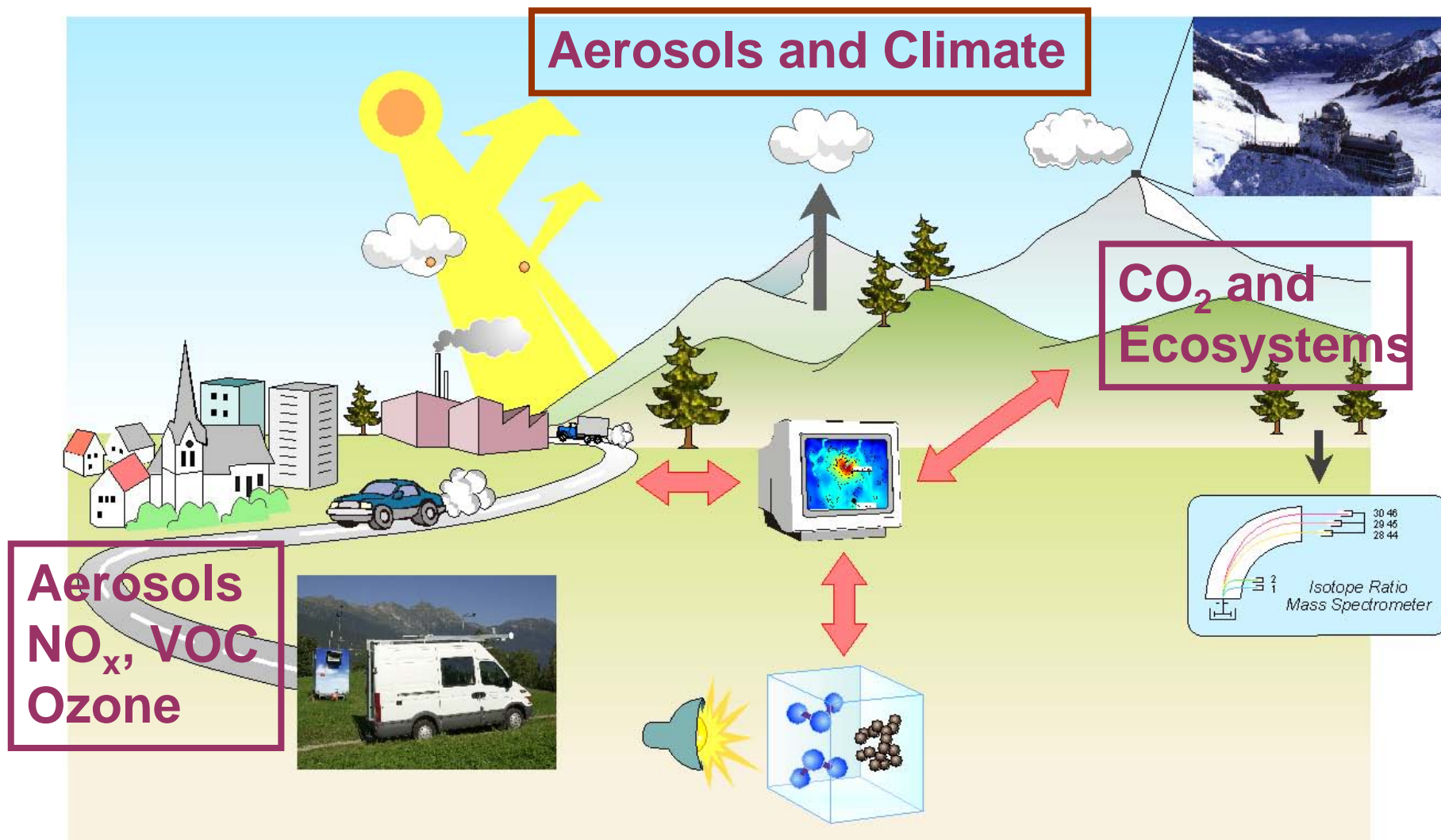


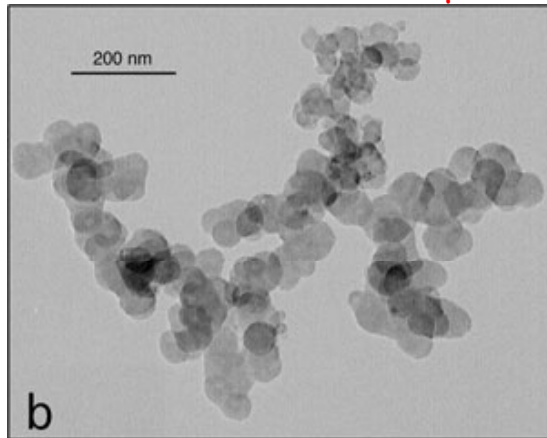
The Laboratory of Atmospheric Chemistry



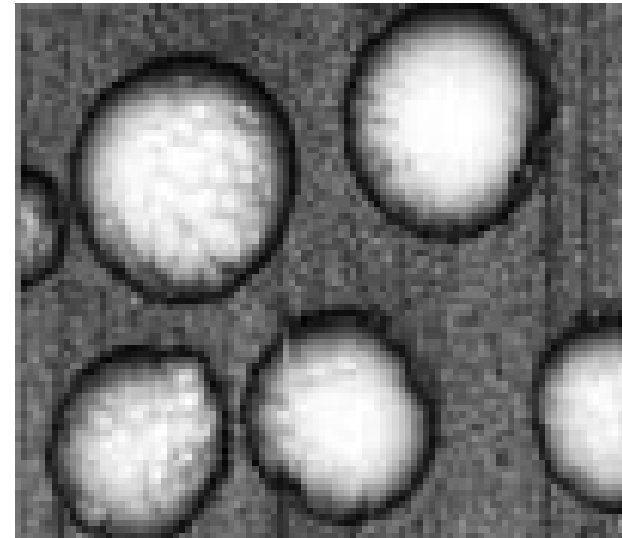
**Definition: PM10 =
Particles with aerodynamic diameter $<10\mu\text{m}$**

Examples:

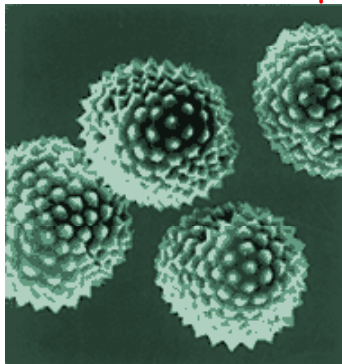
Diesel soot: ca. $0.1\mu\text{m}$



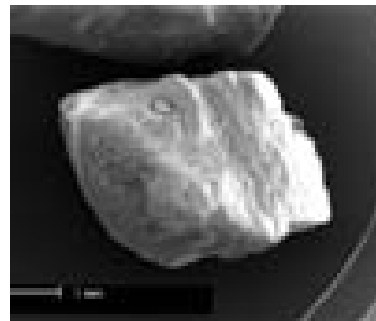
Ammonium sulfate: ca. $0.1\mu\text{m}$



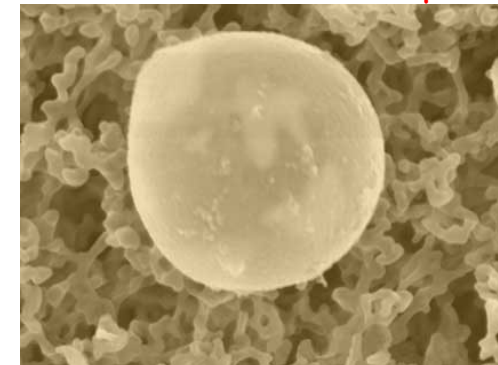
Pollen: $10 - 100\mu\text{m}$



Sea salt: $0.2 - 10\mu\text{m}$

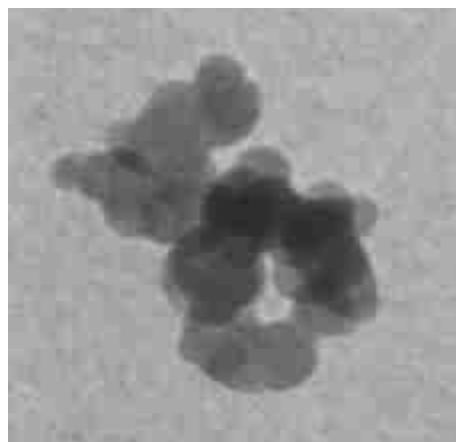


Mineral dust: $0.2 - 10\mu\text{m}$



How big are aerosol particles?

Size relationships



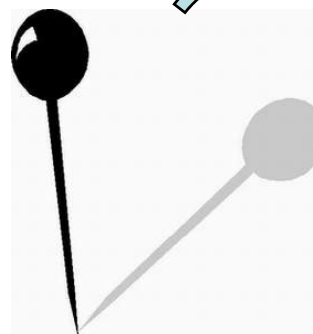
Diesel soot

100 Nanometer (nm)

=
0.1 micrometer (μm)

=
0.0001 millimeter (mm)

x 20'000



x 20'000



Pin head

2'000'000 nanometer (nm)

=
2'000 micrometer (μm)

=
2 Millimeter (mm)



Hot air balloon

40'000'000 micrometer (μm)

=
40'000 millimeter (mm)

=
40 Meter (m)

In one cubiccentimeter of air: typically 10'000 particles

Aerosols

- Primary and secondary particles and size distributions
- Instrumentation
- Climate
- Health
- Source identification

Primary particle emissions in 2000 (Tg yr⁻¹)

