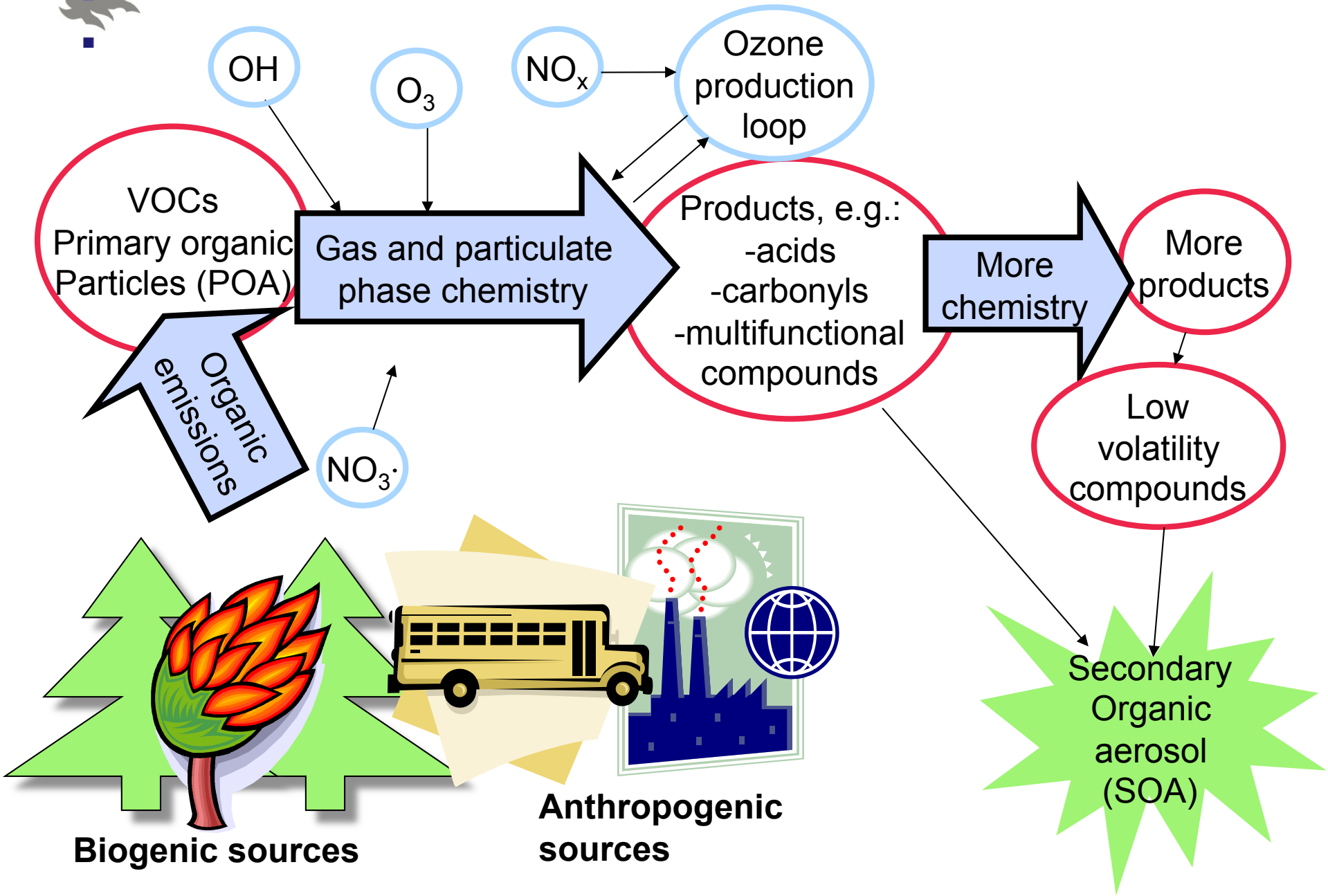
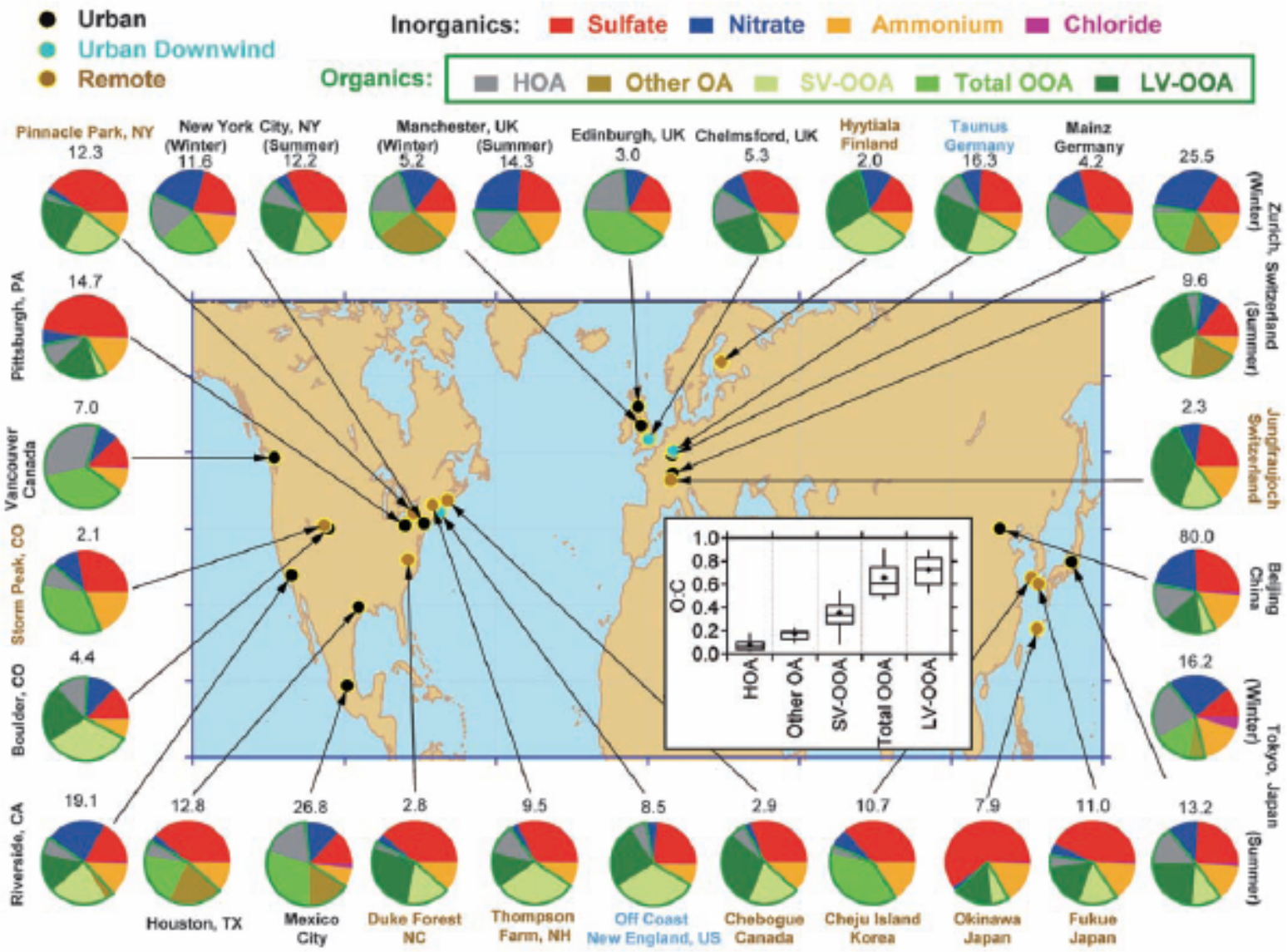
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Organic compounds, atmospheric nucleation and growth

