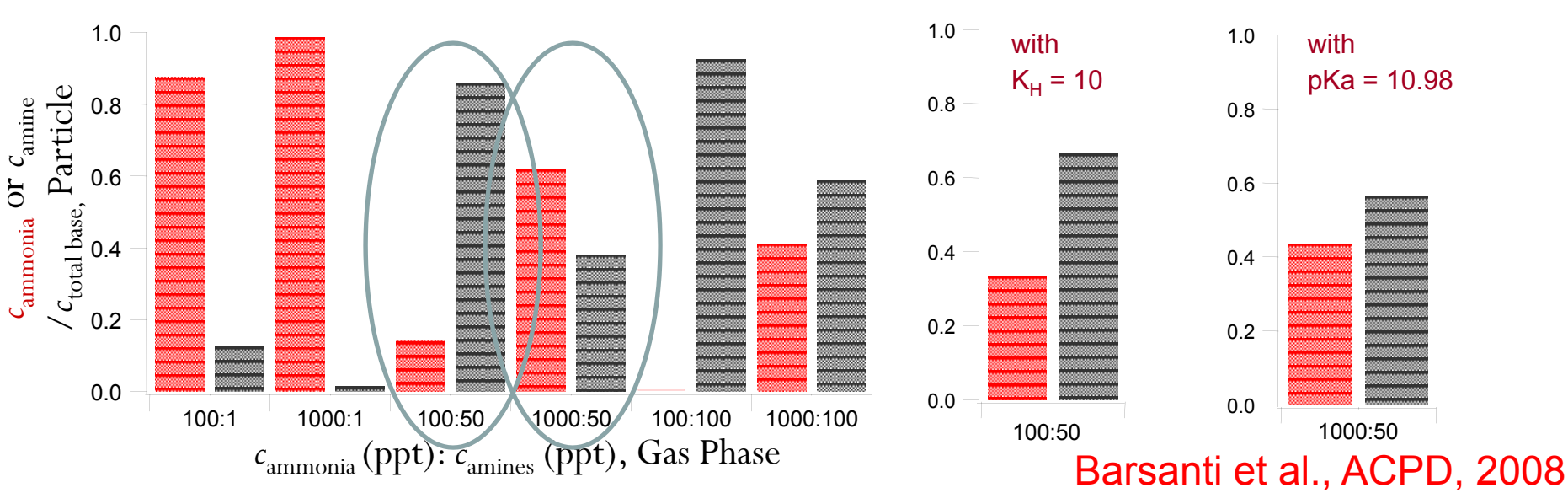




Smith et al., GRL, 2008

# Particulate amine salt formation is thermodynamically favored

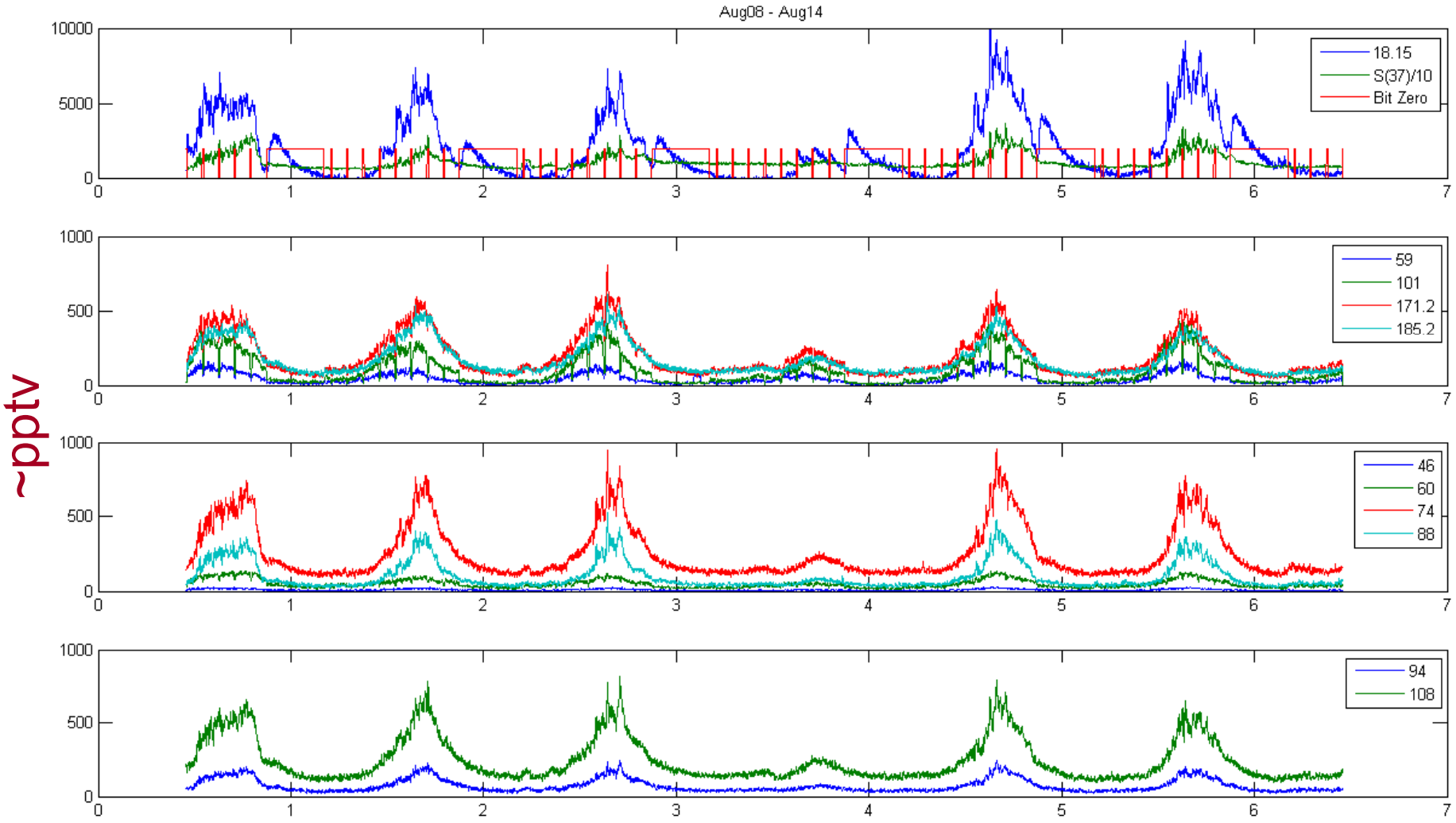
Example: A 10 nm water droplet equilibrated with ambient concentrations of acetic acid, ammonia, and "amines" (methyl, dimethyl, trimethyl, and diethyl). Relevant parameters below.