	Northern Hemisphere	Southern Hemisphere	Global	Low	High	Source
Carbonaceous aerosols						
Organic Matter (0–2 μm)						
Biomass burning	28	26	54	45	80	Liousse <i>et al.</i> (1996), Scholes and Andreae (2000)
Fossil fuel	28	0.4	28	10	30	Cook <i>et al.</i> (1999), Penner <i>et al.</i> (1993)
Biogenic (>1μm)	—	—	56	0	90	Penner (1995)
Black Carbon (0–2 μm)						
Biomass burning	2.9	2.7	5.7	5	9	Liousse <i>et al.</i> (1996); Scholes and Andreae (2000)
Fossil fuel	6.5	0.1	6.6	6	8	Cooke <i>et al.</i> (1999); Penner <i>et al.</i> (1993)
Aircraft	0.005	0.0004	0.006			
Industrial Dust, etc. (> 1 μm)			100	40	130	Wolf and Hidy (1997); Andreae (1995)
Sea Salt						
d < 1 μm	23	31	54	18	100	
d = 1–16 μm	1,420	1,870	3,290	1,000	6,000	
Total	1,440	1,900	3,340	1,000	6,000	Gong <i>et al.</i> (1998)
Mineral (Soil) Dust ^b						
d < 1 μm	90	17	110	—	—	
d = 1–2 μm	240	50	290	—	—	