Atmospheric organics, sources and evolution



Organic compounds constitute a significant fraction of particulate mass



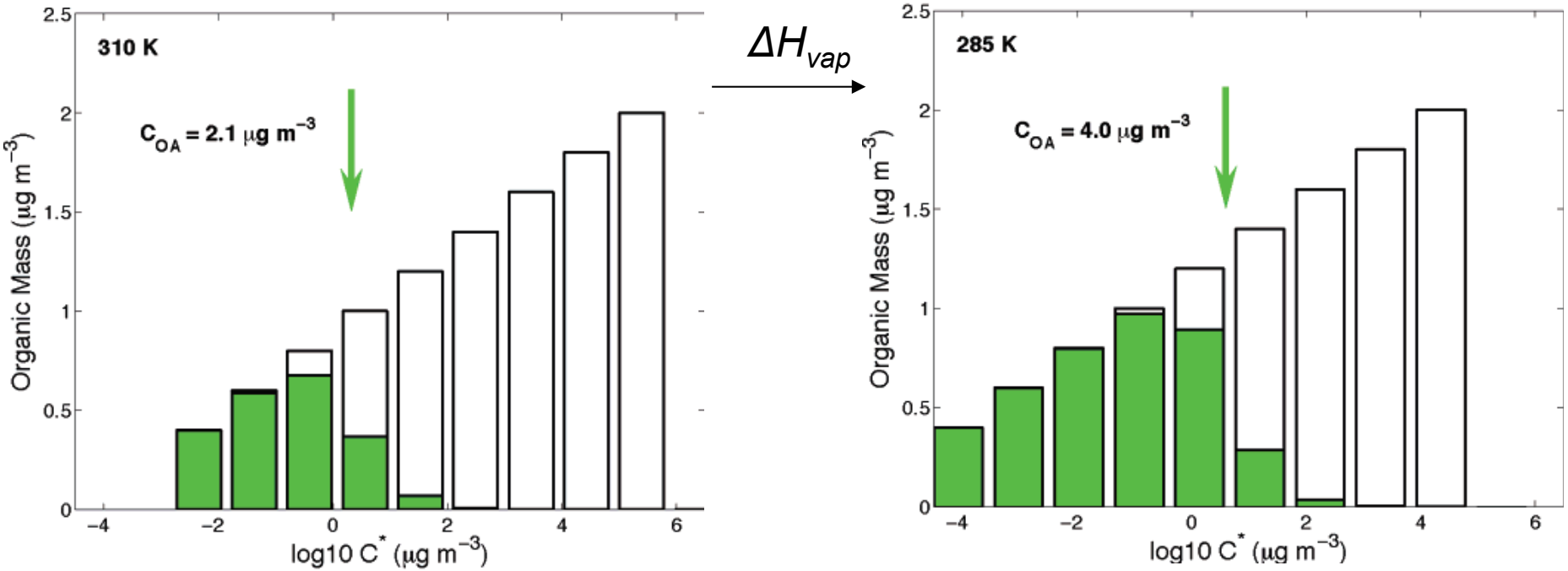
Jimenez et al, Science 2010

Why are organics so challenging?