| HA/B | $K_H$ (M atm$^{-1}$) | p*K*a | $c_i$. gas phase (ppt) |
|---|---|---|---|
| Acetic | 8800 | 4.76 | 100 |
| Ammonia | 60 | 9.25 | 100,1000 |
| "Amines" ($MeNH_2$, $Me_2NH$, $Me_3N$, $Et_2NH$) | 10, **30** ($Me_3N \approx 10$, $Et_2NH \approx 40$) | 9.76, **10.64**, 10.98 ($Me_3N = 9.76$, $Et_2NH = 10.98$) | 1, 50, 100 (based on urban/rural measurements in Sweden, Grönberg et al., 1992) |




Barsanti et al., ACPD, 2008

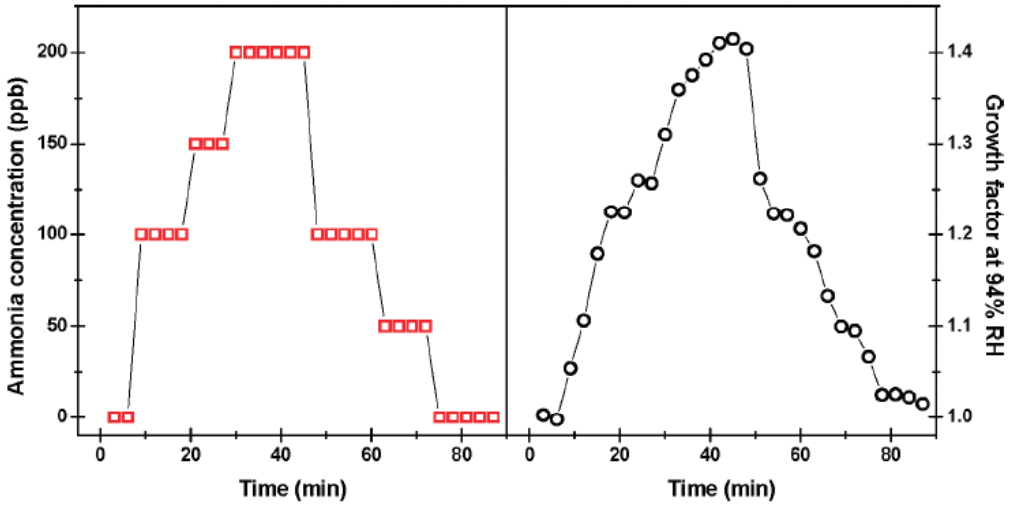
# Gas phase amines can be abundant (e.g., Atlanta 2009)