d = 2–20 μm	1,470	282	1,750	—	—	
Total	1,800	349	2,150	1,000	3,000	

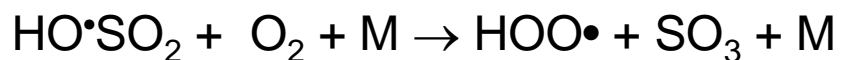
^a Range reflects estimates reported in the literature. The actual range of uncertainty may encompass values larger and smaller than those reported here.

^b Source inventory prepared by P. Ginoux for the IPCC Model Intercomparison Workshop.

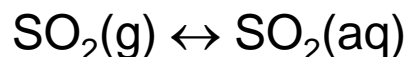


Formation of secondary aerosol

- **Sulfate, homogeneous reaction:**

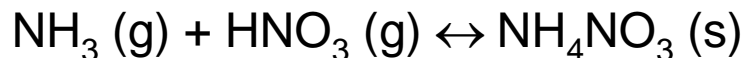


- **Sulfate, heterogeneous reaction:**

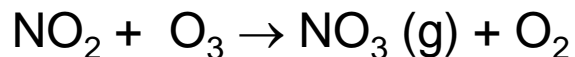


Oxidation with H_2O_2 , Ozon, NO_2 , ...

- **Nitrate, homogeneous reaction :**



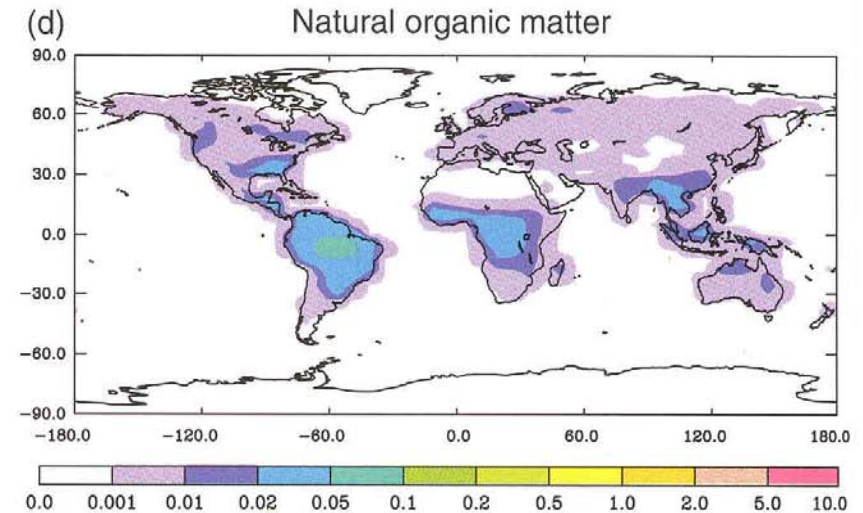
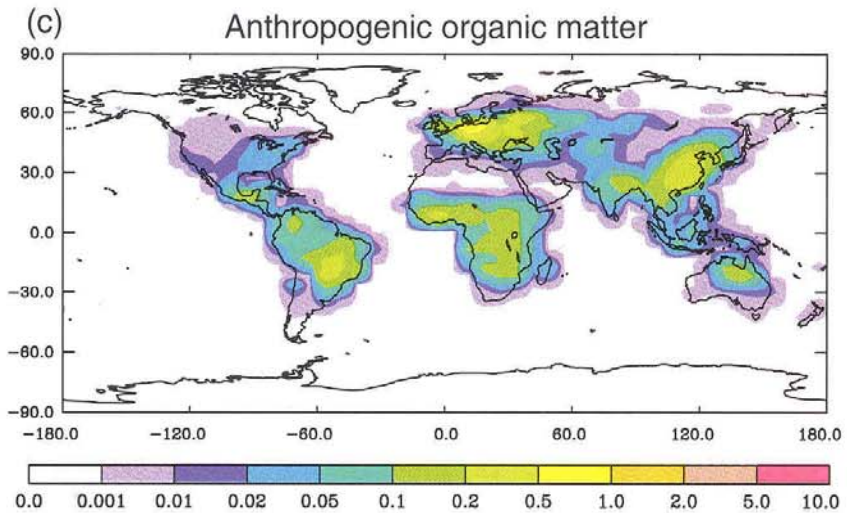
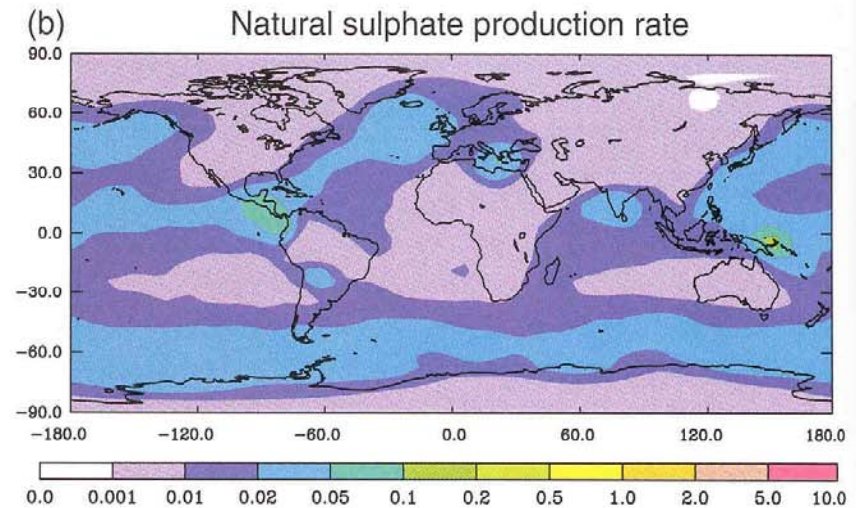
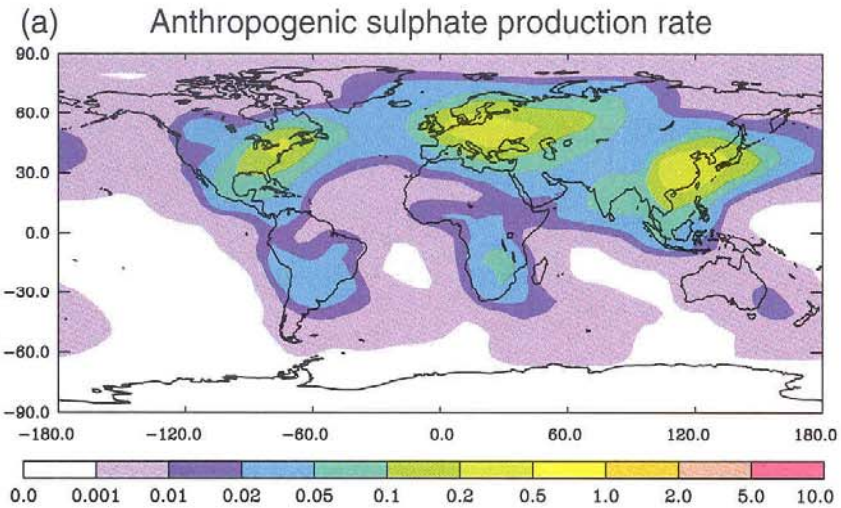
- **Nitrate, heterogeneous reaction :**