- Huge number of compounds
  - Atmospheric processing
    - Phase transitions, oxidation, aging
- Properties poorly known
  - Saturation vapour pressures, activities
  - Gas phase chemistry
- Mechanistic understanding of the behaviour of each compound would take ages
  - Answers on e.g. climate issues probably needed earlier
  - Integrative approaches, selecting representative compounds

An example of an integrative approach: Volatility Basis Set (VBS)

- Organics distributed to logarithmic bins based on their volatility – gas-aerosol equilibrium changes with conditions



- Improves predictions of particle mass concentrations
  - Number?
- Volatilities of atmospheric organics needed!

Murphy et al., *ES&T* 2010

Condensational growth: Mass flux and diameter growth rate

- Mass flux to particles from the laws of mass and heat transfer
  - Kinetic regime: Kinetic gas theory
  - Continuum regime: Diffusion theory
  - Transition regime in between

R↯R²↯R³

Transition regime correction factor

Ambient concentration

$$I_{1c} = \frac{\mathrm{d}m_p}{\mathrm{d}t} = \frac{4\pi a p \beta D_{12} M_1}{RT_\infty} \ln\left(\frac{1-\frac{p_{1a}}{p}}{1-\frac{p_{1\infty}}{p}}\right) \approx \frac{4\pi a \beta D_{12} M_1}{RT_\infty}\left(p_{1\infty} - p_{1a}\right)$$

Equilibrium vapour pressure over the particle

$$\frac{\mathrm{d}m_p}{\mathrm{d}t} = \rho_p \cdot \frac{\mathrm{d}v_p}{\mathrm{d}t} = \rho_p \cdot \frac{4}{3}\pi \cdot 3r_p^2 \cdot \frac{\mathrm{d}r_p}{\mathrm{d}t} = \frac{1}{2}\pi D_p^2 \cdot \rho_p \cdot \mathrm{GR}$$

- In reality mass transfer ALWAYS coupled with heat transfer
  - Latent heat

$$P_{i,s}(x,T,r) = \Gamma_i(x,T) \cdot x_i \cdot P_{i,pure}(T) \exp\left(\frac{2\sigma v}{kTr}\right)$$

Role of kinetics and thermodynamics

- Nucleation :

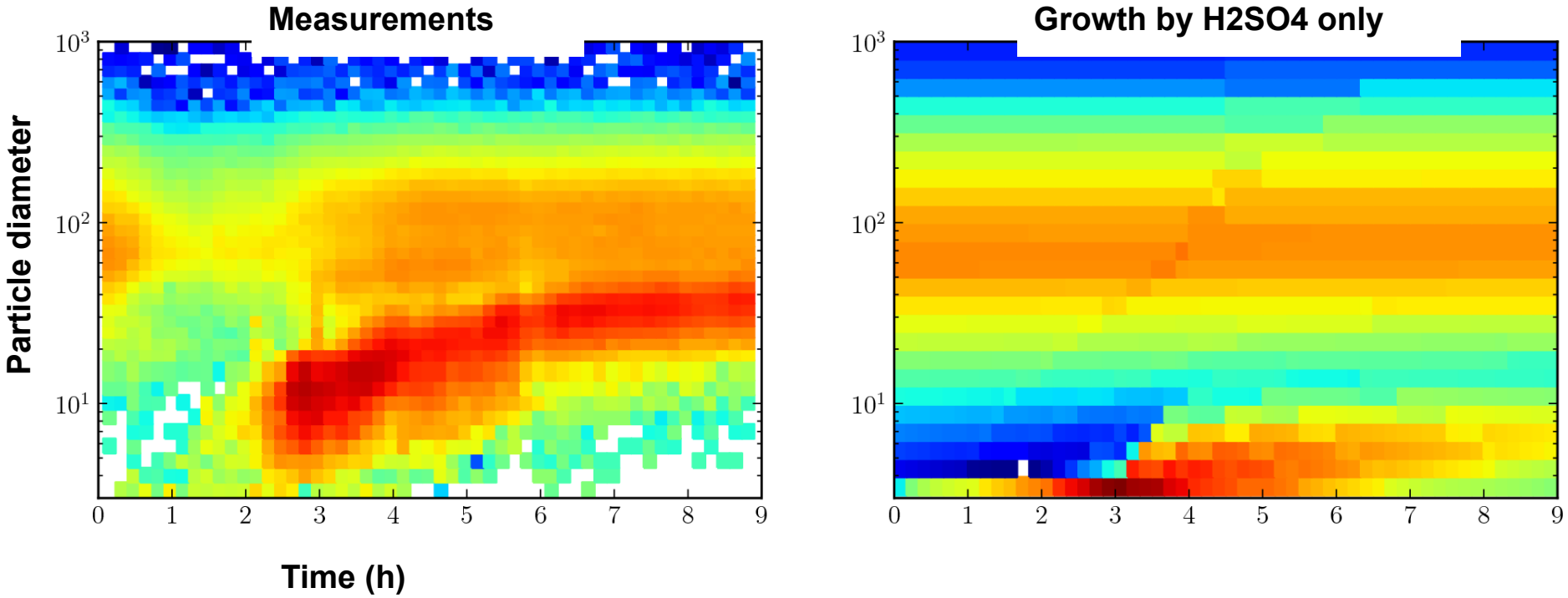
KINETICS × exp(-N*× ln S)= KINETICS× $1/S^{N*}$

- Condensation:

KINETICS×(S-1)

Role of organics in particle growth: Measured sulphuric acid does not explain atmospheric growth in Hyytiälä