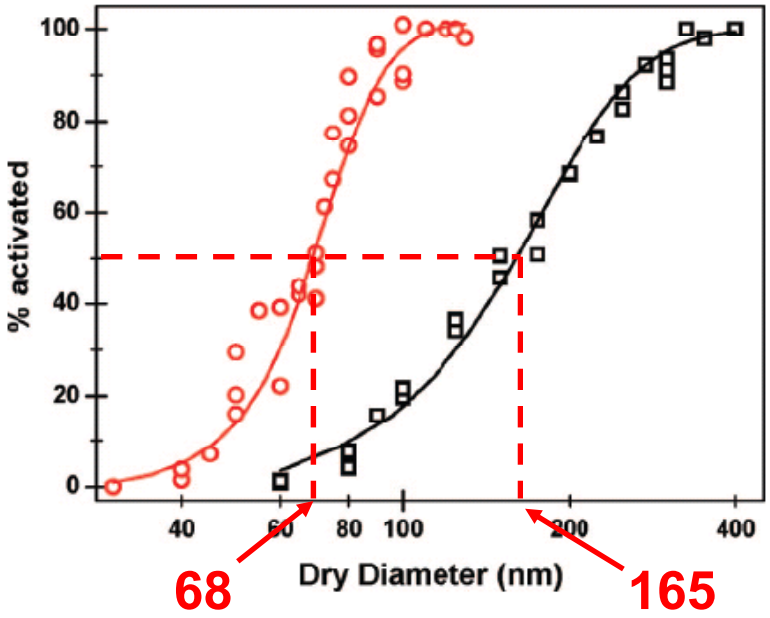

Dave Hanson, unpublished

# Neutralization of aerosol by atmospheric bases increases hygroscopicity

hygroscopic growth of wet adipic acid particles exposed to $NH_3$




CCN activation at 0.64% SS

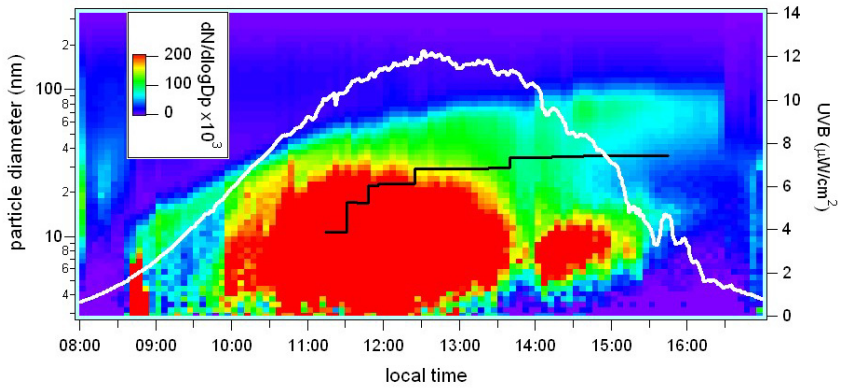



**CCN Activity and Hygroscopic Growth of Organic Aerosols Following Reactive Uptake of Ammonia**

E. DINAR,† T. ANTTILA,‡ AND Y. RUDICH*,†

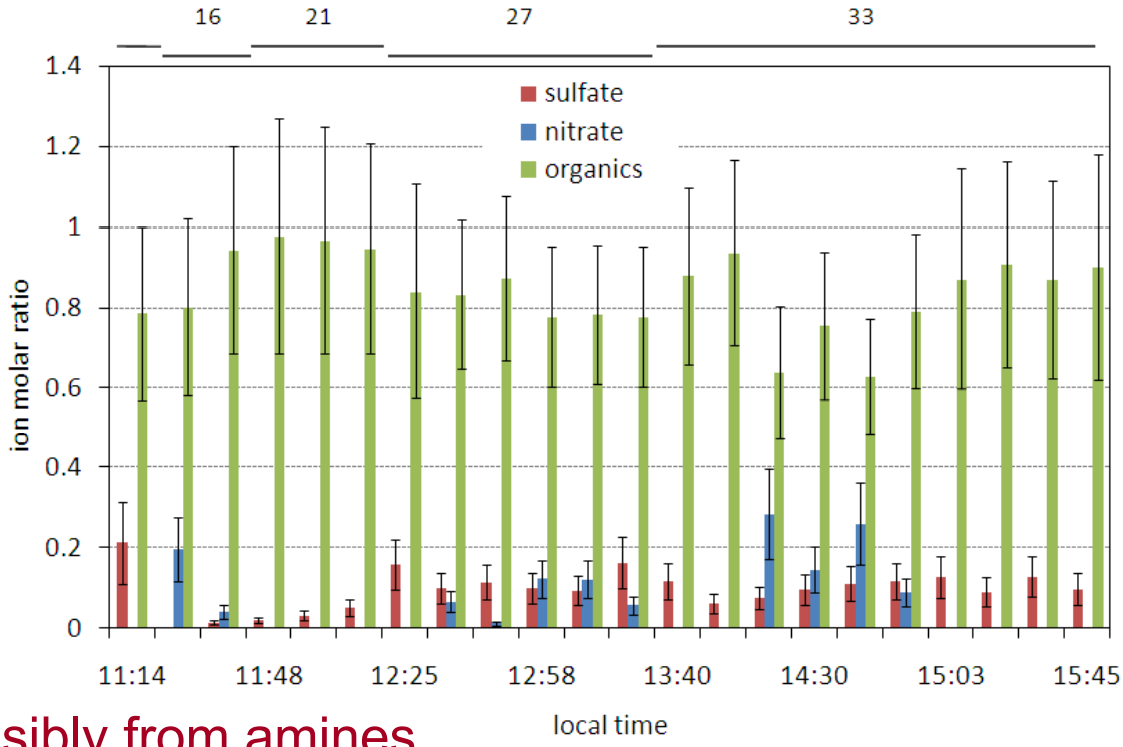
*Environ. Sci. Technol.* **2008**