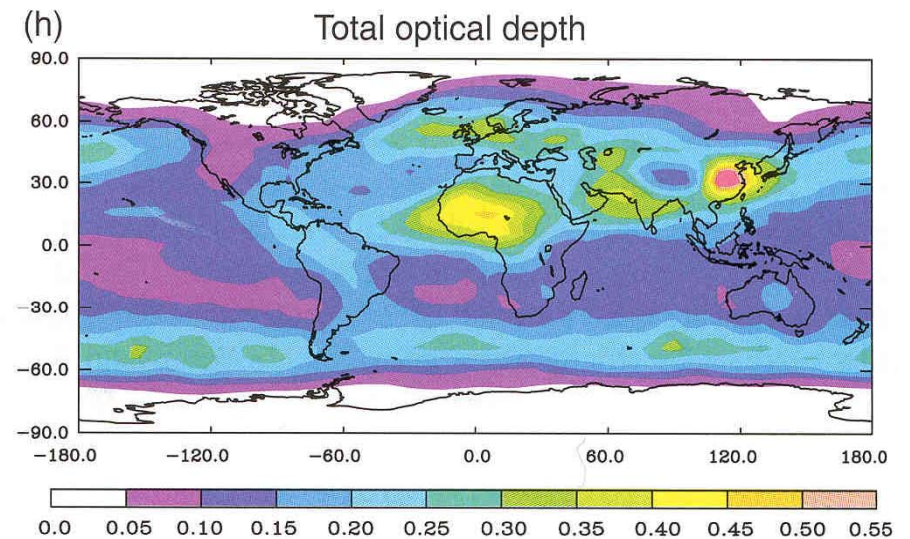
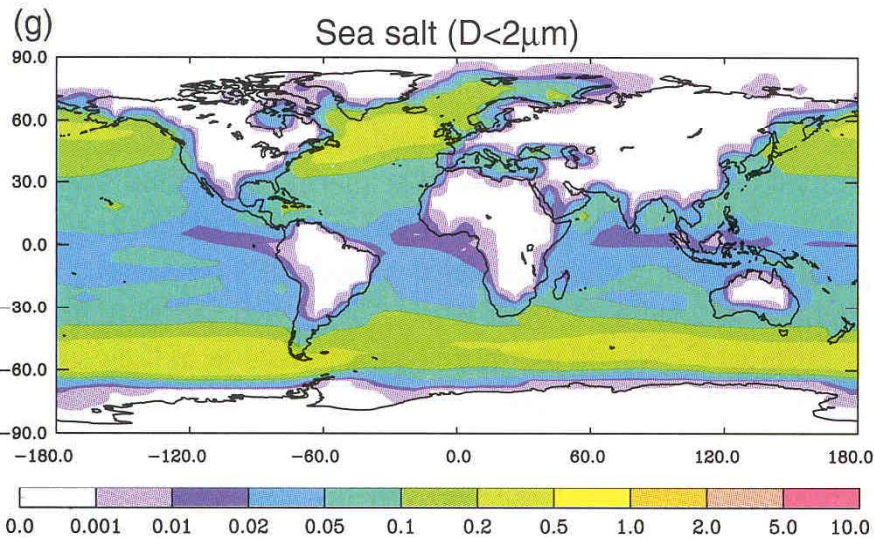
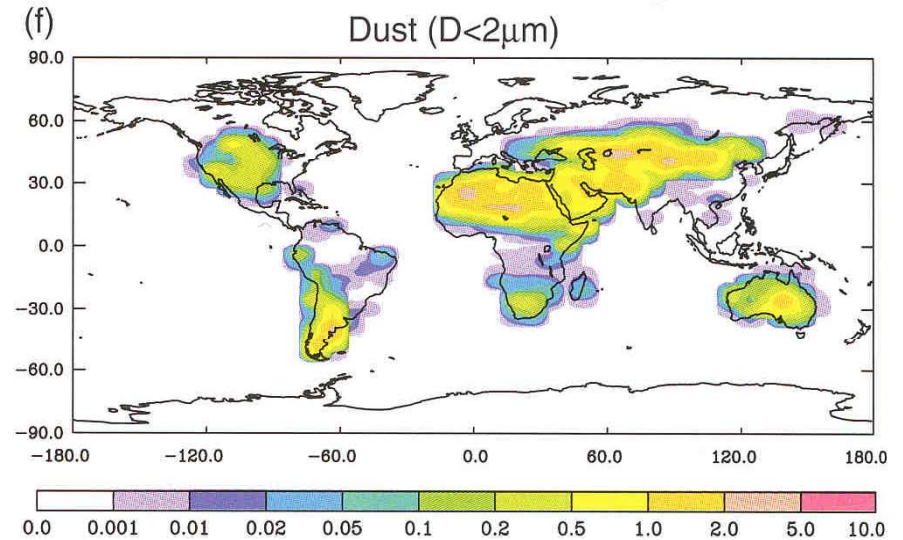
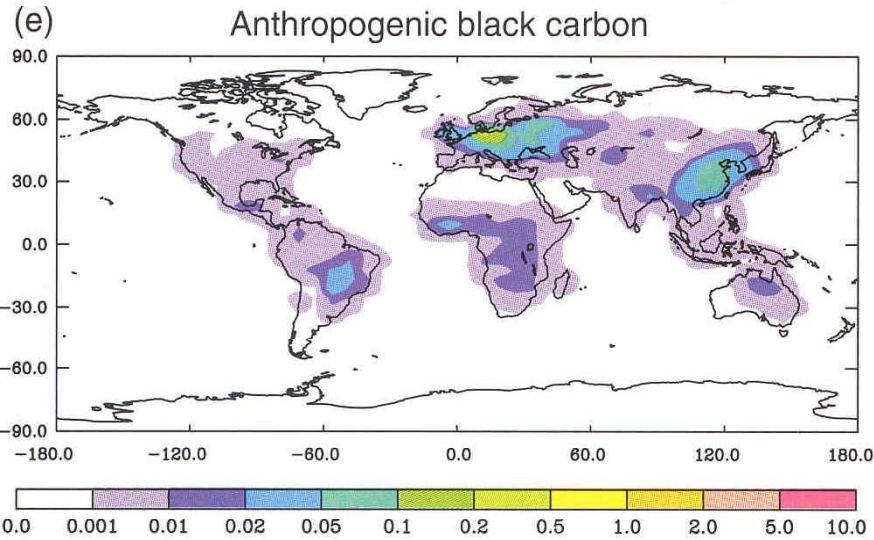
- **Organics:**