- Measured sulphuric acid can explain < 10 % of the nucleation mode growth

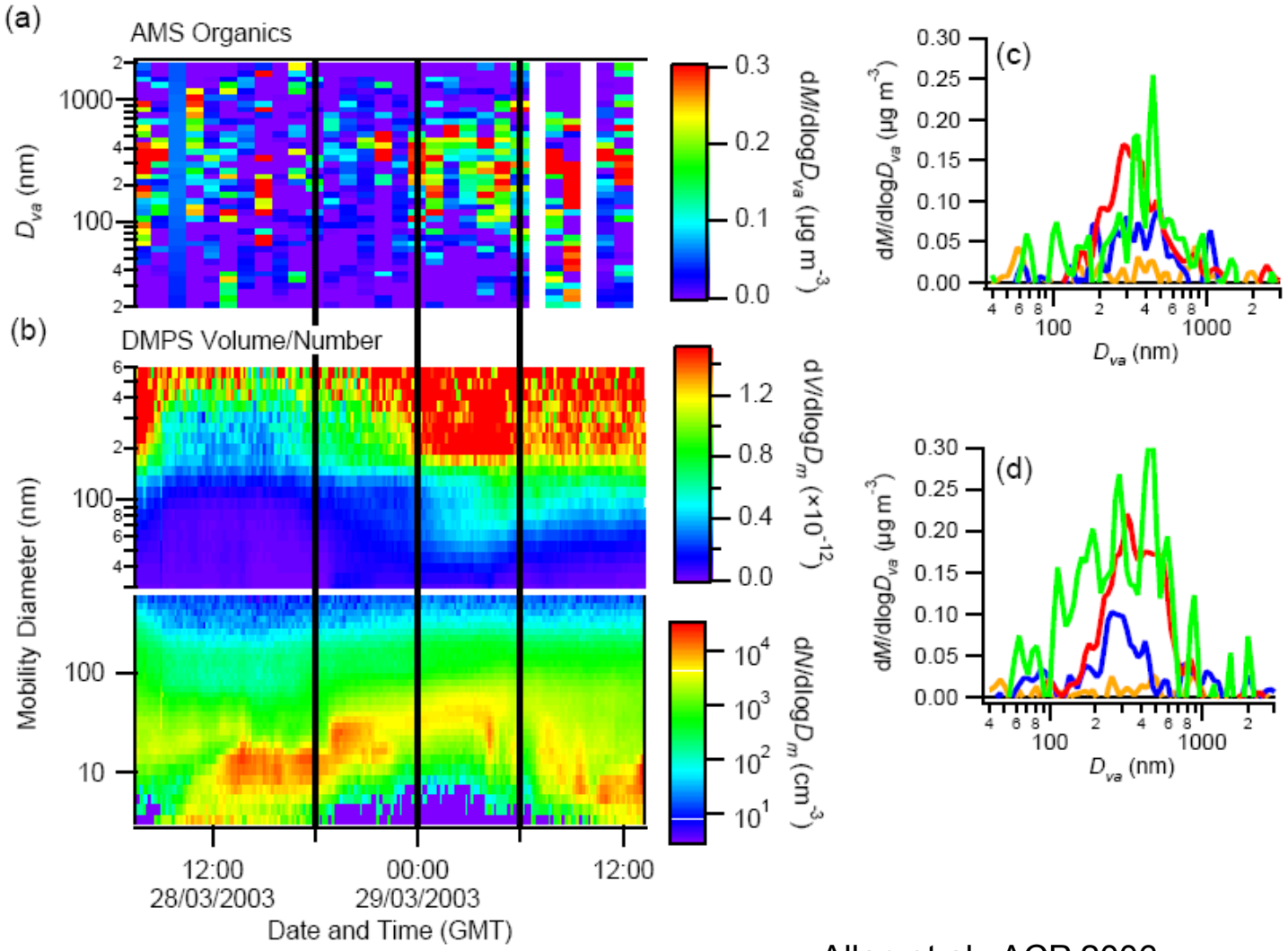


- Something else is condensing on the particles
- Organics make most of the growth

Figure by Jeffrey R. Pierce

Organics and particle growth: AMS data from Hyytiälä (> 20 nm)

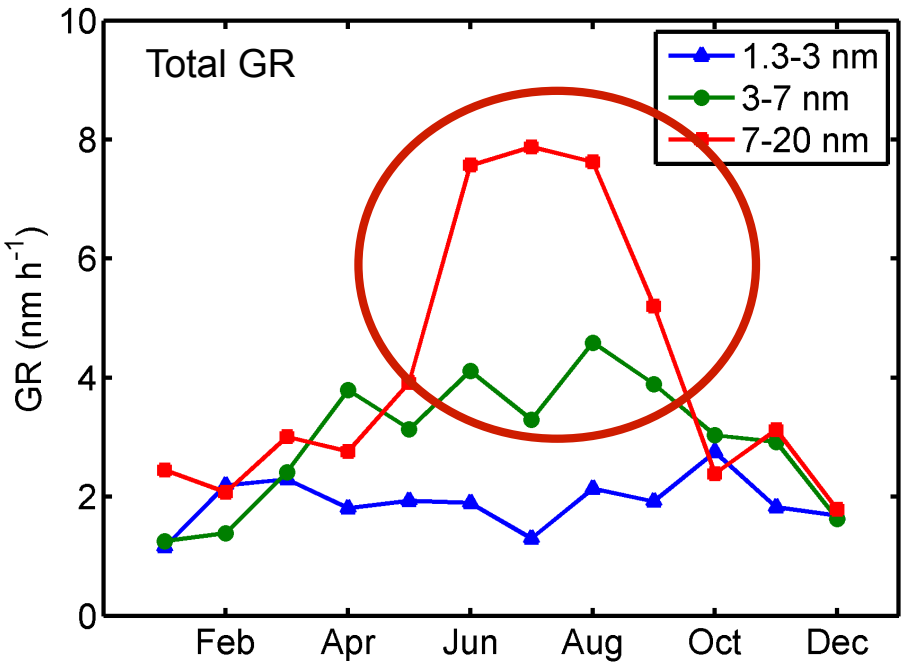
- Organics dominate when nucleation mode growing