# TDCIMS measurements: Following the growth of particles formed from nucleation during MILAGRO (16 March 2006)




Sulfate accounts for only ~10% of detected negative ions

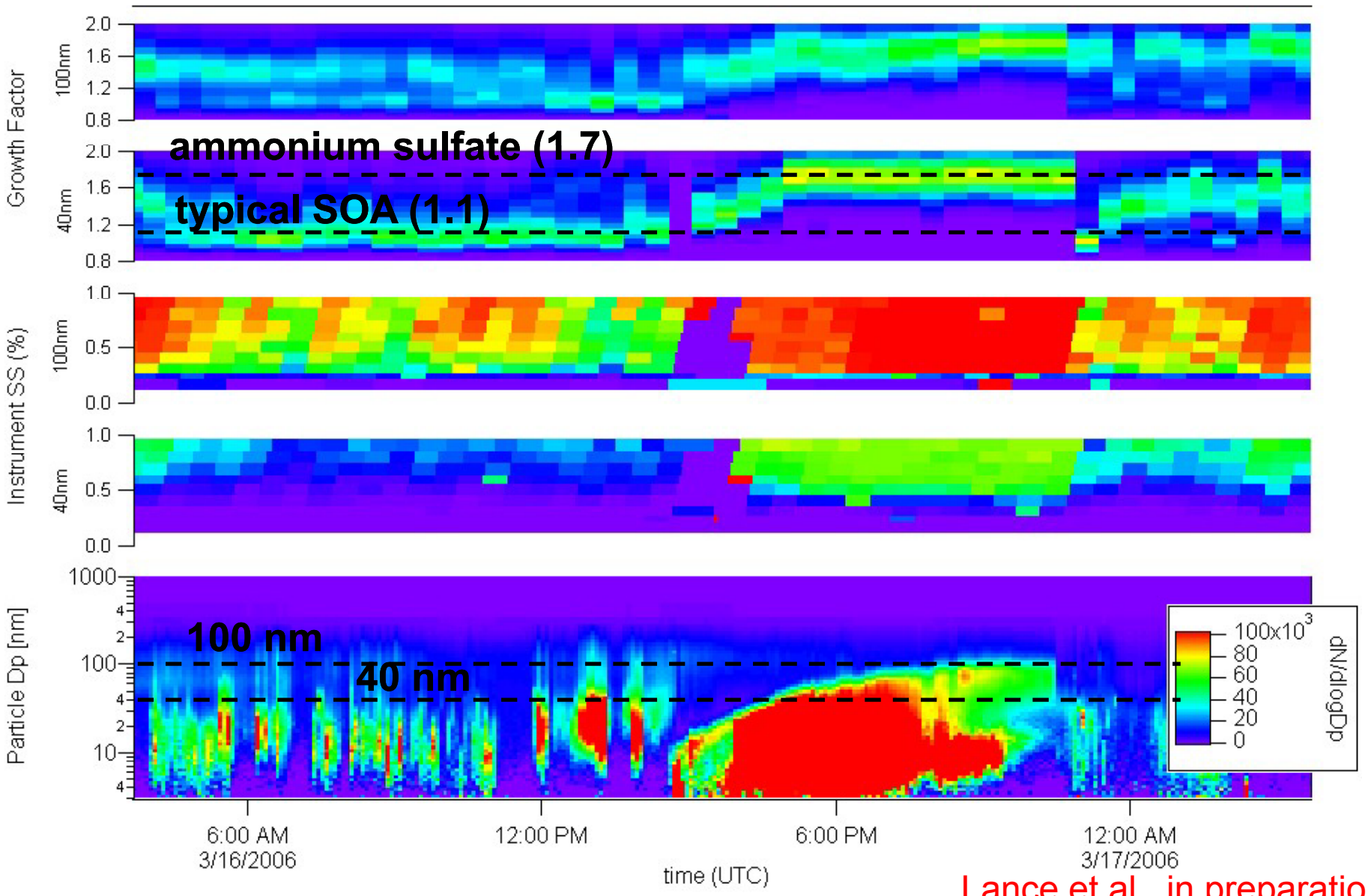
| m/z | species | % total |
|---|---|---|
| 26 | $CN^-$ | 12 |
| 42 | $C_2H_4N^-$, $CNO^-$ | 28 |
| 45 | formate | 21 |
| 59 | acetate | 12 |
| 62 | nitrate | 8 |
| 64 | $SO_2^-$ | 10 |
| 75 | deprotonated hydroxyacetic acid | 1 |
| 80 | $SO_3^-$ | 0.5 |
| 96 | $SO_4^-$ | 0.1 |
| | total identified | 93 |




