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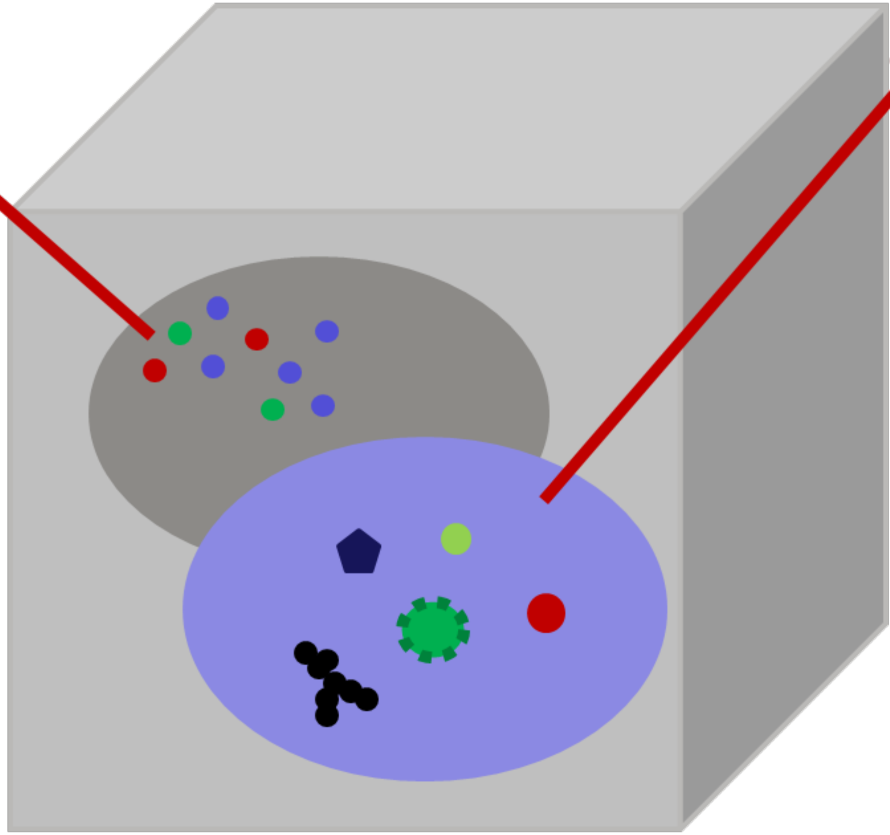
Atmospheric aerosols: Observations on atmospheric particle formation and growth

Putting things to scale: One cubic centimetre of atmospheric air

Gases:

- Single molecules
- N_2, O_2, Ar, H_2O, CO_2, ...
- 10^{19} molecules
- 1 mg = 10^{-6} kg

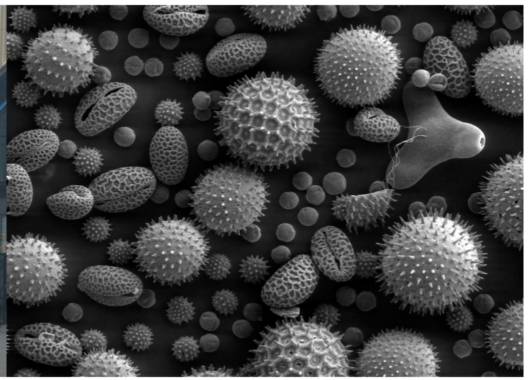


Aerosol particles:

- In condensed (liquid or solid) phase
- Soot particles, road dust, sulfate particles, diesel particles, fog droplets, bacteria, pollen, ...
- 10^{4} particles
- 10^{-5} µg = 10^{-14} kg

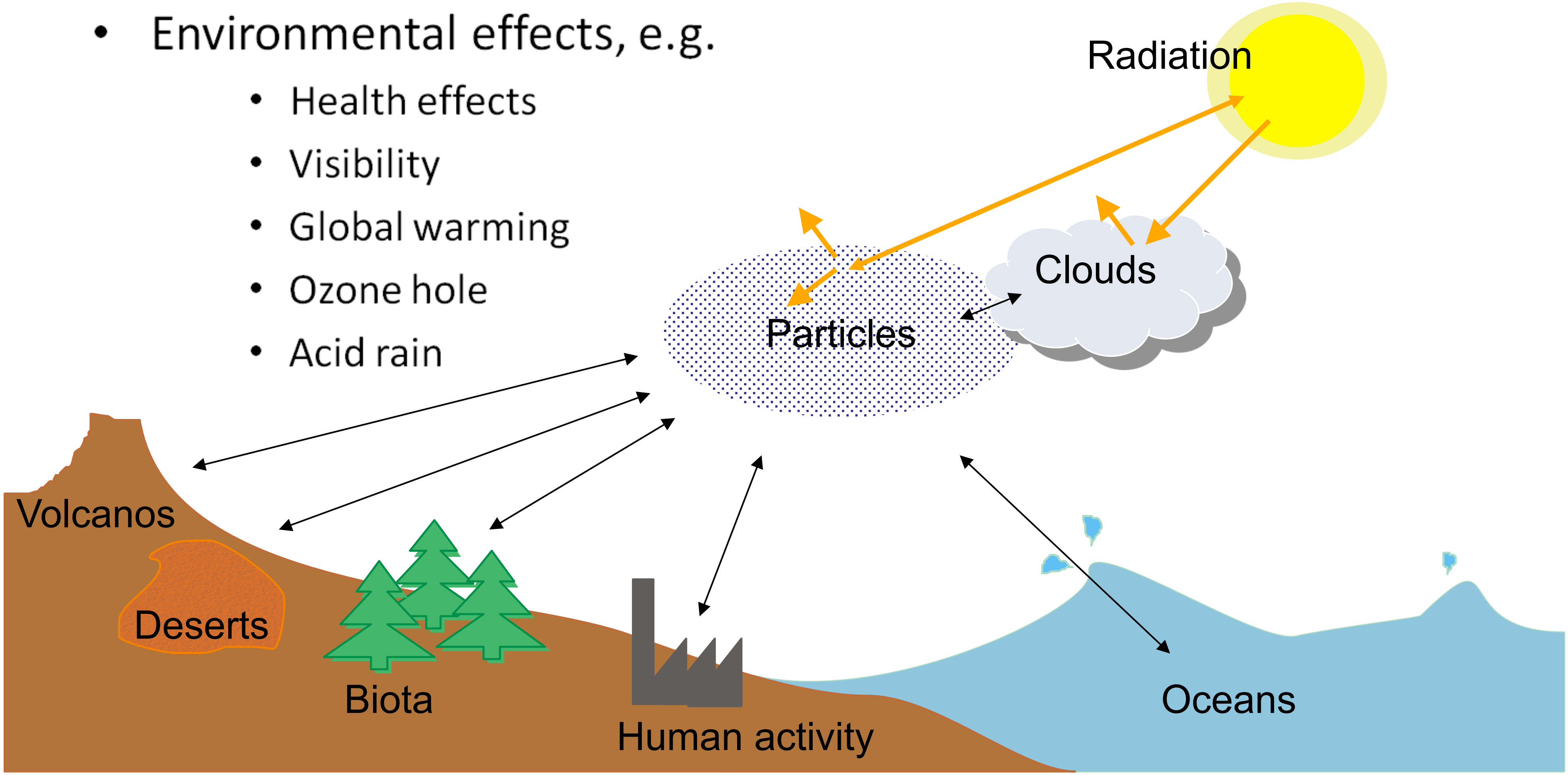
Atmospheric aerosols: Ubiquitous and variable

- Liquid or solid particles suspended in air
- Diameters ~10^{-9} – 10^{-4} m
- Concentrations ~10^{0} – 10^{5} cm^{-3} (10^{-1} – 10^{2} µg m^{-3})

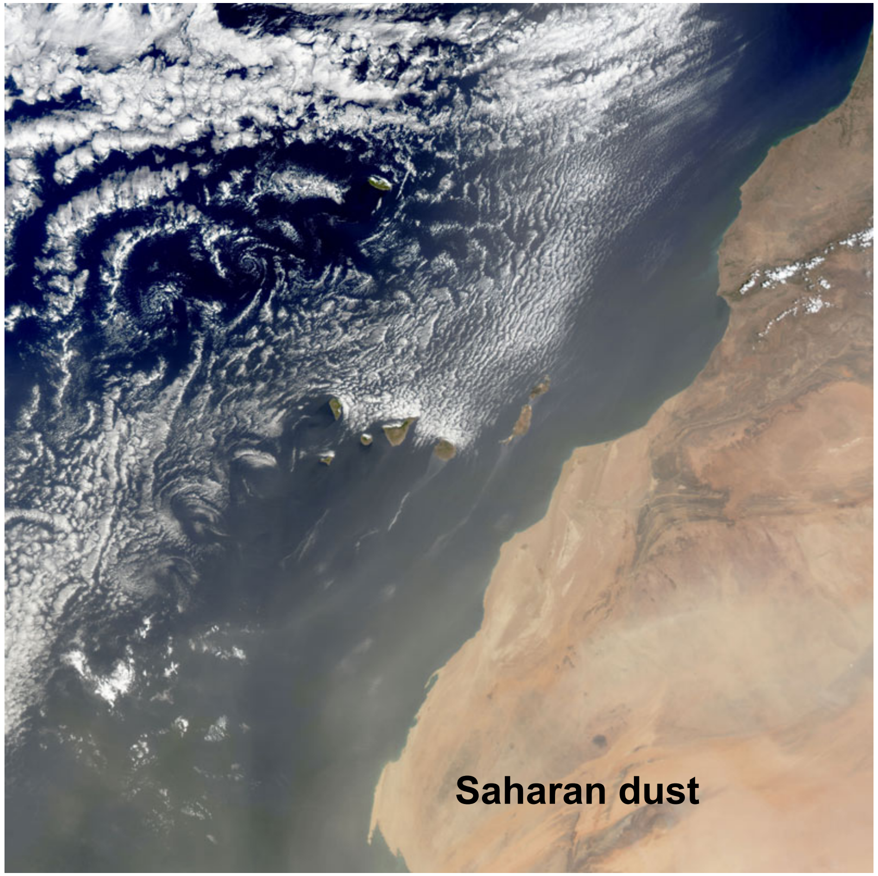


Sources and effects of atmospheric aerosols

- **Primary particles** = emitted in the condensed phase
- **Secondary particles** = formed in the atmosphere from vapours
- Environmental effects, e.g.
    - Health effects
    - Visibility
    - Global warming
    - Ozone hole
    - Acid rain



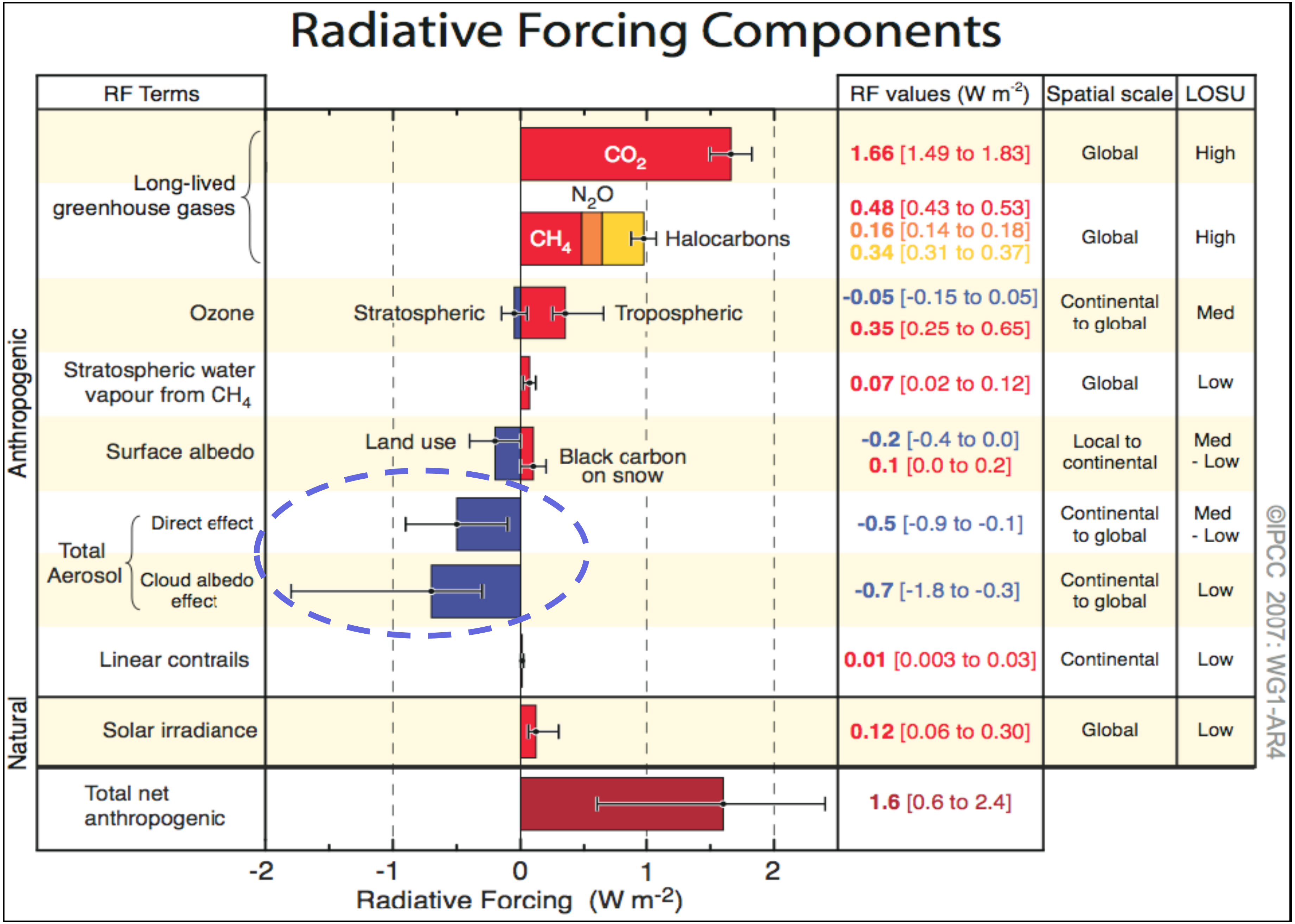
Aerosols directly scatter and absorb solar radiation → direct effect on climate