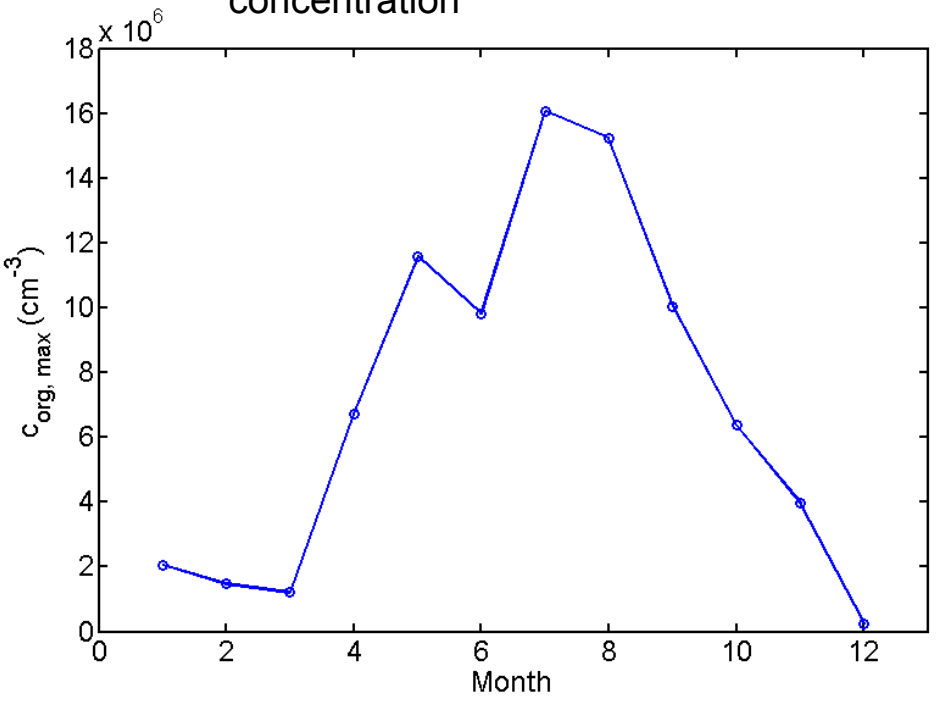
Allan et al., ACP 2006

Indications on the role of organics: Seasonality of particle growth rates

- Peak in GRs coincide with peak in organic emissions

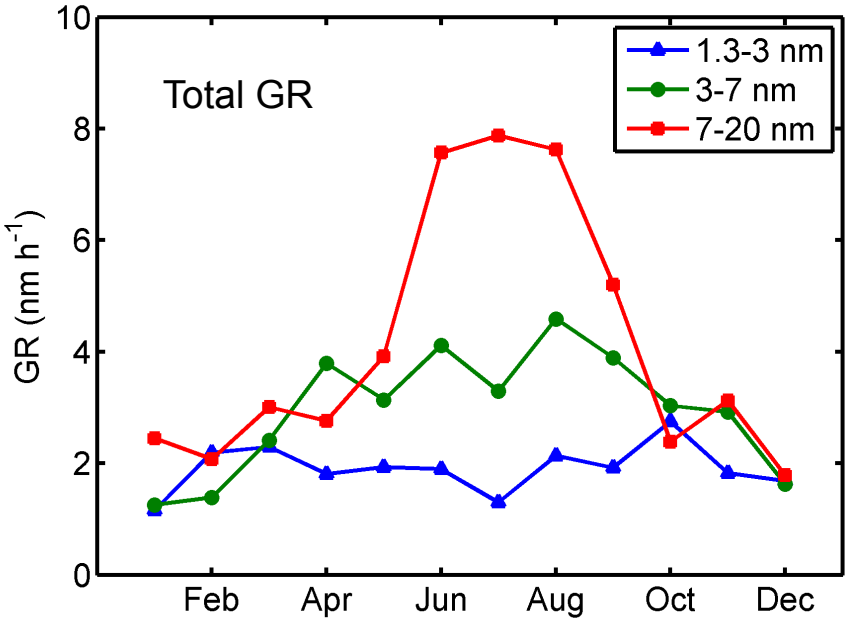


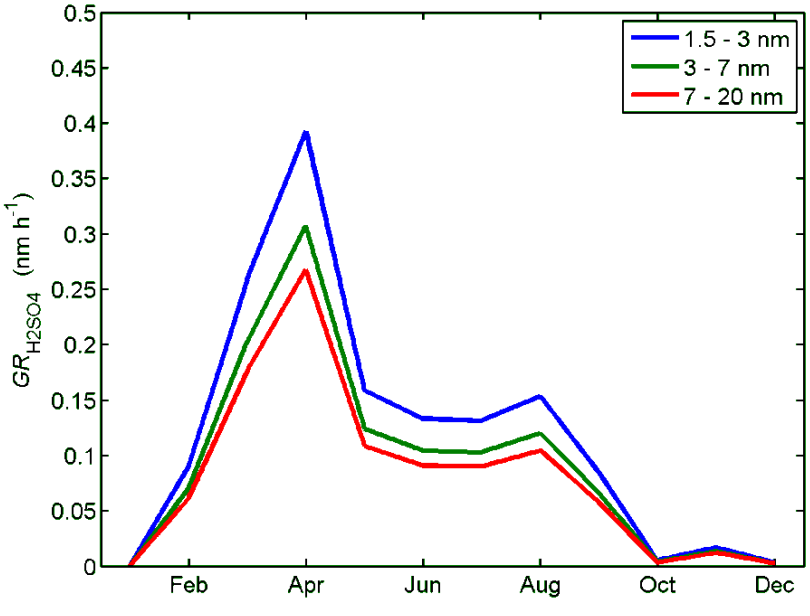
Estimated condensable organic vapour concentration