negative ion fragments possibly from amines

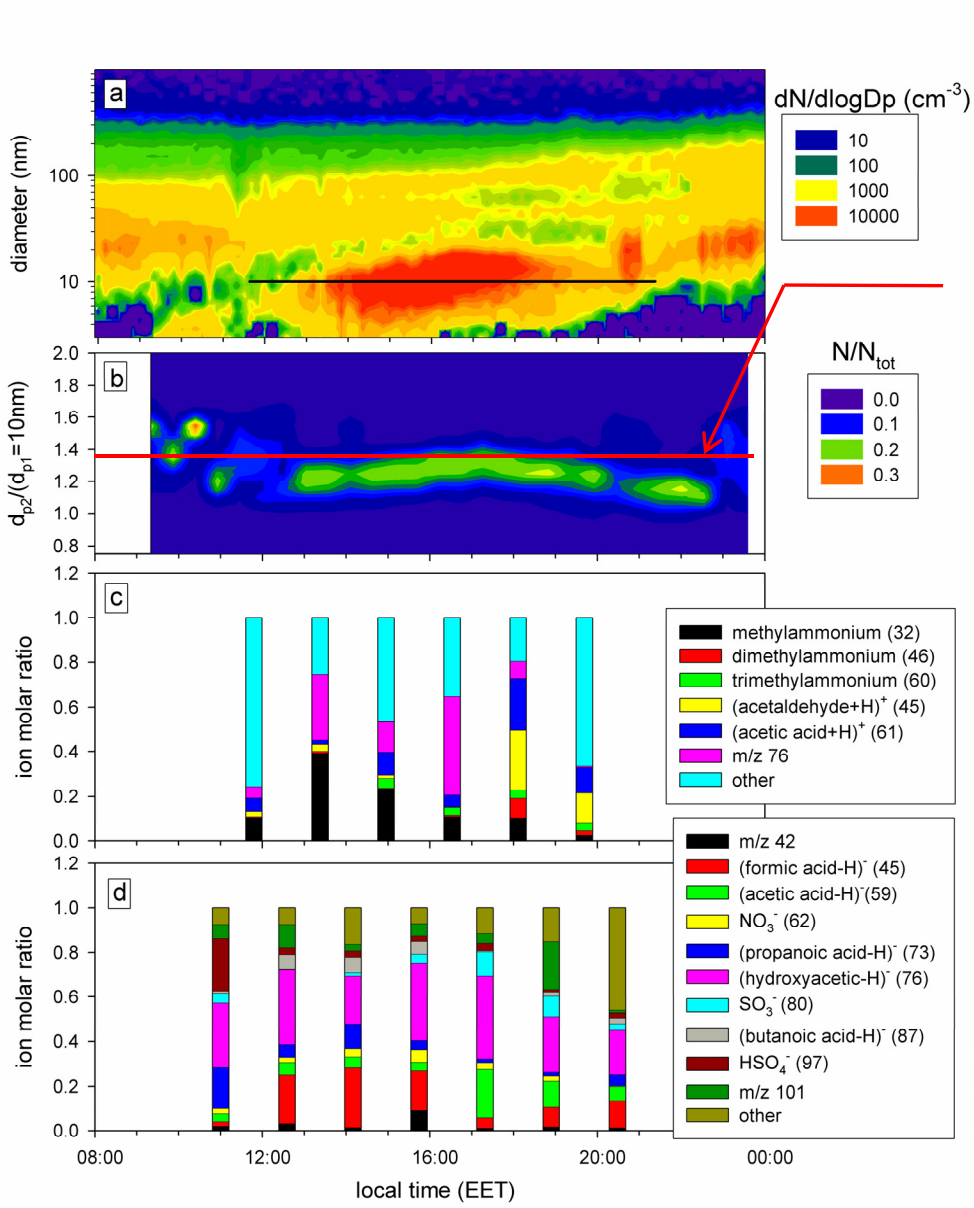
Smith et al., GRL, 2008

# Hygroscopicity and CCN activity of ultrafine aerosol during 16 March event




Lance et al., in preparation

# TDCIMS observations at Hyytiälä on 9 April 2007 show aminium ions with deprotonated acids in 10nm particles




GF for 10nm $(NH_4)_2SO_4$

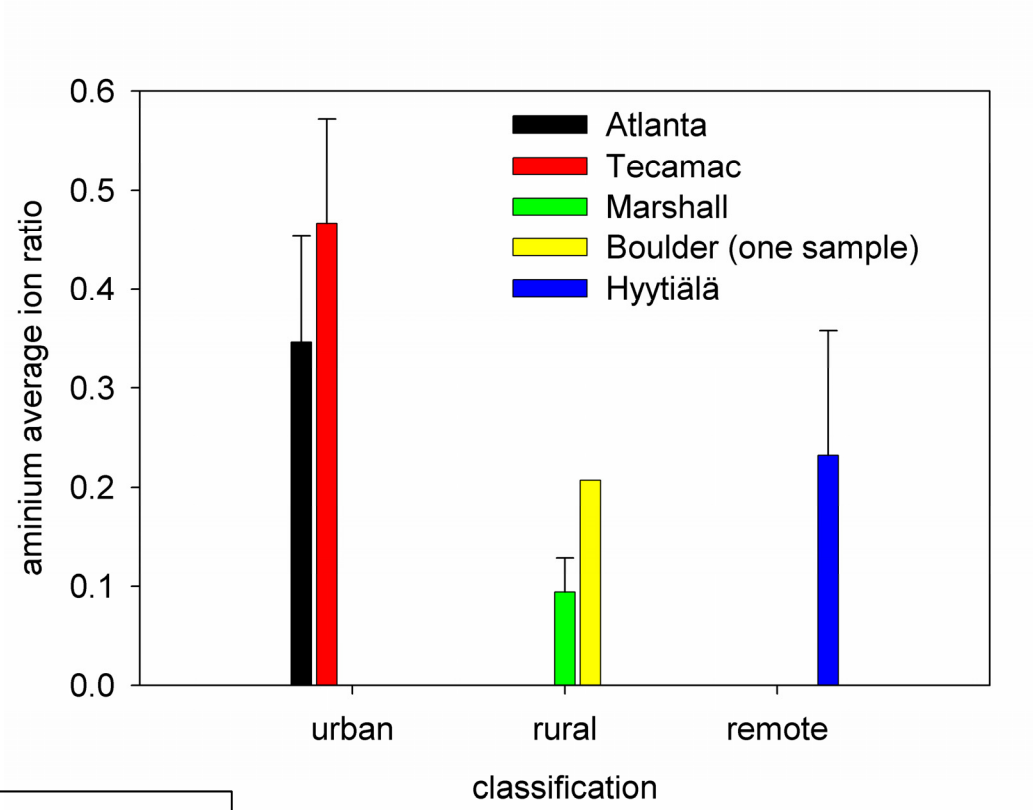
- On average, aminium ions comprise about 23% of positive ion spectrum
- 10 nm particles had an average 90%RH growth factor of 1.27