Figures: NASA

Aerosols act as cloud condensation nuclei → Indirect effect on climate

Figure: NASA



Radiative Forcing Components
RF Terms
RF values (W m-2)
Spatial scale
LOSU
Anthropogenic
Natural
Long-lived greenhouse gases
CO2
N2O
CH4
Halocarbons
1.66 [1.49 to 1.83]
Global
High
0.48 [0.43 to 0.53]
0.16 [0.14 to 0.18]
0.34 [0.31 to 0.37]
Global
High
Ozone
Stratospheric
Tropospheric
-0.05 [-0.15 to 0.05]
0.35 [0.25 to 0.65]
Continental to global
Med
Stratospheric water vapour from CH4
0.07 [0.02 to 0.12]
Global
Low
Surface albedo
Land use
Black carbon on snow
-0.2 [-0.4 to 0.0]
0.1 [0.0 to 0.2]
Local to continental
Med - Low
Total Aerosol
Direct effect
-0.5 [-0.9 to -0.1]
Continental to global
Med - Low
Cloud albedo effect
-0.7 [-1.8 to -0.3]
Continental to global
Low
Linear contrails
0.01 [0.003 to 0.03]
Continental
Low
Solar irradiance
0.12 [0.06 to 0.30]
Global
Low
Total net anthropogenic
1.6 [0.6 to 2.4]
-2
-1
0
1
2
Radiative Forcing (W m-2)
©IPCC 2007: WG1-AR4

IPCC, 2007

Significance of uncertainties?

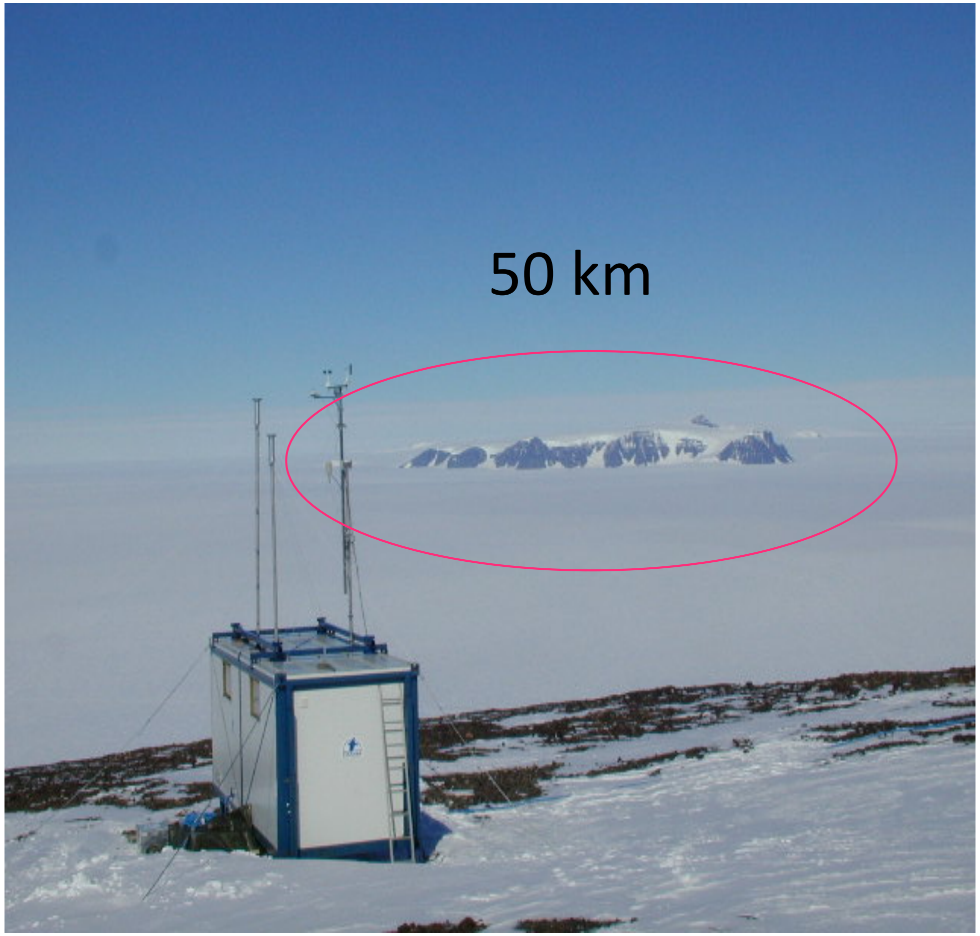
- How much doubling the CO_2 concentration in the atmosphere rise the average temperature of the Earth?