$\text{VOC} + \text{OH}, \text{O}_3, \dots \rightarrow \text{SOA}$ (secondary organic aerosol)

Source strengths of sulfate and organic carbon ($\text{kg m}^{-2} \text{hr}^{-1}$)



Source strengths of black carbon, mineral dust and sea salt ($\text{kg m}^{-2} \text{hr}^{-1}$)



Size distributions of aerosol particles

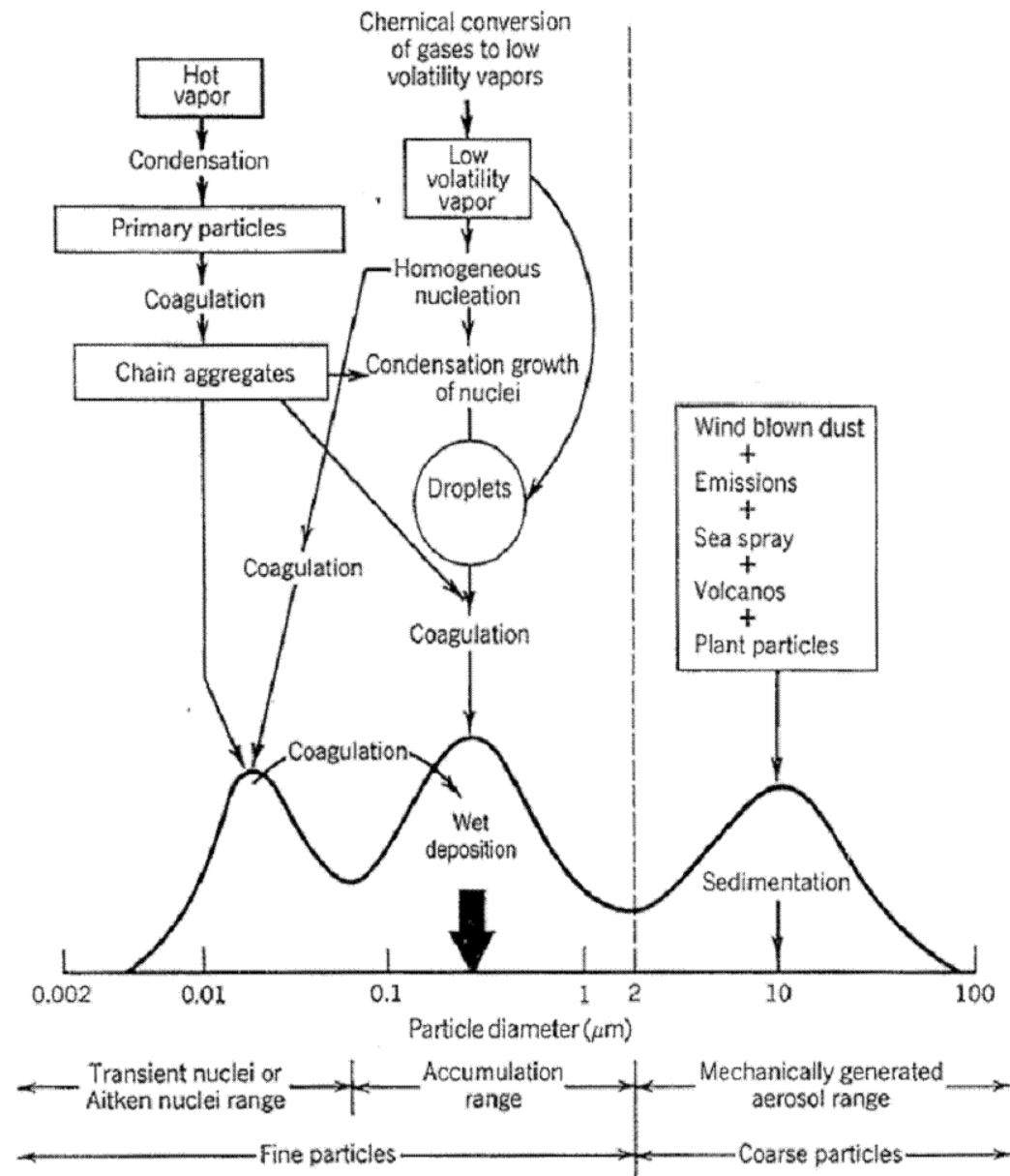
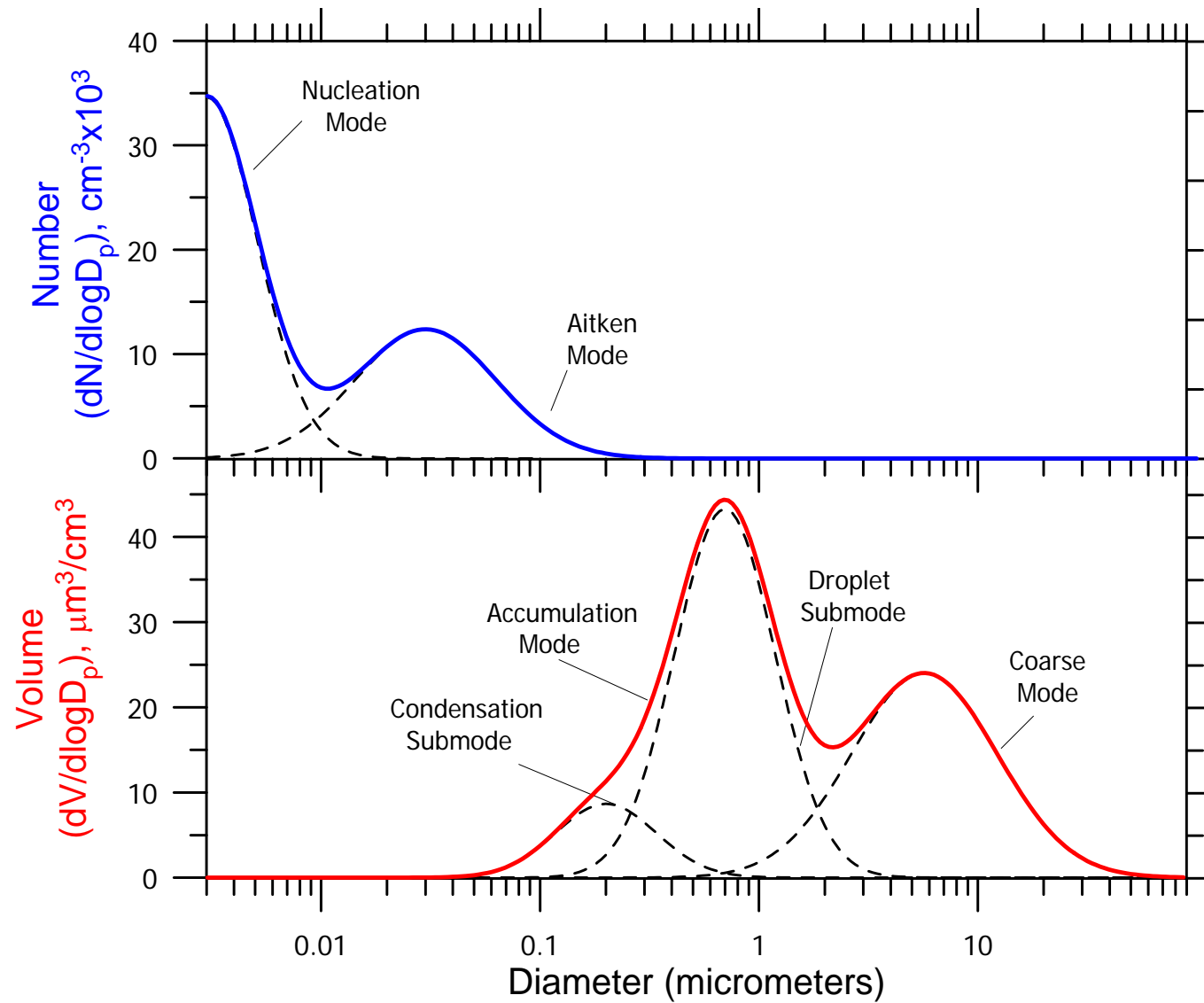
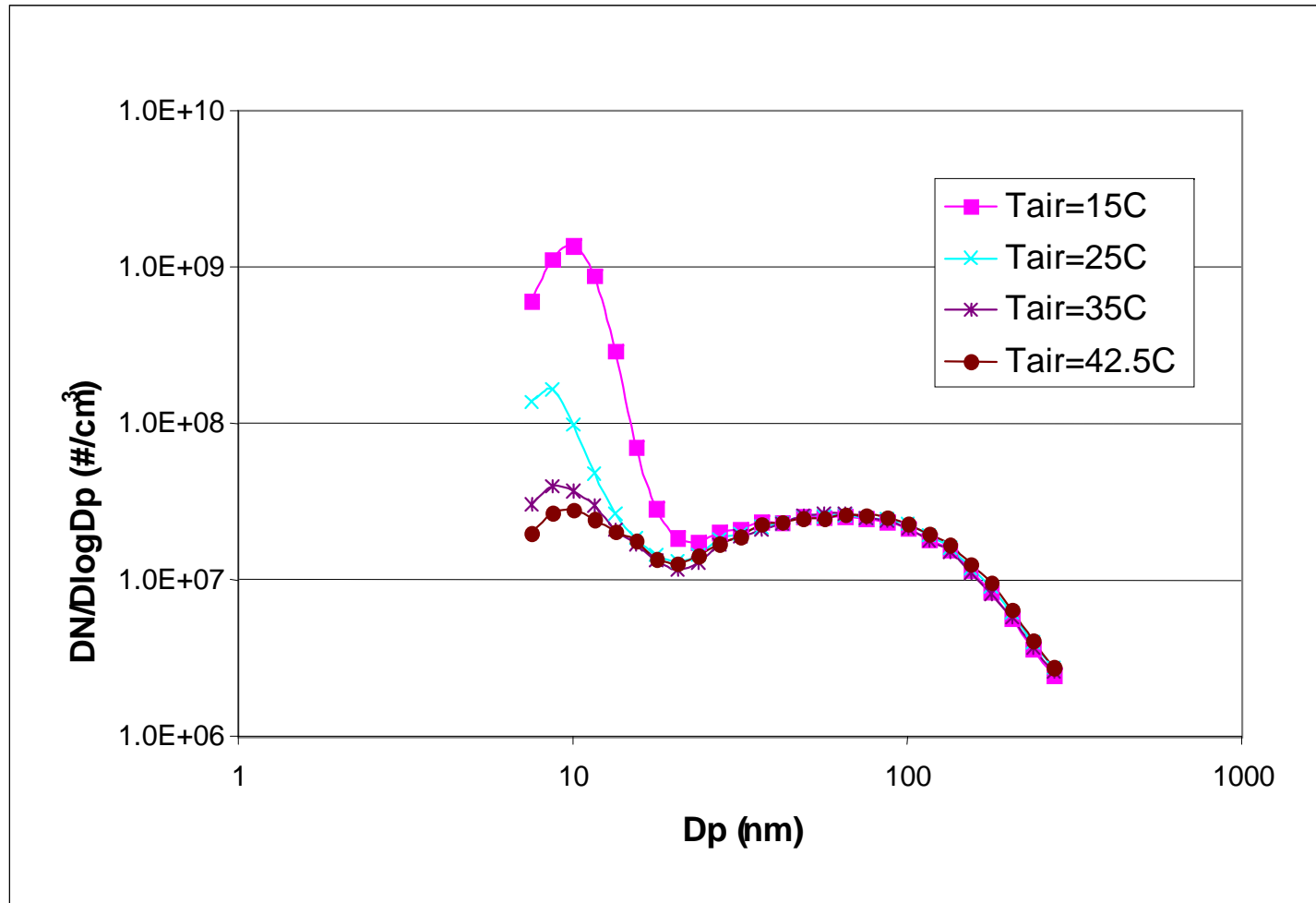