Smith et al., PNAS, 2010

# Aminium ion ratios suggest that organic and inorganic salt formation may be a universal, and important, growth process

**To equate aminium ion ratios from mass spectra to those in particles**

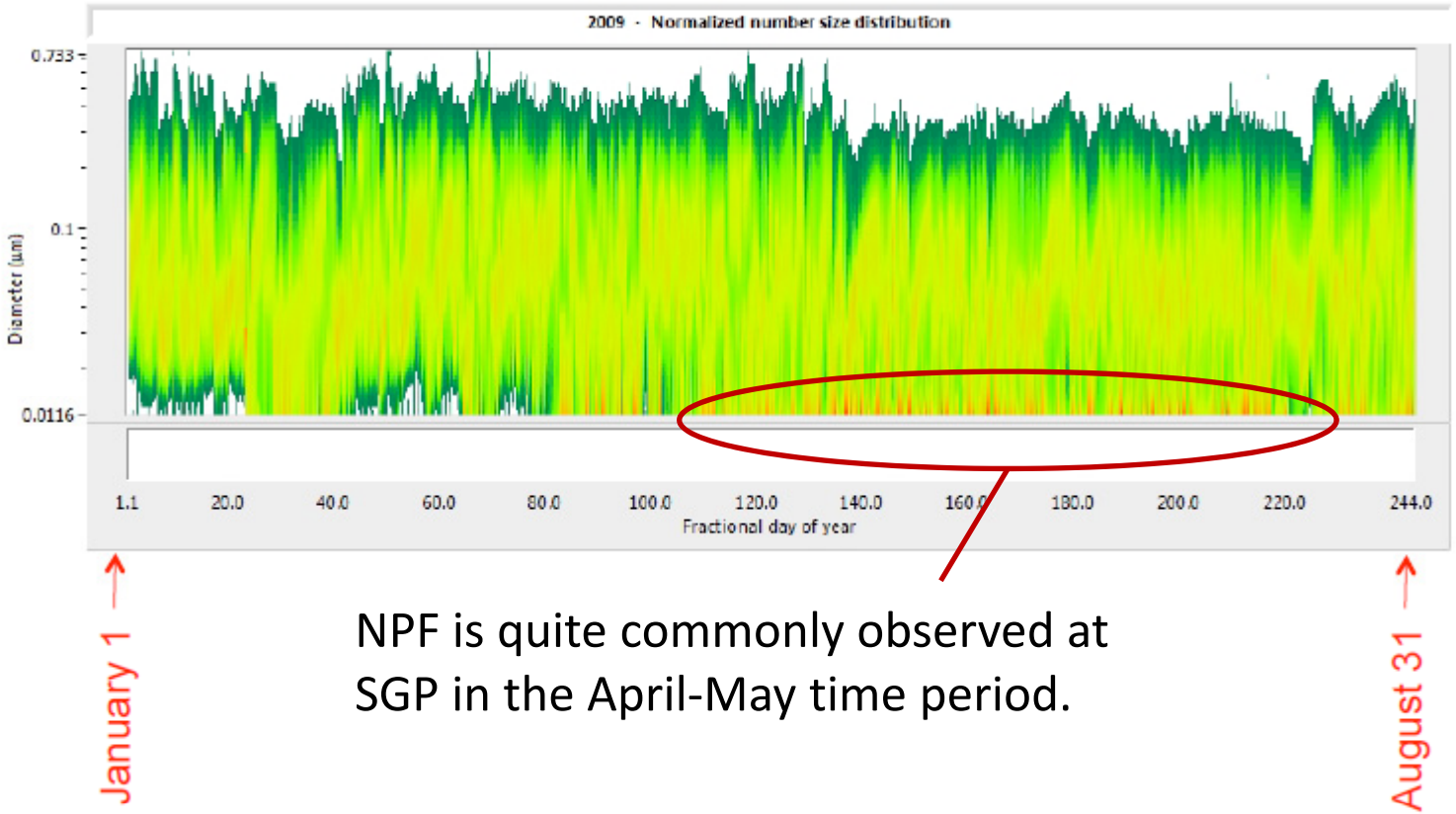
- Nanoparticles formed from nucleation are composed of non-refractory oxidized species (thus are quantified by TDCIMS).