- Aerosols -0.3 W/m^2 → +1.5 °C

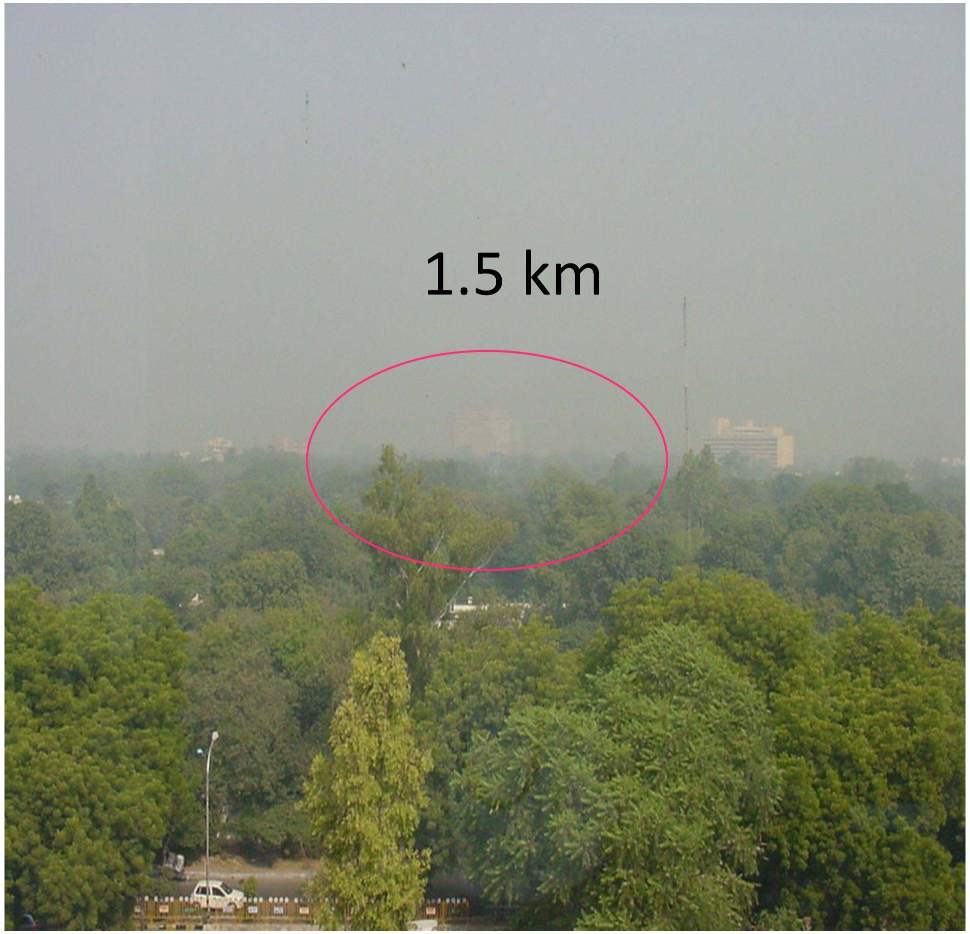
- Aerosols -1.8 W/m^2 → +10 °C

Andreae et al. 2005

Aerosols and air quality: Visibility



Antarctica

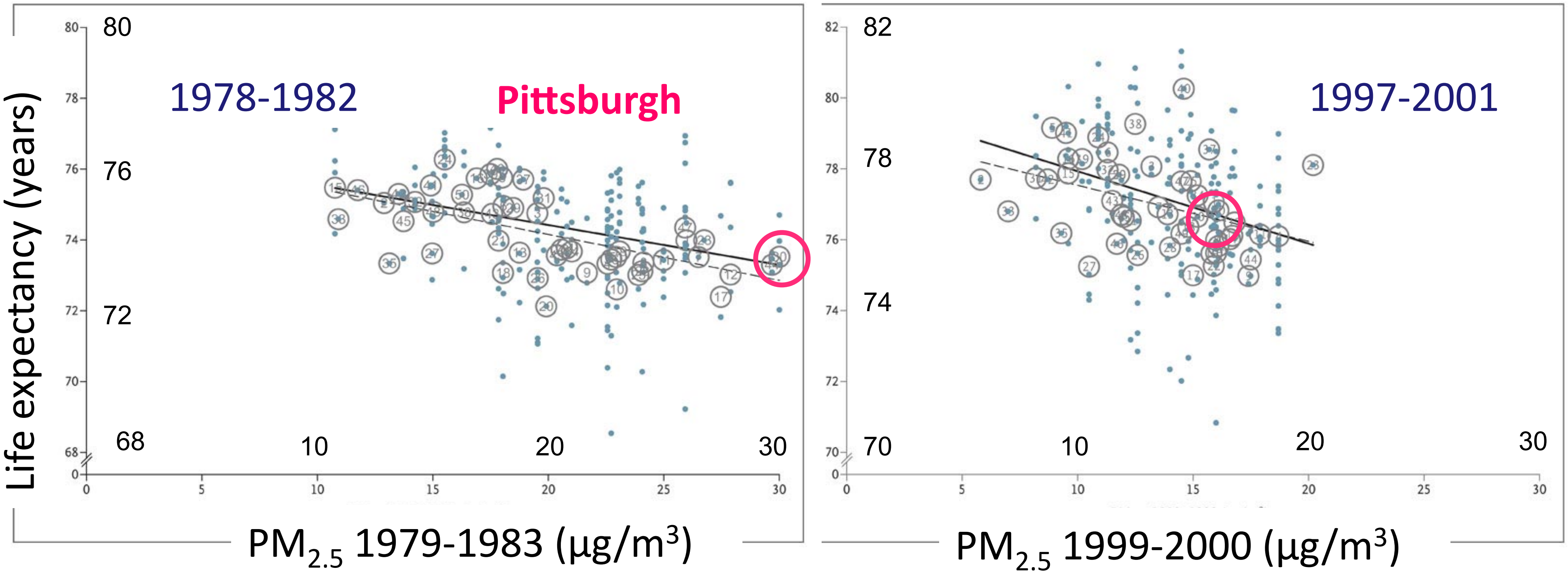


New Delhi

Figures: I. K. Koponen, P. Mönkkönen

Aerosols and air quality: Life expectancy and PM

- Negative correlation with particulate mass



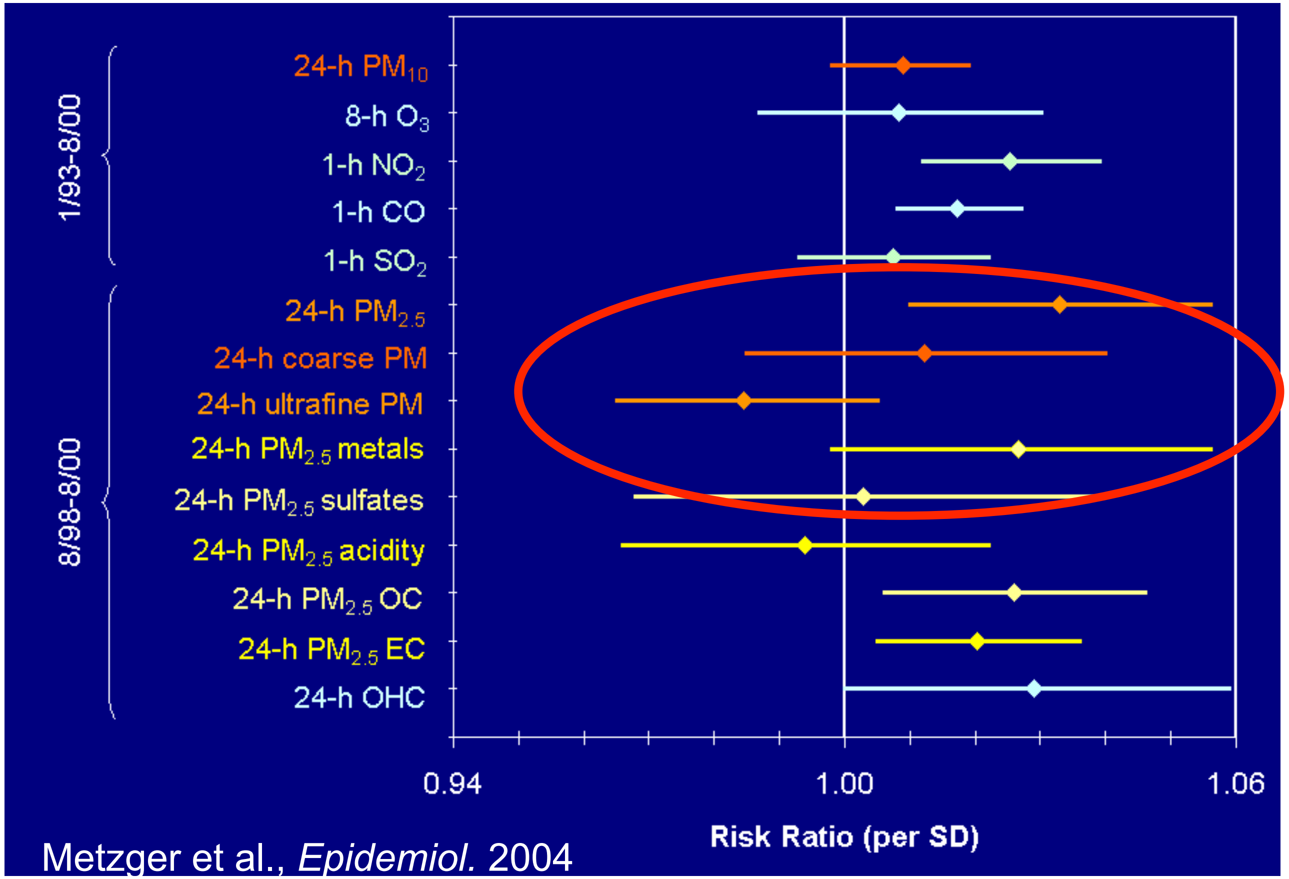
- Air quality improvements worthwhile!

Pope et al., *NEJM* 2009

Aerosols and air quality:

Cardiovascular ER visits and pollution

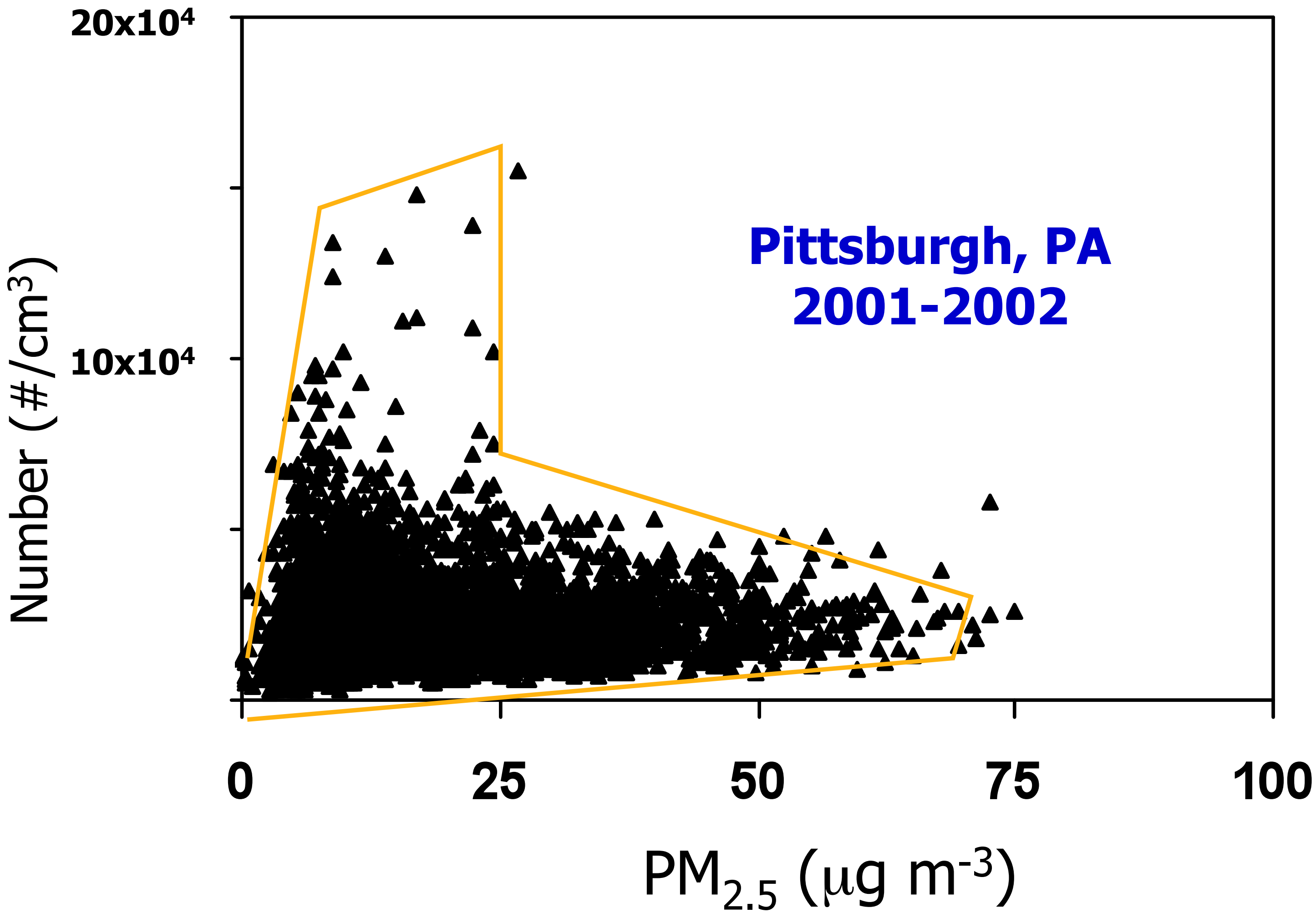
- Ultrafine particles seem to anticorrelate with risk



- On the other hand: Nanoparticles known to penetrate deep into lungs

Particle mass and number are not independent!

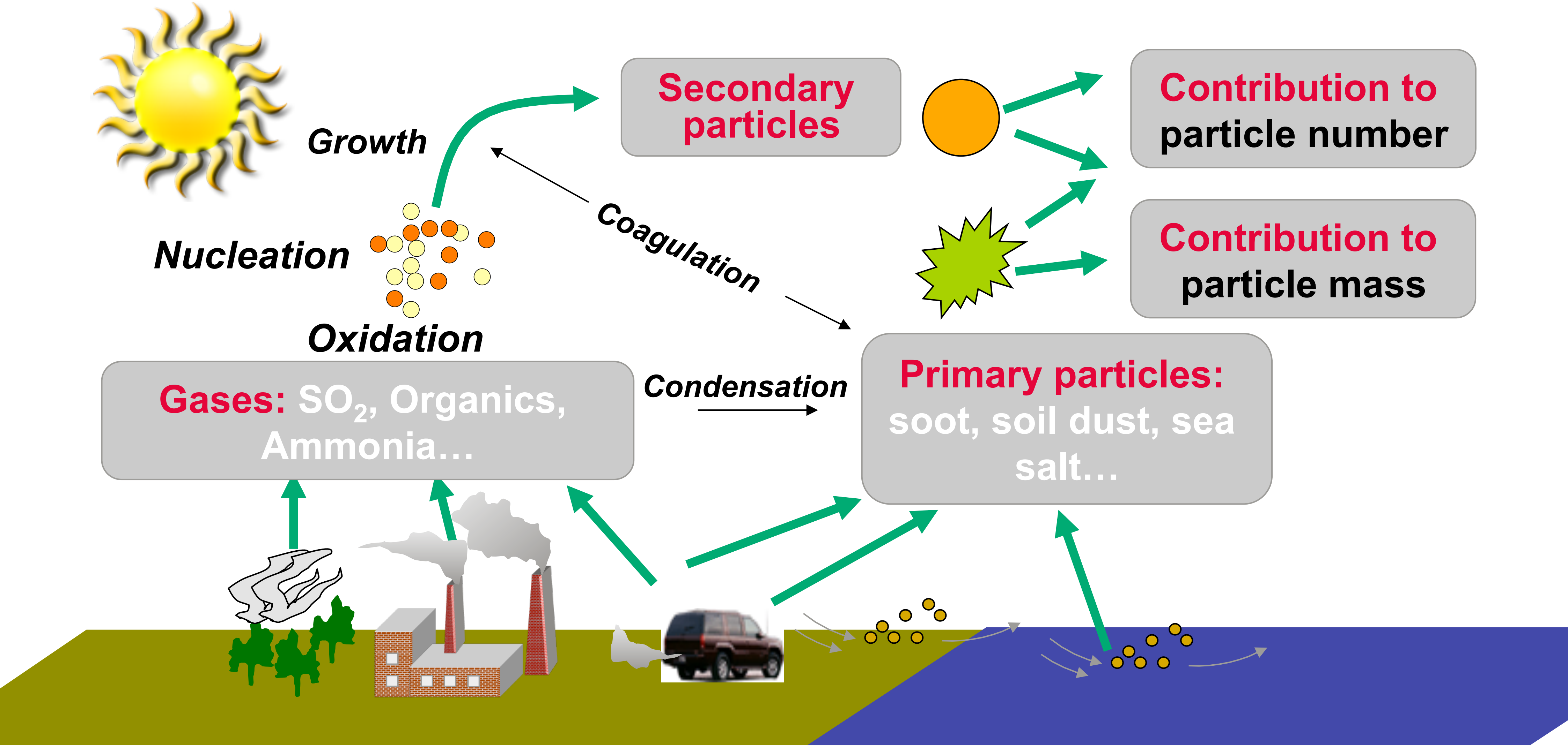
- Negative correlation due to nucleation activity



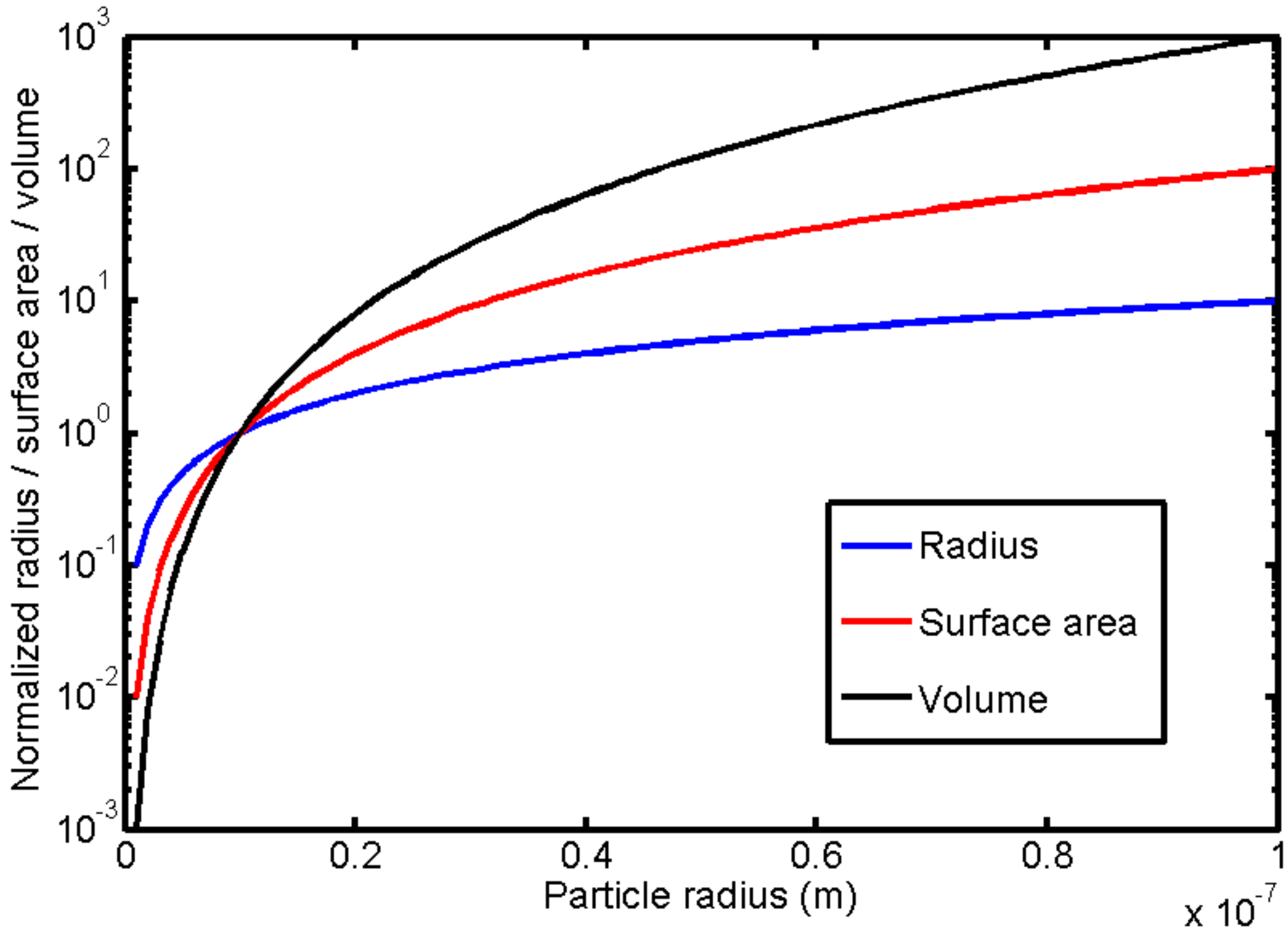
- Challenge: Representing the mass-number interactions correctly!