Seasonality of GRs: Total growth vs. growth by sulphuric acid

- Sulphuric acid not enough even at the smallest sizes

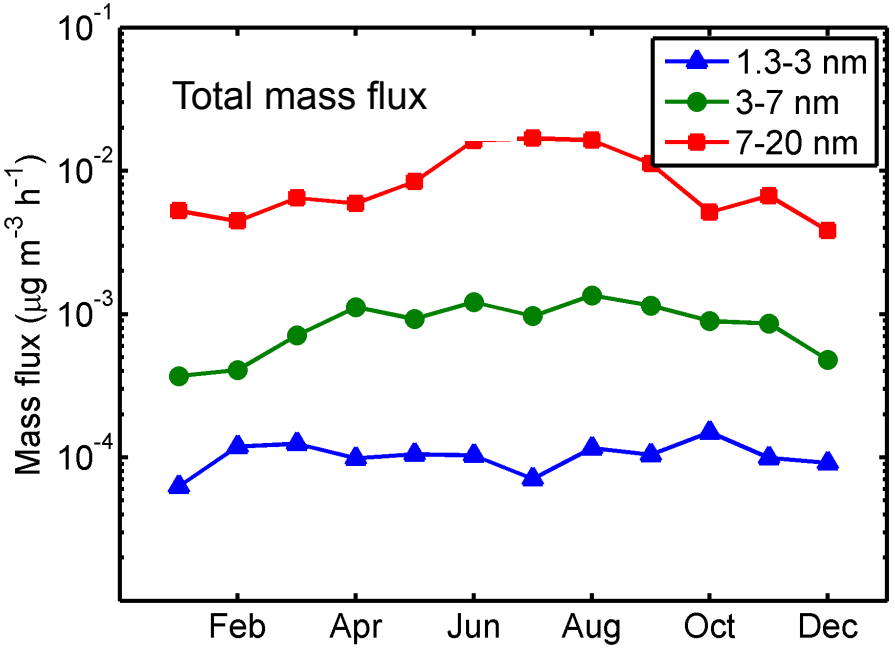


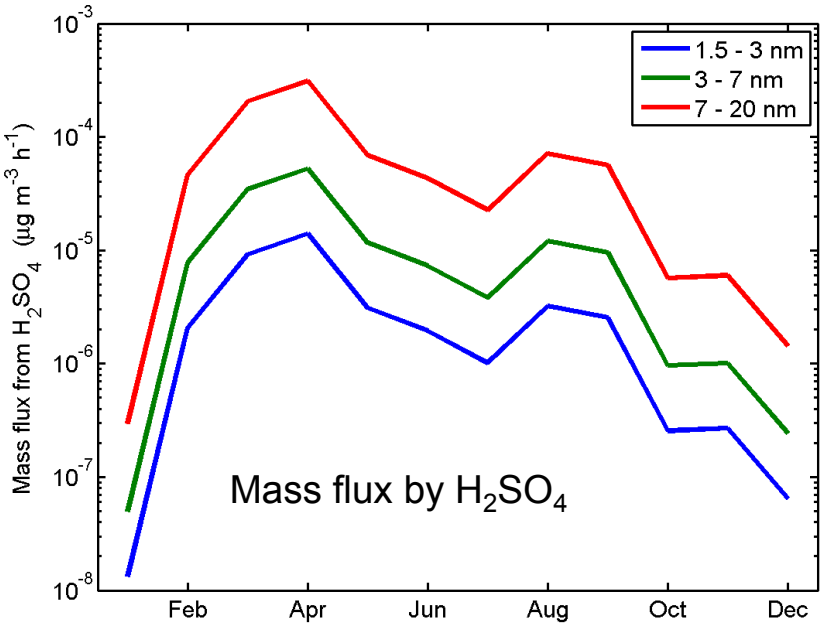


- Organic condensation onto ultrafine aerosol needs to be considered to predict the lifetimes of freshly-nucleated particles