- Normalize ratio by non-acid ion peaks in positive ion spectrum.
- TDCIMS has equal sensitivity towards bases, acids, and other oxidized organics (see Winkler).




Aminium salt formation is an important mechanism for nanoparticle growth

Smith et al., PNAS, 2010

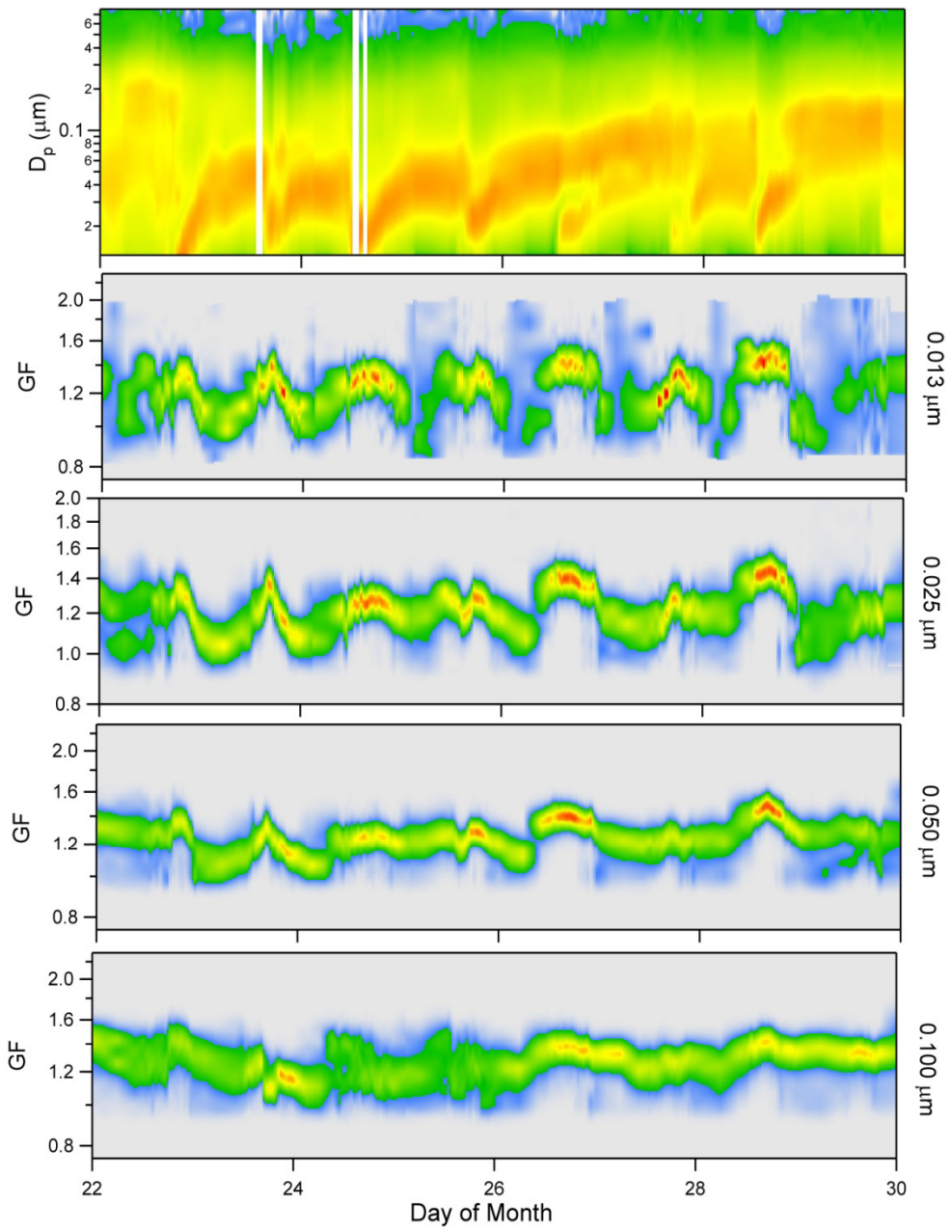
# New particle formation (NPF) at the Southern Great Plains ARM site