Primary vs. secondary aerosol, particle number vs. particle mass

- Particles interact with each other and gases



Remember: The basic relationships between radius, area, volume



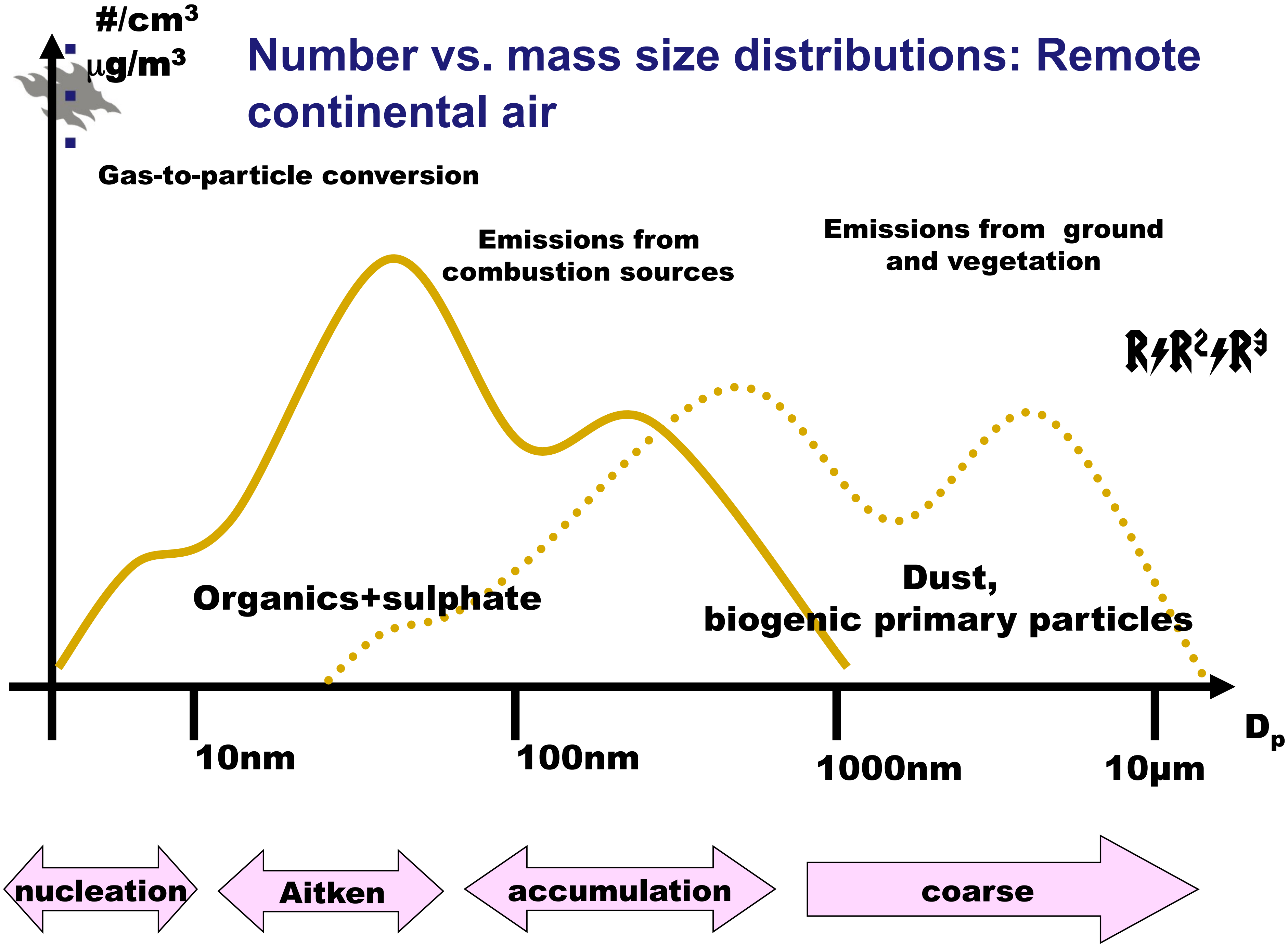
$$A_p = 4\pi r_p^2$$

$$v_p = \frac{4}{3}\pi r_p^3$$

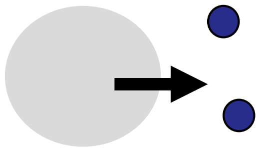
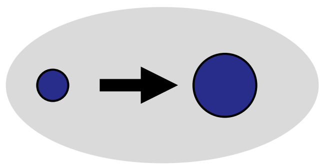
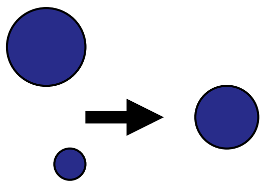
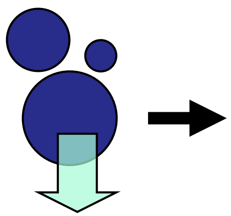
$$m_p = \rho_p \cdot v_p$$

R ⚡ R² ⚡ R³

Number vs. mass size distributions: Remote continental air

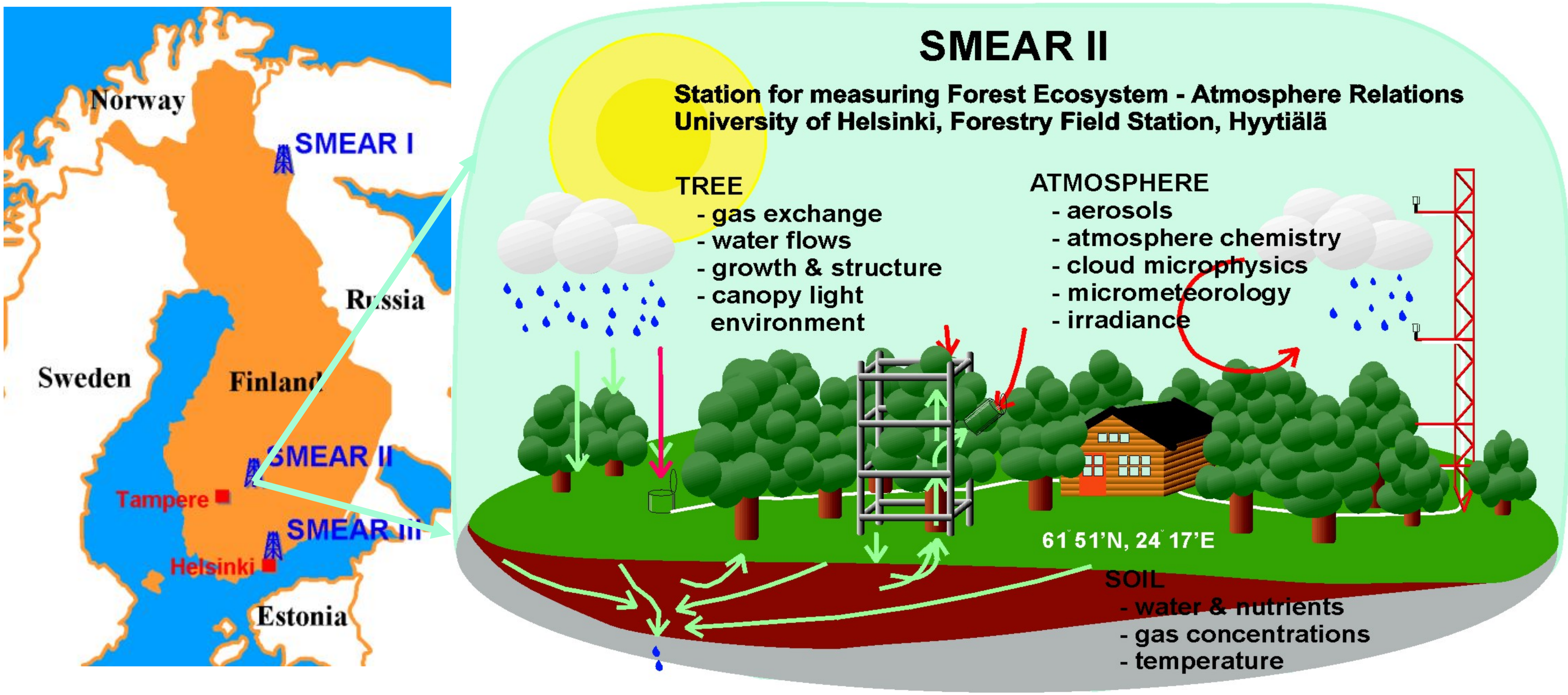


Aerosol dynamic processes

Process	Schematic	Number	Mass	Depends on
Nucleation -Homo-/ heterogeneous		Increase/ -	Increase	Vapour conc
Condensation /Evaporation		-	Increase/ decrease	Vapour conc, particle size
Coagulation		Decrease	-	Particle conc and size
Deposition		Decrease	Decrease	Particle size, surface properties

Long-term data sets from SMEAR stations

- Particle number size distribution measurements from 1996 on
  - Longest data series in the world

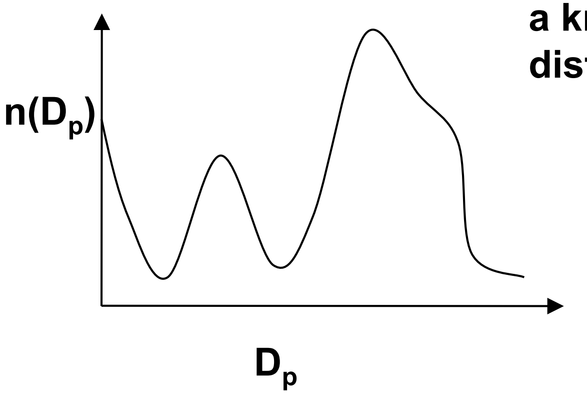


The DMPS system at the SMEAR II: particle size distribution measurements since 1996

Sample in

Charger

Bipolar charging to a known charge distribution



DMA

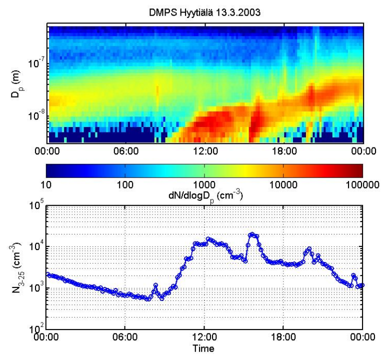
E

Mobility (size) classification with an electric field

Concentration measurement

CPC

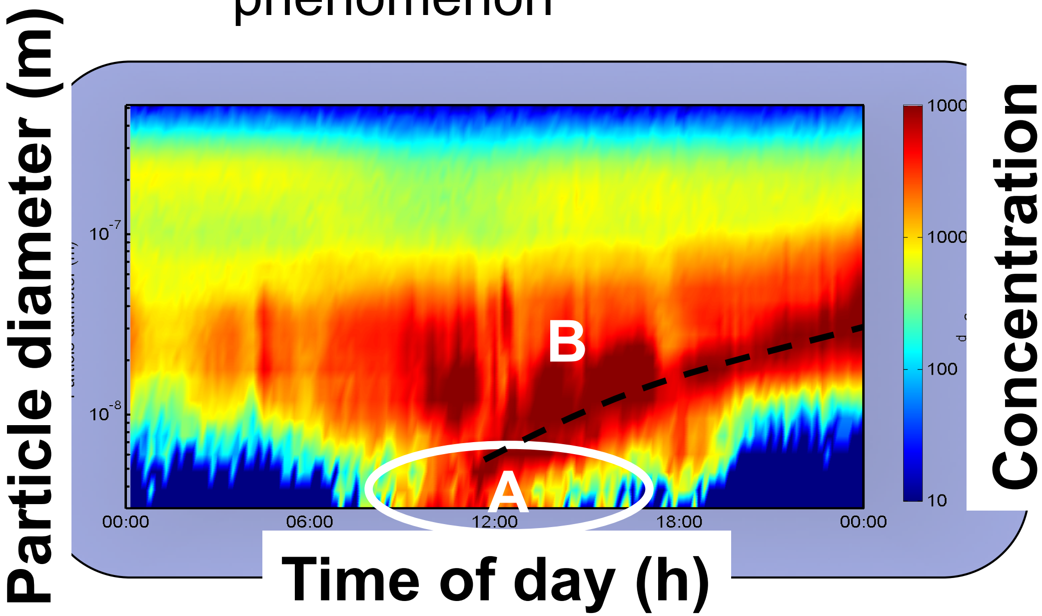
- Condensation of butanol on particles
- Optical counting



- Size range 3 – 1000 nm
- Time resolution 10 min

New particle formation events at the SMEAR II station

- New particles appearing in the 3-25 nm size range (**A**)
- Newly-formed particles growing, sometimes to sizes where they can act as cloud condensation nuclei (**B**)
- Persistence of mode indicates regional scale phenomenon



How do we know this is nucleation / condensation?