Mass fluxes to nucleation mode particles

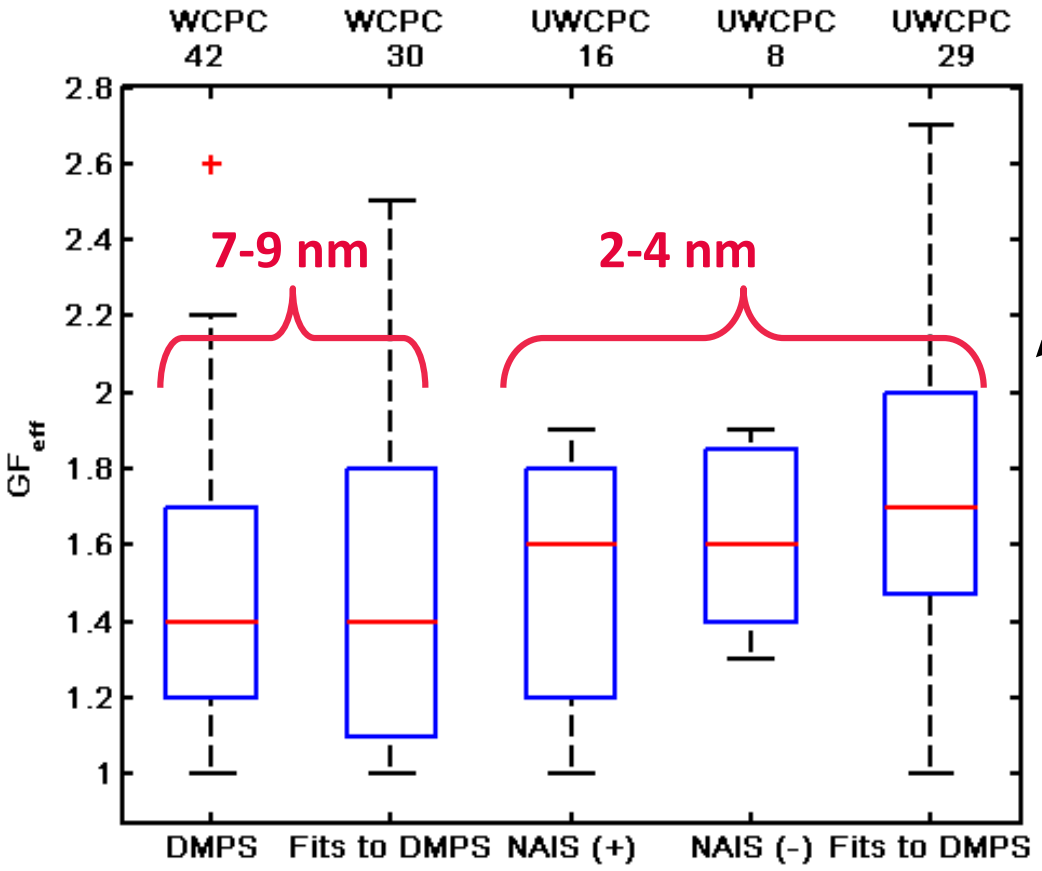
- Note: the material condensing onto ultrafines very small compared to total organic mass
  - Identities and properties of these compounds unknown





Indications on the role of organics in particle formation and growth: Water-affinity of nanoparticles

- CPCB: particles seem to be less hygroscopic than ammoniumsulphate even close to 2 nm

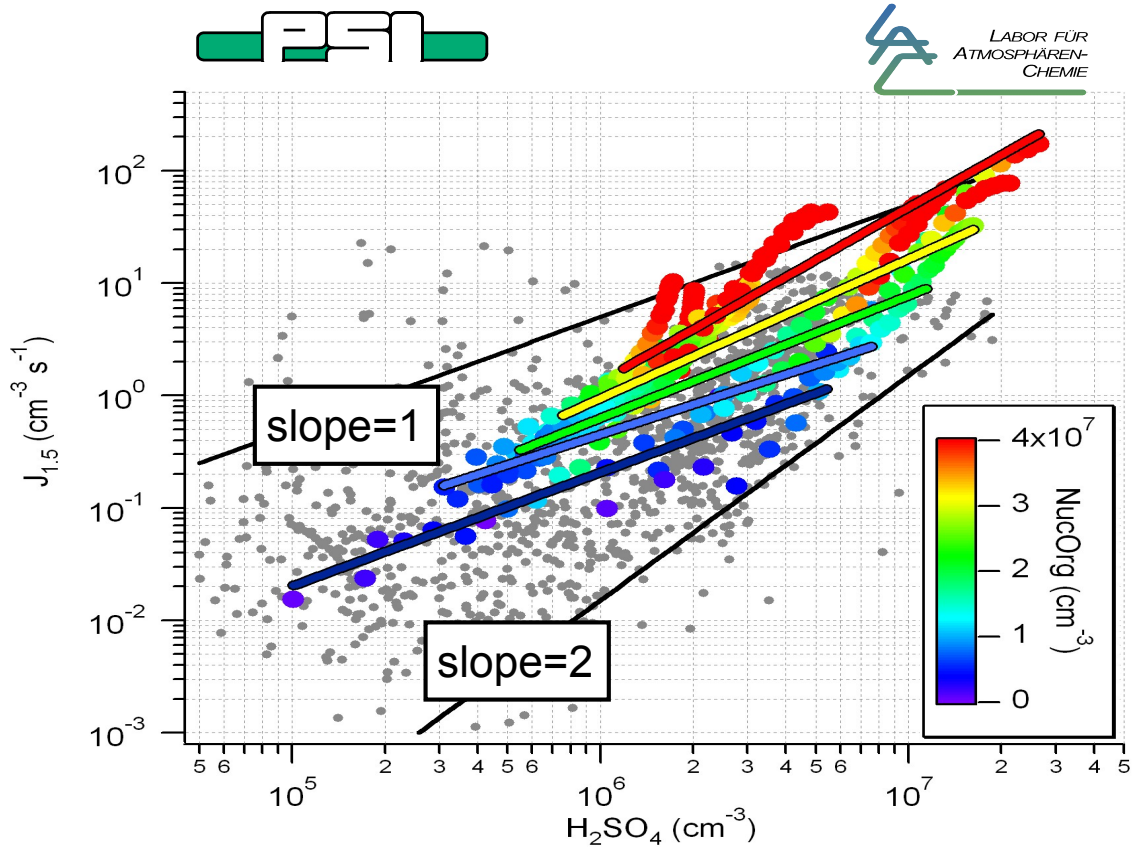


Small particles more hygroscopic:

Role of organics increases with particle size

Organics and nucleation?