NPF is quite commonly observed at SGP in the April-May time period.

Collins, unpublished

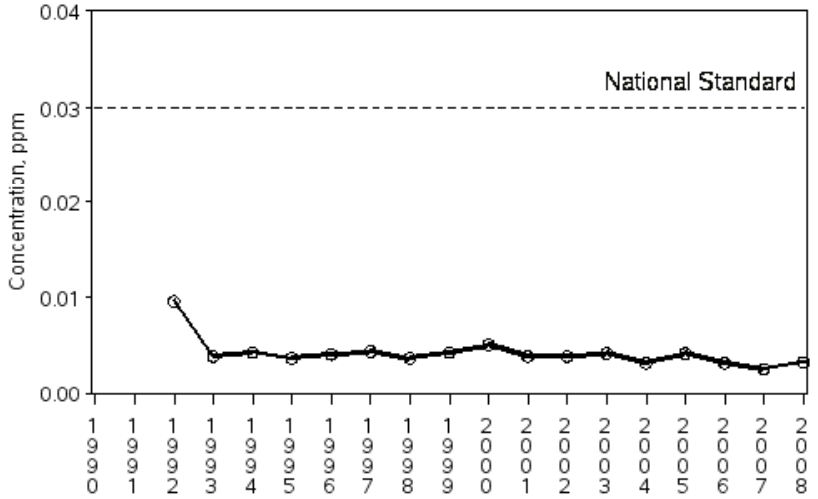
# New particle formation at the Southern Great Plains ARM site




Newly formed particles at SGP are also quite hygroscopic and can be potential CCN.

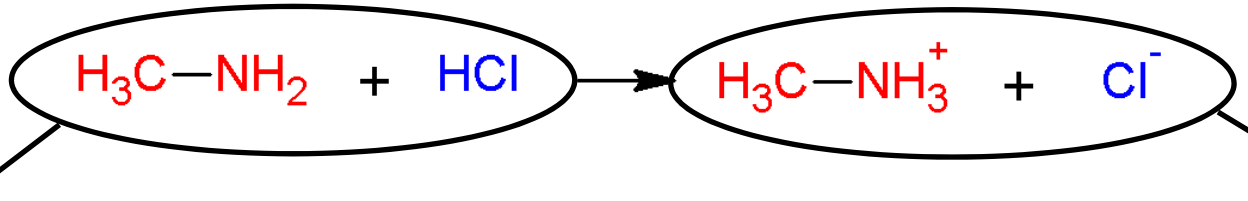
Note that SO2 is not particularly high in Kay Cnty.

SO2 Air Quality, 1990 - 2008
(Based on Annual Arithmetic Average)
Kay County
SITE=400710602 POC=1




Collins, unpublished and USEPA

# New particle formation – a simple demonstration




volatile!

non-volatile!

a base ($CH_3NH_2$)

an acid (HCl)

Experiment performed by H. Friedli