Figure by M. Dal Maso

Nucleation (usually) connected to daylight and atmospheric mixing

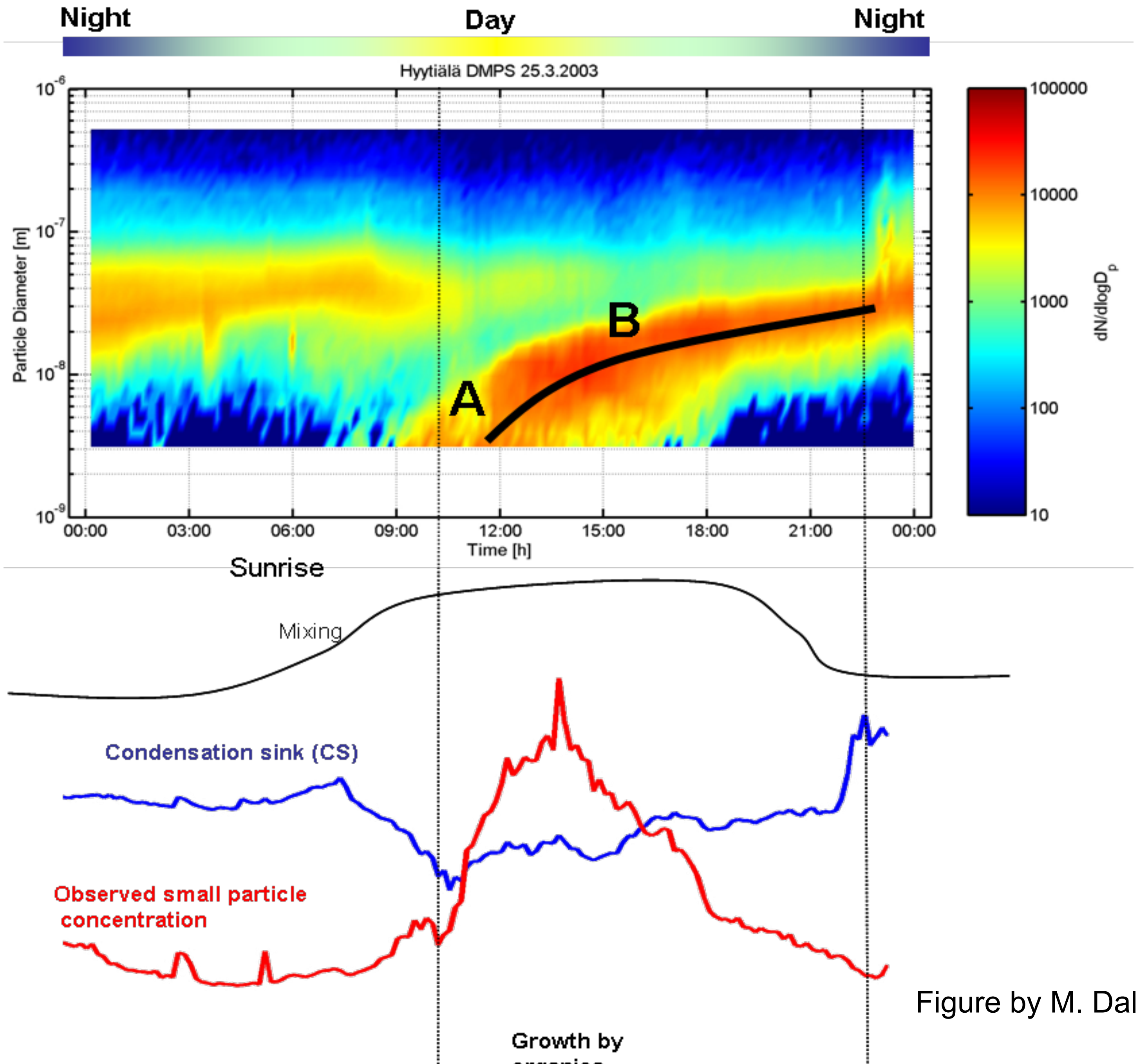
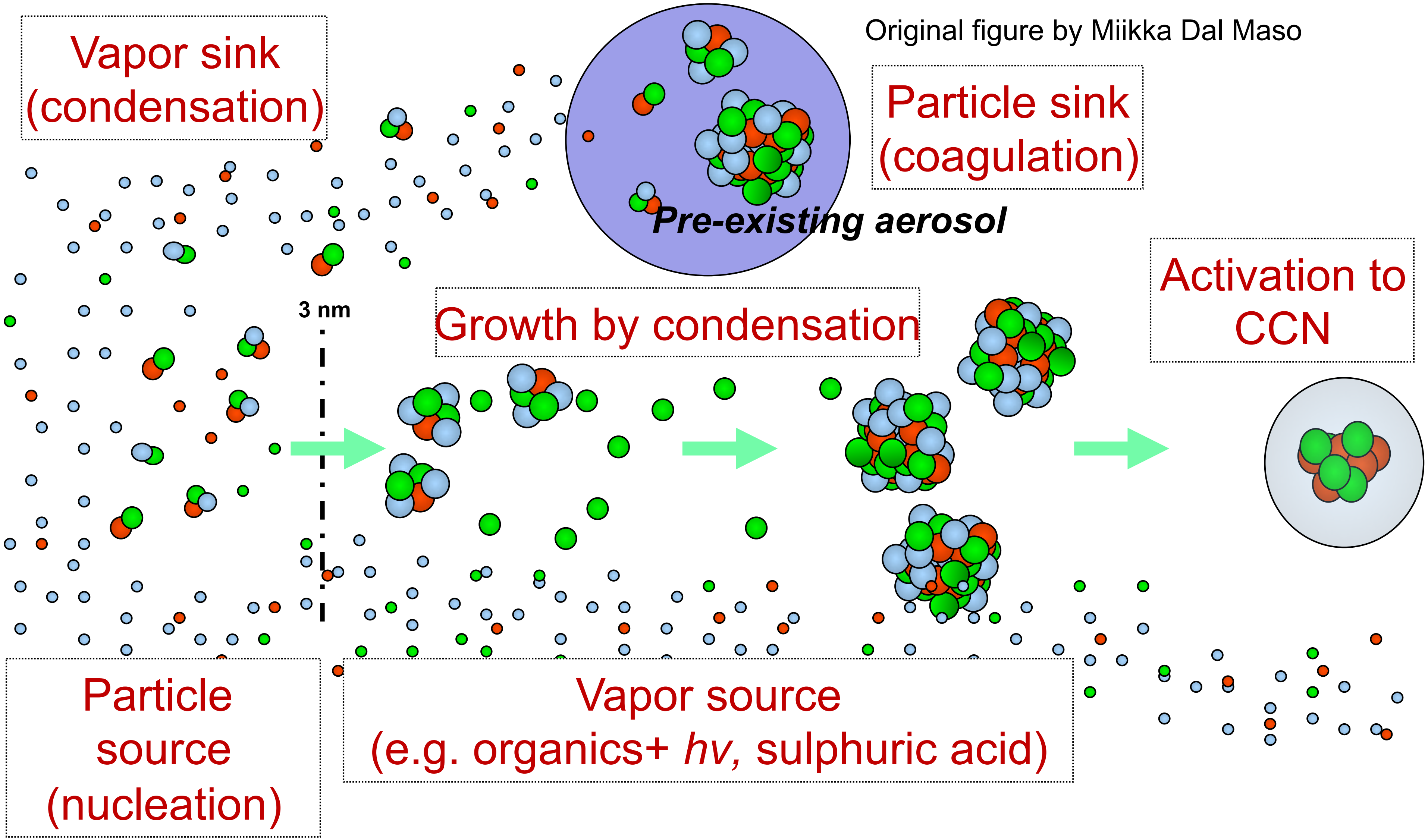


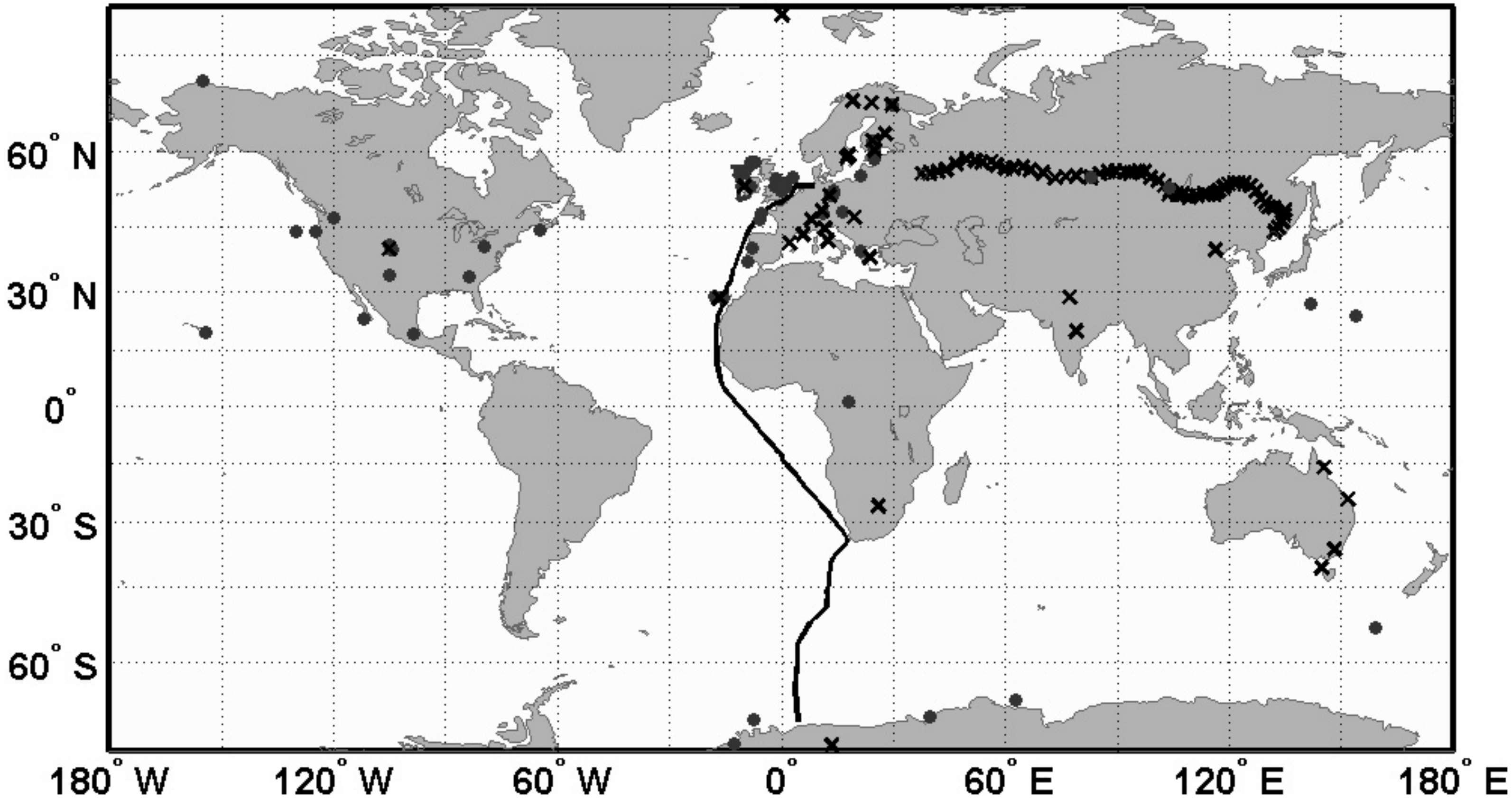
Figure by M. Dal Maso

Lifetimes of freshly formed aerosol determined by competition of growth and coagulation