- Sulphuric acid and TMB



$$J \propto [H_2SO_4]^n [Org]^m,$$

$$n = 1.0 \pm 0.042,$$

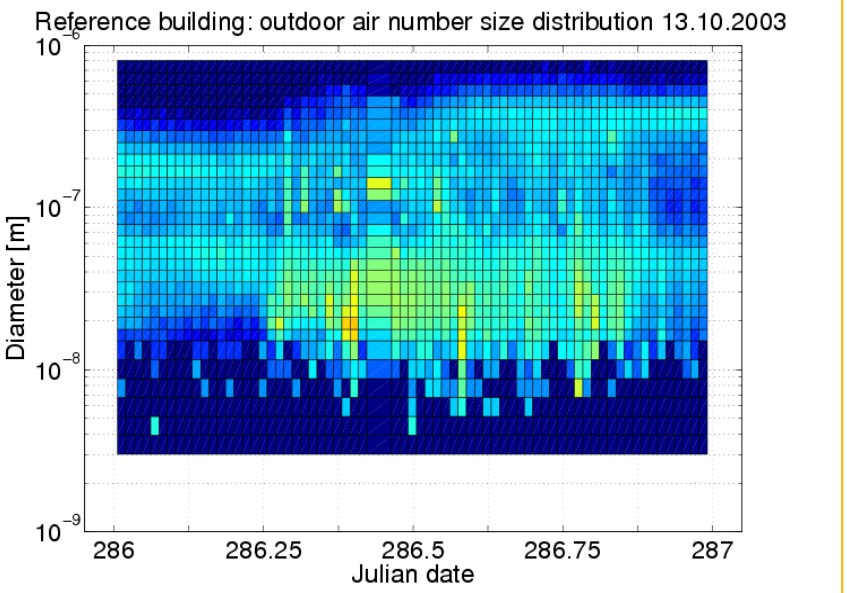
$$m = 0.8 \pm 0.04$$

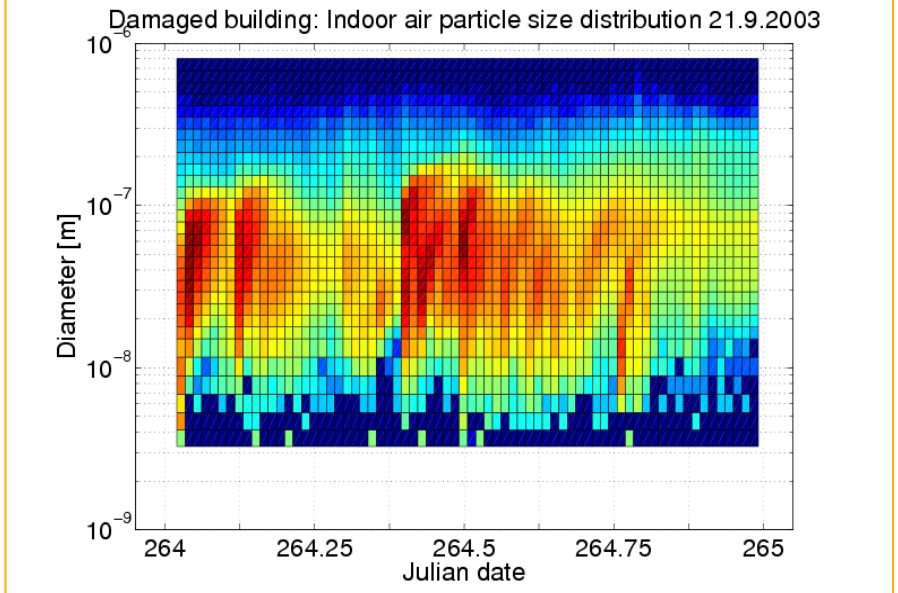
- Good agreement with atmospheric data

Metzger et al., *PNAS* 2010

Vartiainen et al, Atmos. Env. 2006

Organics CAN nucleate even on their own: Case of limonene





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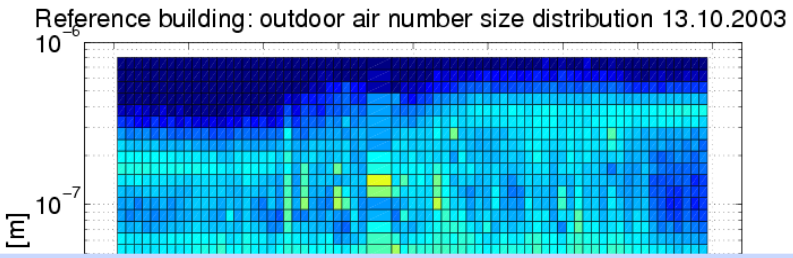

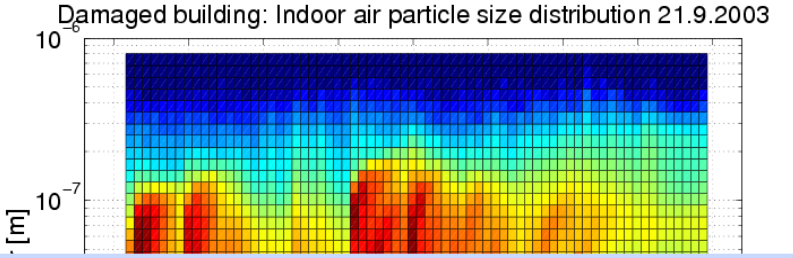

It's a matter of concentration!