Nucleation and particle growth observed all over the world

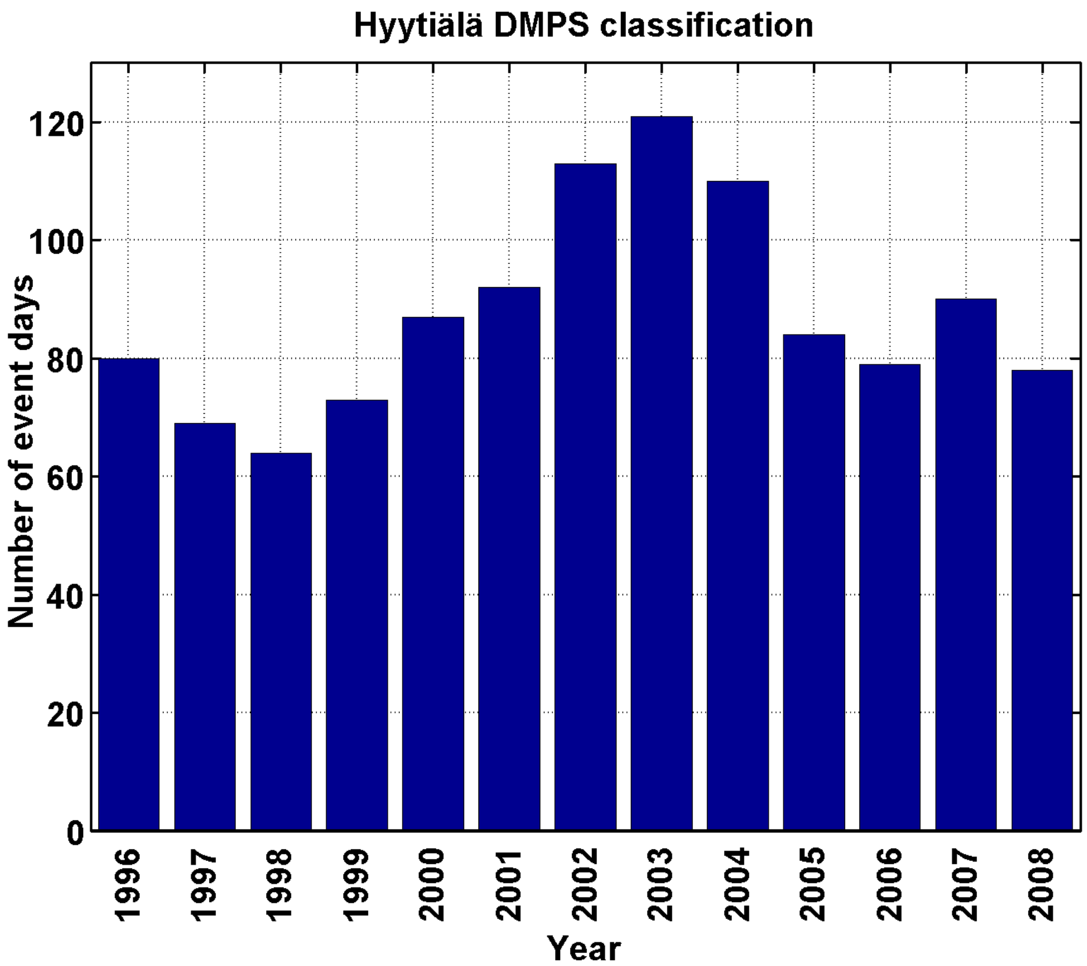
- Potentially an important source of aerosol particles!
  - Global and regional models useful tools to investigate how important nucleation is for total aerosol budgets



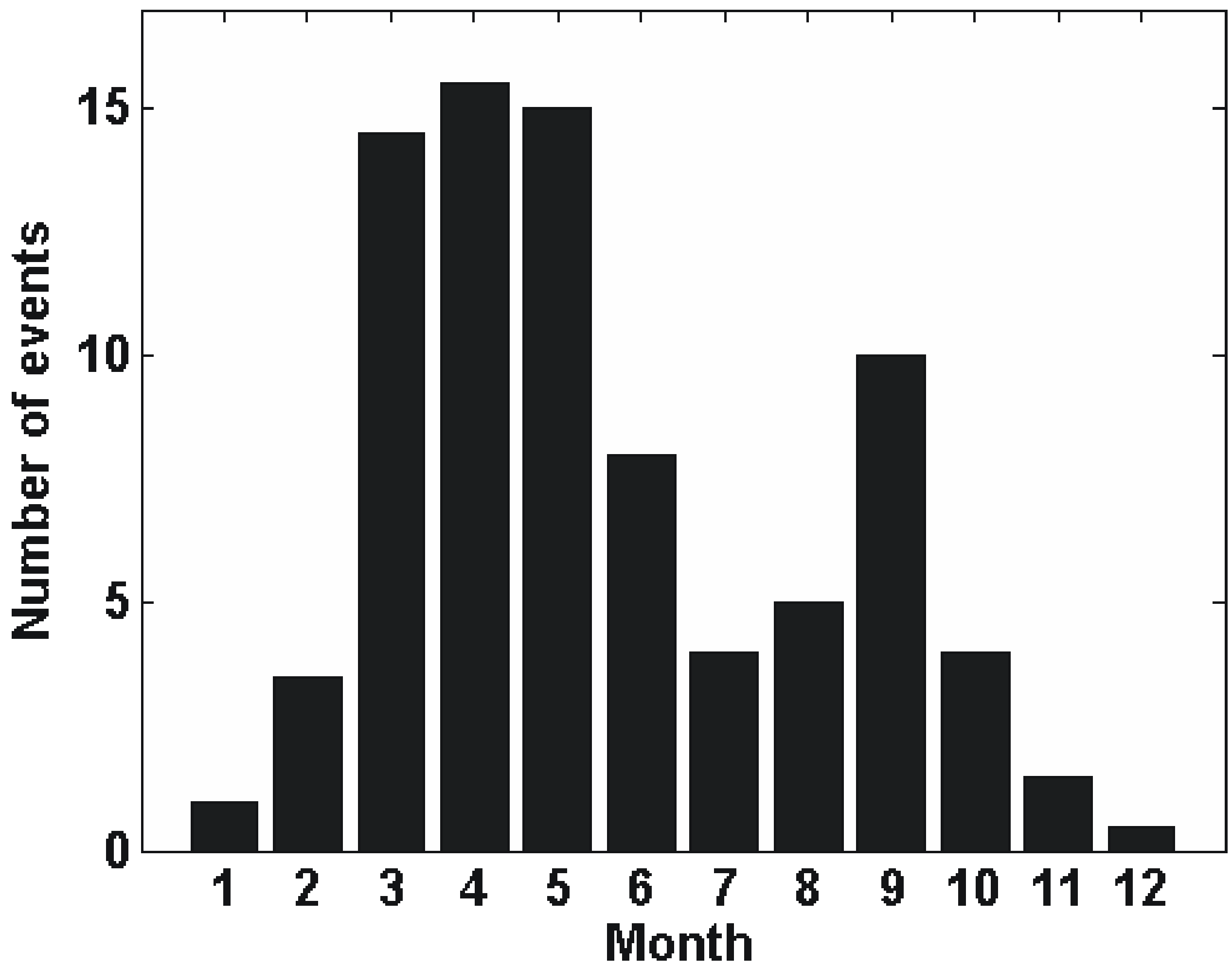
Kulmala et al., *J. Aerosol Sci.* 2004

Particle formation and growth events, SMEAR II in Hyytiälä, Finland

- Particle formation most frequent in spring and autumn

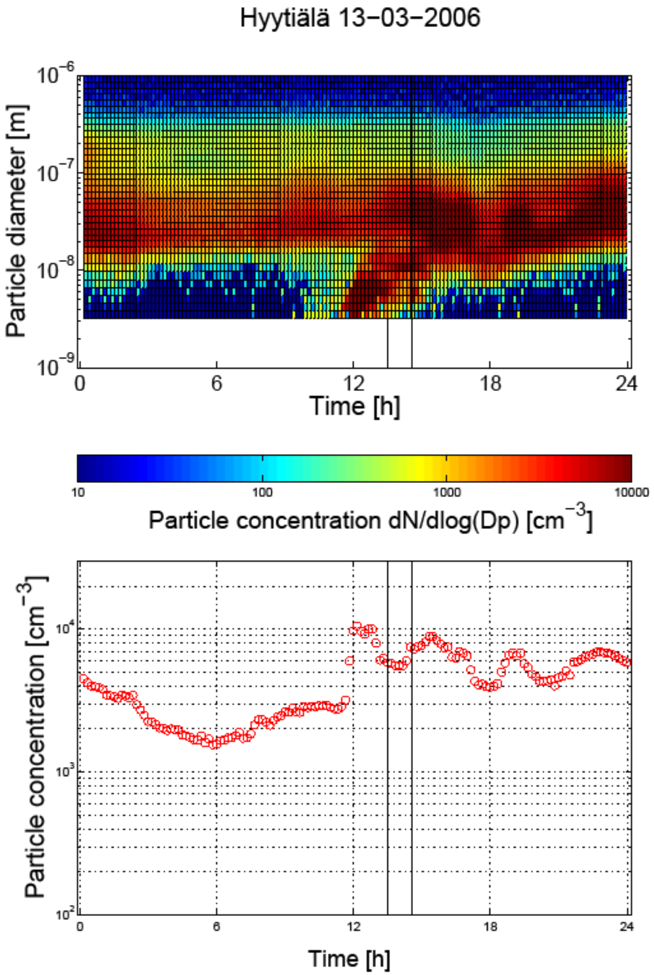


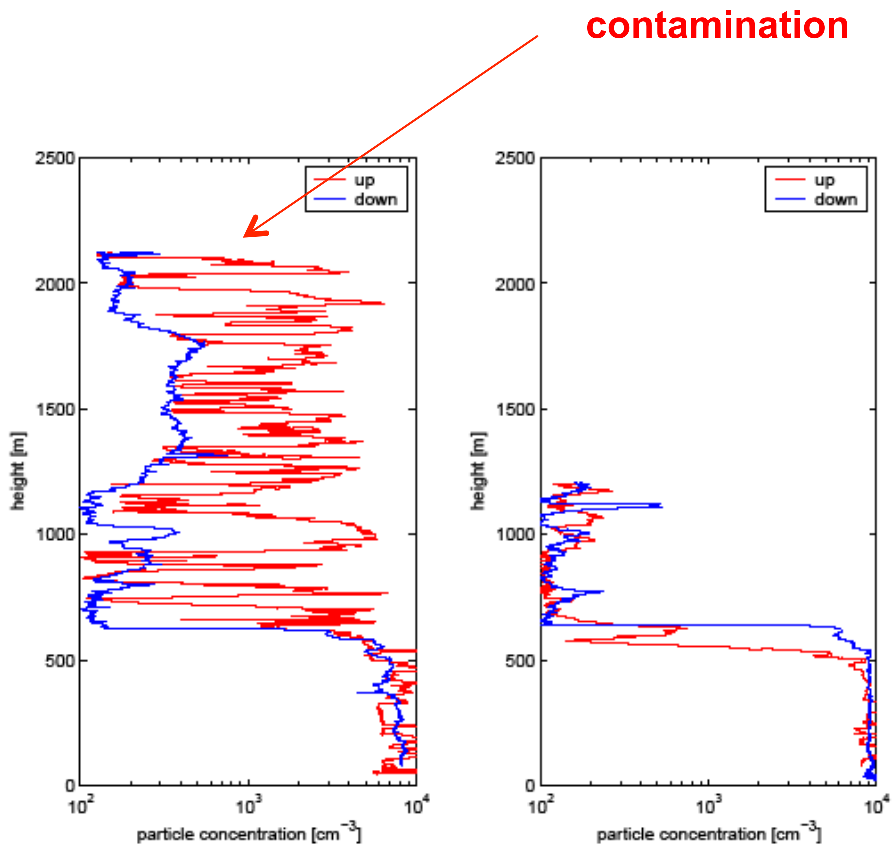
Particle formation in Hyytiälä: seasonal distribution of particle formation events



Nucleation in boundary layer or upper troposphere?

- **BL**: More vapours – **UT**: Lower temperature, lower sink
- Hot air balloon measurements near SMEAR II indicate particle formation inside BL (but which part of BL?)

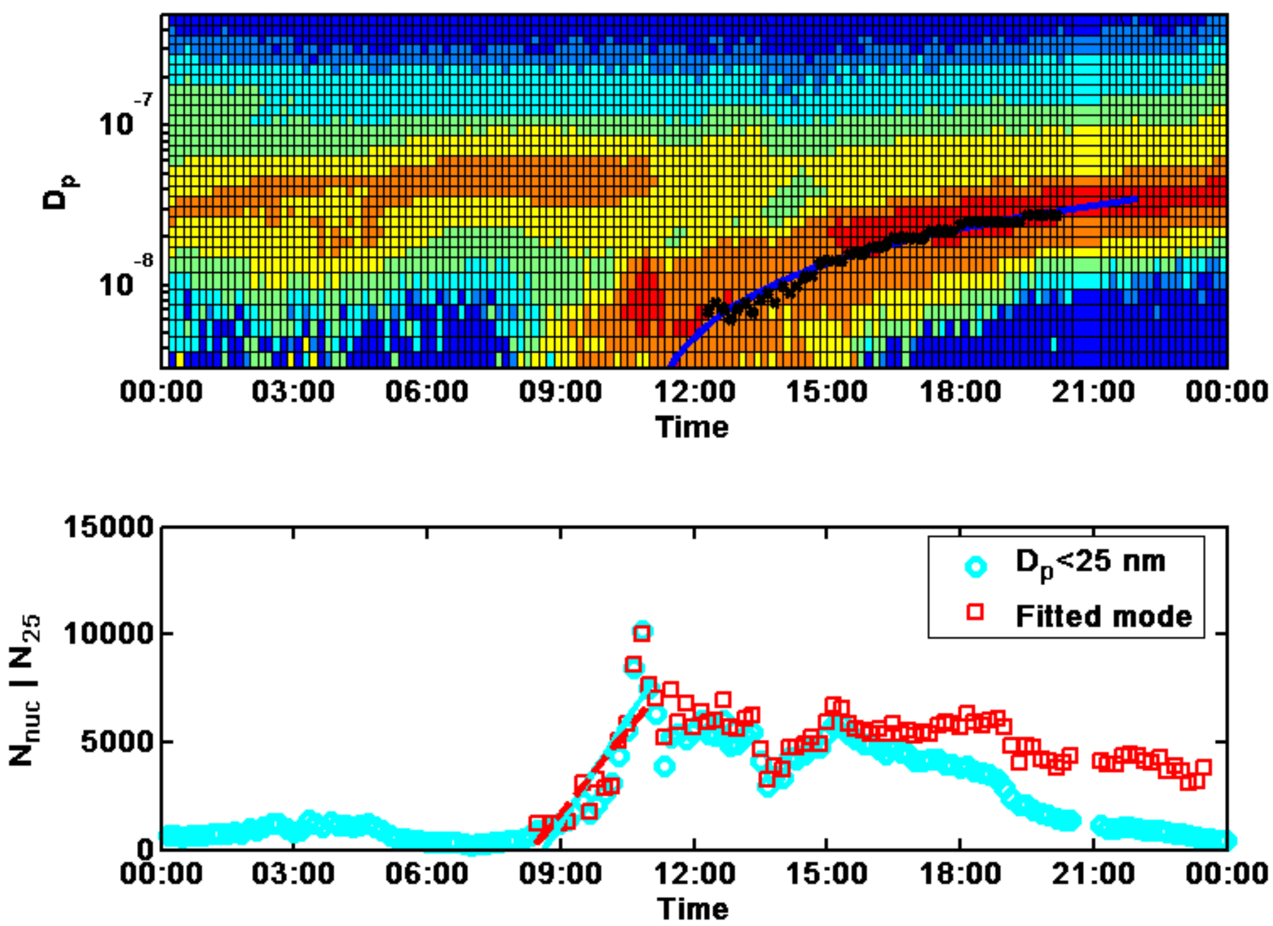




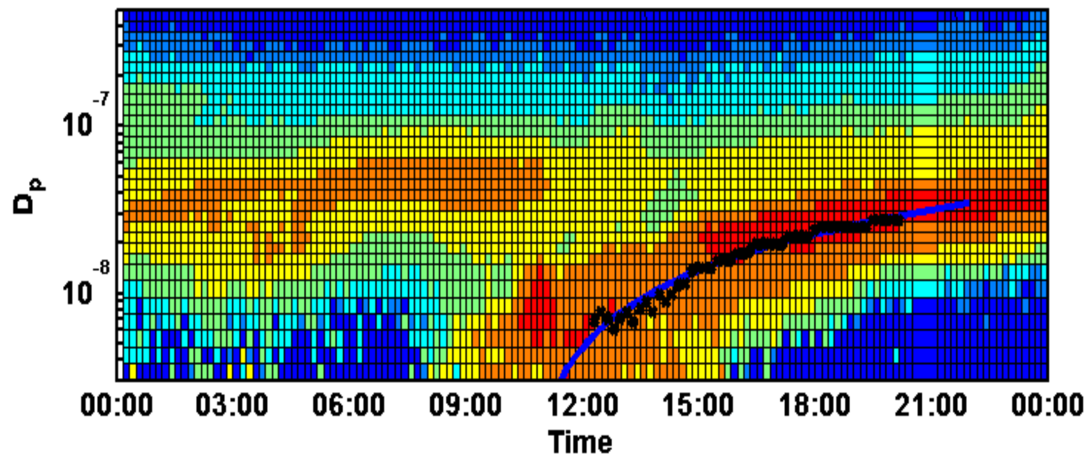
Laakso et al., *BER* 2007

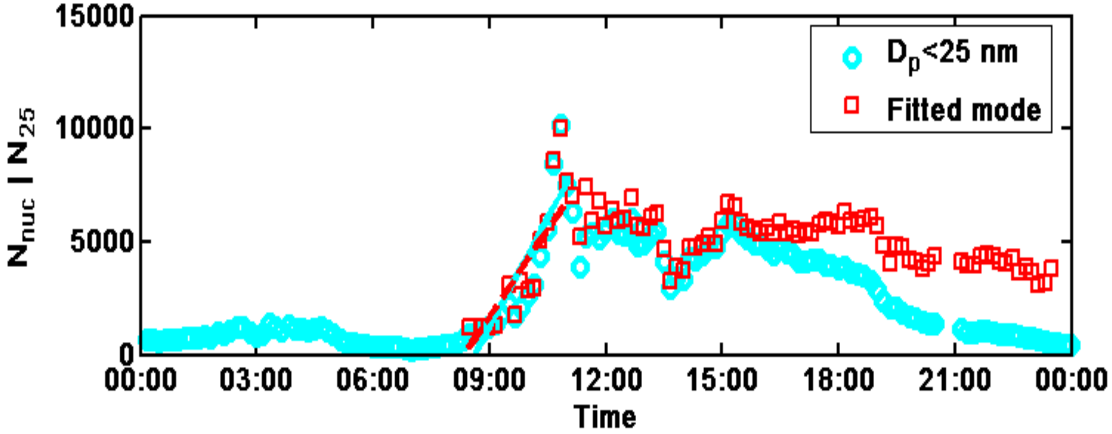
Characteristics of particle formation events

- Intensity of formation, particle growth, background aerosol



Characteristics of particle formation events





Dal Maso et al., *BER* 2005

- Growth rate (GR)
  - Diameter or mass
  - Related to condensable vapour concentrations

Formation rate *(J_3)*

- Related to nucleation rate

$$J_{nuc} = \frac{dN_{nuc}}{dt} + F_{coag} + F_{growth}$$

Condensation sink (CS)

- Describes the background aerosol
- Related to vapour sink and coagulational loss rate

Condensation and coagulation sinks

- Condensation sink (**CS**): $$CS = 4\pi D \int_0^\infty r\, \beta_M(r)\, n(r)\, dr = 4\pi D \sum_i \beta_M\, r_i\, N_i$$
  - describes the aerosol population's ability to remove vapor by condensation

- Coagulation sink (**CoagS(D_p)**) $$CoagS(D_p) = \int_{D_p}^\infty K(D_p, D_p', T, \ldots)\, n(D_p')\, dD_p'$$
  - describes the aerosol population's ability to remove particles of size D_p

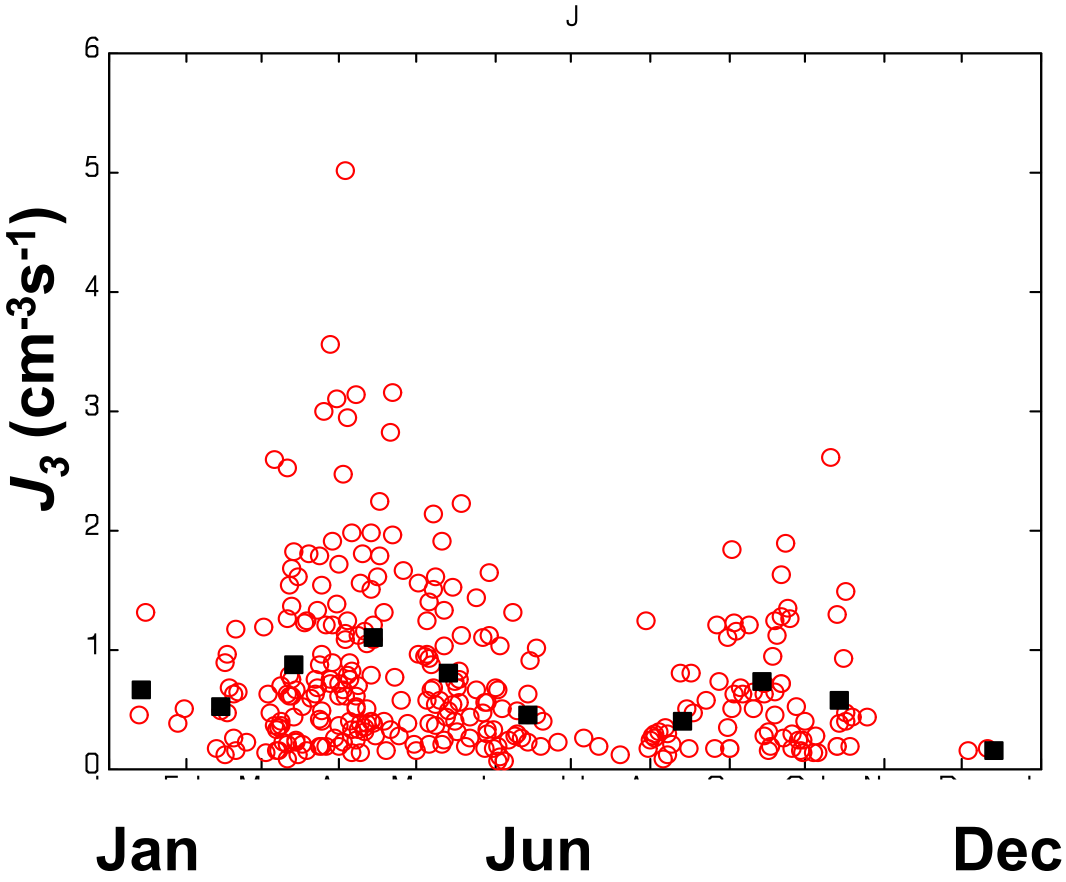
- Sinks sensitive to particle size changes
  - hygroscopic growth must be accounted for
  - ➔ parameterization (Laakso et al., *JGR* 2004):

$$GF(D_p, RH) = \left(1 - \frac{RH}{100}\right)^{\gamma(D_p)}$$

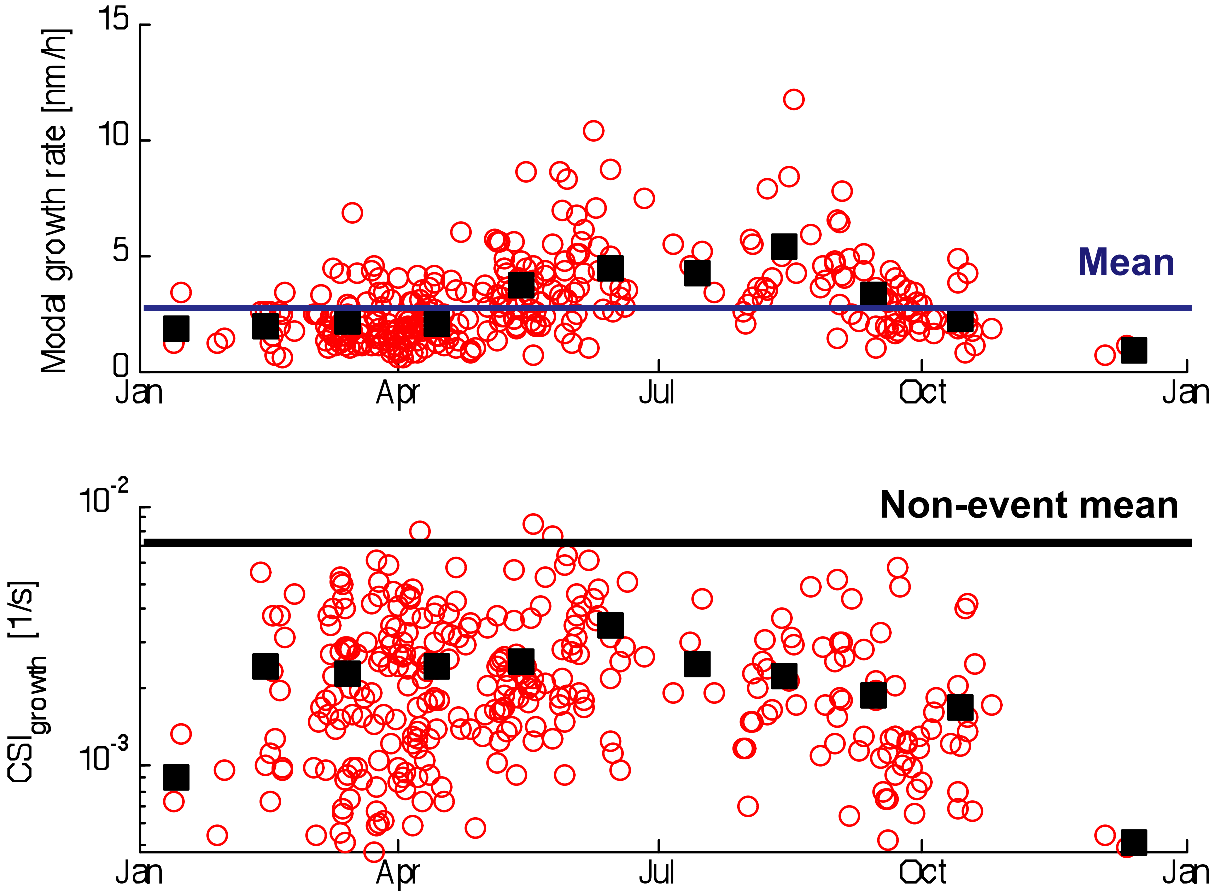
  - CS greater by up to factor of 4, usually ca. 1.5...2.0

Observations from Hyytiälä: 3 nm particle formation rates

- Mean J_3: 0.8 $cm^{-3}s^{-1}$
- Maxima coincide with frequency maxima



Observations from Hyytiälä: Growth rates and CS



- Mean GR: 3 nm/h
- Growth rate peaks during summer
- Mean CS during growth period: 2.4 $\cdot 10^{-3}\ s^{-1}$
- Sink lower during events than non-events

Dal Maso et al., *BER* 2005

Global observations: Formation and growth rates

(Kulmala et al., *JAS* 2004)

- Formation rate J_3:
  - Regional background
    - 0.01 – 10 $cm^{-3}s^{-1}$
  - Urban areas
    - 10 – 100 $cm^{-3}s^{-1}$
  - Coastal zones
    - 1000 – 1 000 000 $cm^{-3}s^{-1}$
- Growth rate **GR:**
  - usually 1 – 20 nm/h
  - 0.1 nm/h (Arctic areas, initial growth below 3 nm)

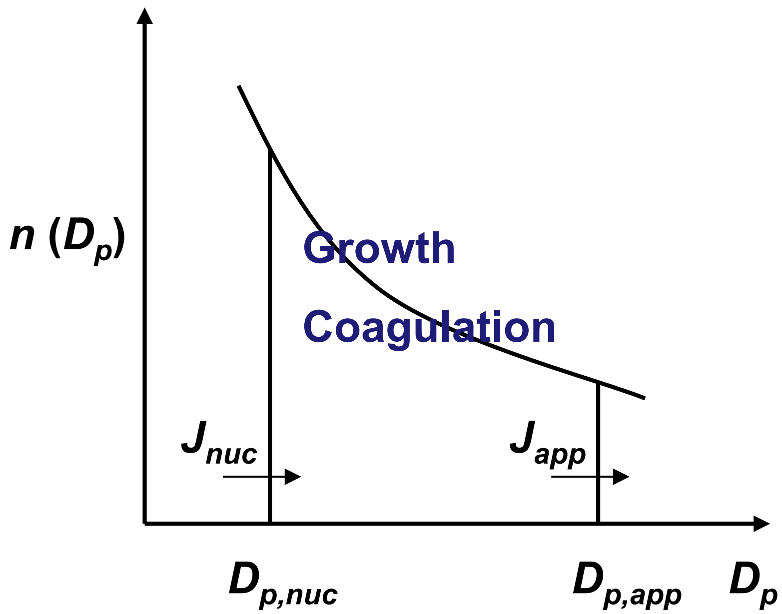
How to estimate nucleation rate from the 3 nm formation rate?

- The DMPS cut-off size at 3 nm – J_3 needs to be scaled back to the nucleation size (1-2 nm) (Kerminen and Kulmala, *JAS* 2002):

$$J_{nuc} = J_{app}(t')\exp\left[\frac{\gamma CS'}{GR}\left(D_{p,nuc}^{-1} - D_{p,app}^{-1}\right)\right]$$

$$\gamma \approx 0.23$$

- Calculation sensitive to
  - Coagulation sink
  - Particle growth rate at 1-3 nm
  - Initial particle size



- $J_{1.5}$ in Hyytiälä ~ 0.1 – 10 cm^{-3} s^{-1}

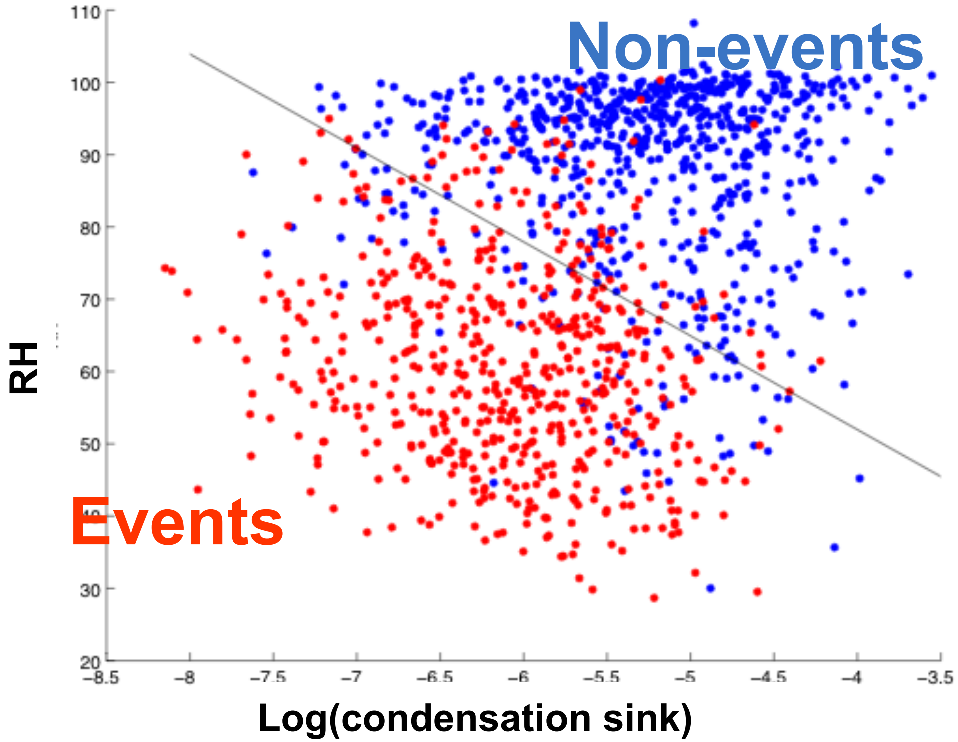
Towards direct observation of atmospheric nucleation

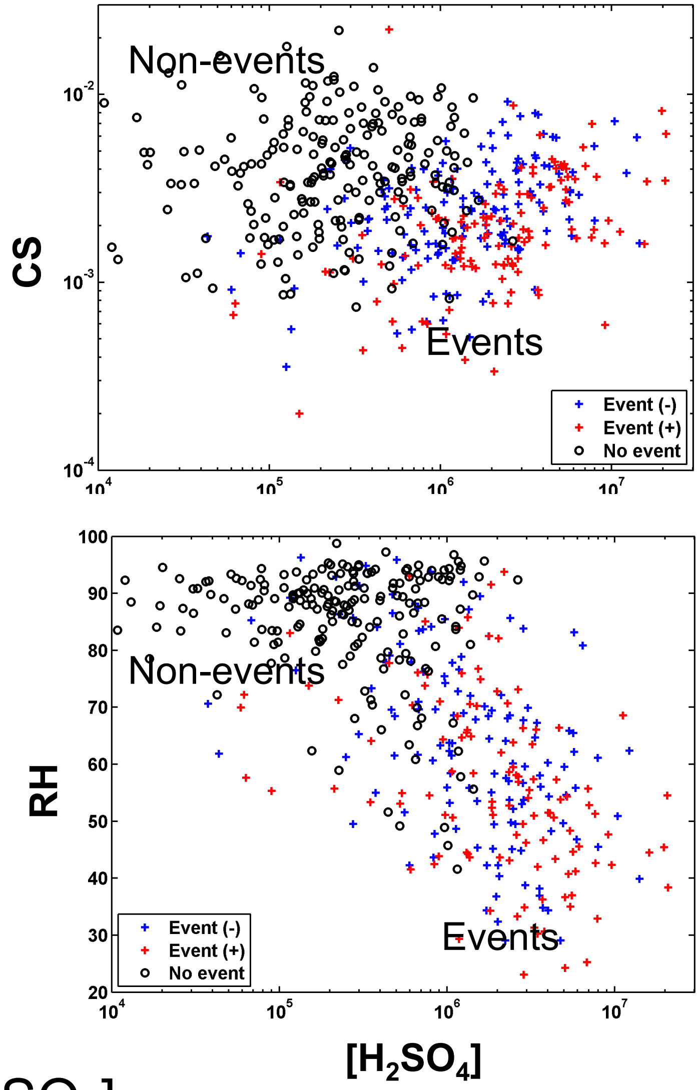
- Scaling back 3 nm formation highly uncertain

- During recent years significant progress has beed made in developing instruments that measure down to ~ 1 nm
  - Ion spectrometers (AIS, BSMA), NAIS
  - Condensation particle counters

- Allows for separate investigation of e.g. electrically charged and neutral aerosol size distributions

What is required for particle formation and growth events in boreal forest?





- Low condensation sink, low RH, high $[H_2SO_4]$
  - RH more significant than e.g. temperature or radiation

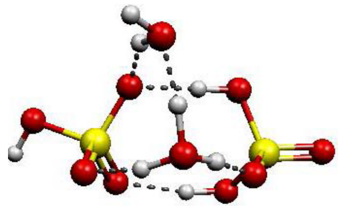
Hyvönen et al., *Atmos. Chem. Phys.*, 2005

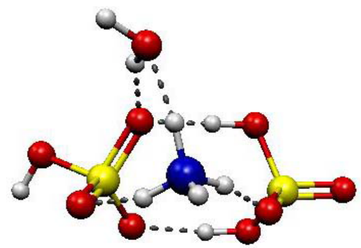
Figure by Tuomo Nieminen

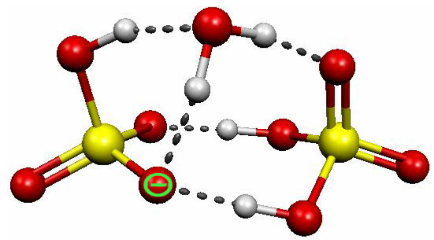
Proposed mechanisms of atmospheric particle formation

- 2-component homogeneous nucleation
  - Sulphuric acid and water
- 3-component homogeneous nucleation
  - Sulphuric acid, water, ammonia
  - Sulphuric acid, water, something else (e.g. organics, amines)

CNT predictions do not work in BL!

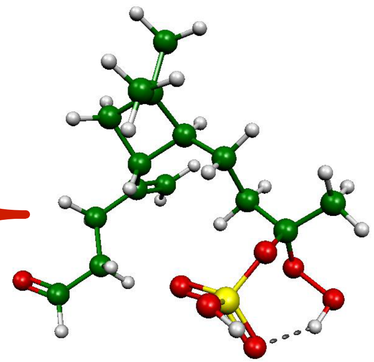




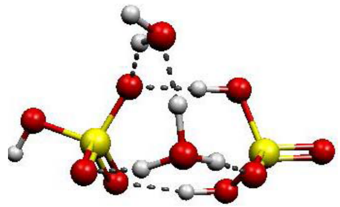


- Ion-induced or ion-mediated nucleation
- ”Cluster activation”
  - Pre-existing clusters act as seeds for condensable vapours

Inspired by observations



Proposed mechanisms of atmospheric particle formation



- 2-component homogeneous nucleation
  - Sulphuric acid and water

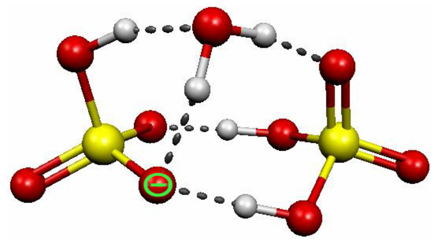
CNT predictions do not work in BL!

- 3

- Mechanistic understanding still missing

- Sulphuric acid seems to be a common factor

amines)



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  - Pre-existing clusters act as seeds for condensable vapours

Inspired by observations