Figure 2.1. Schematic of aerosol sources, transformation mechanisms and sinks (modified after Whitby and Sverdrup (1980)).

Aerosol Size Distribution

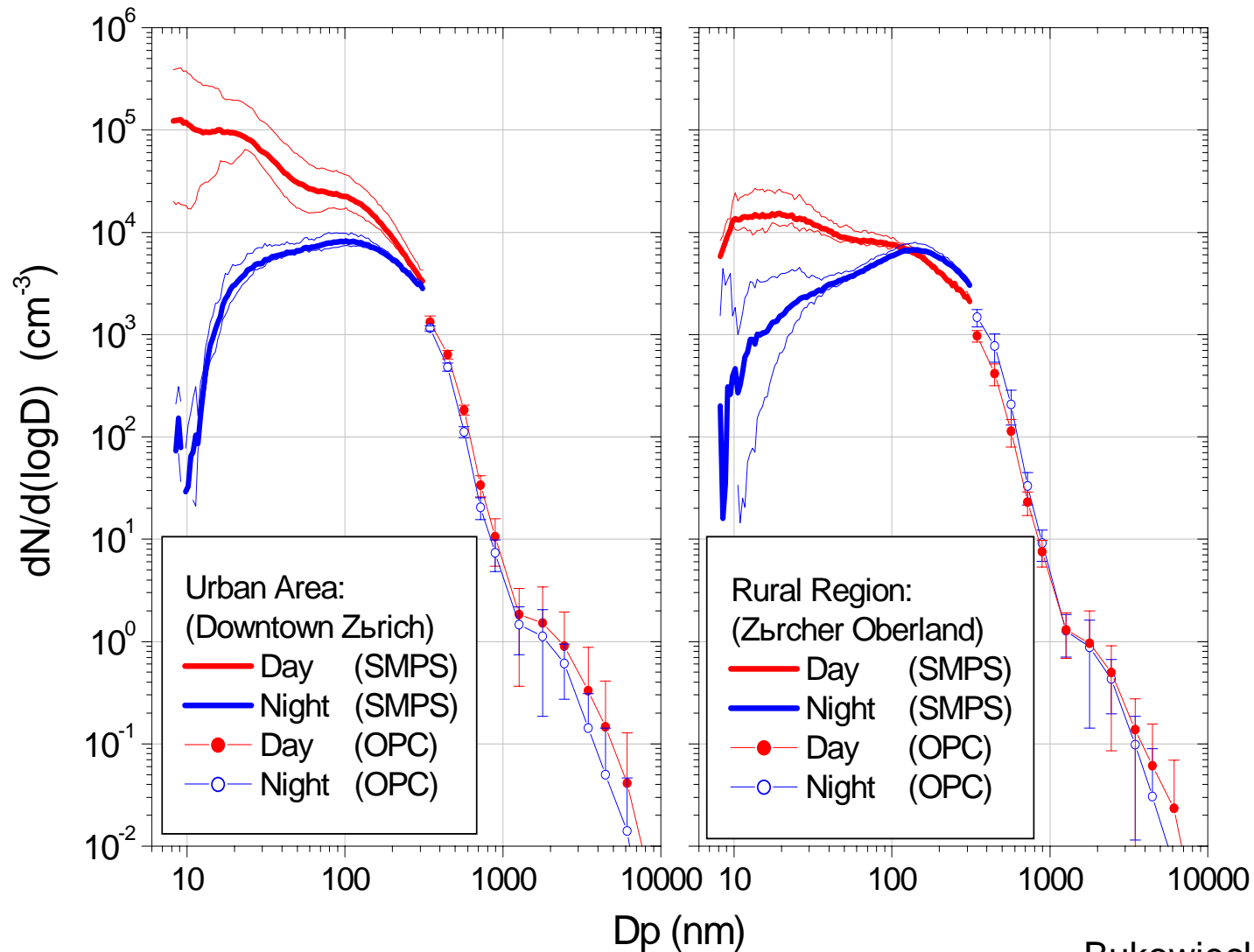


Traffic emissions: Influence of dilution temperature

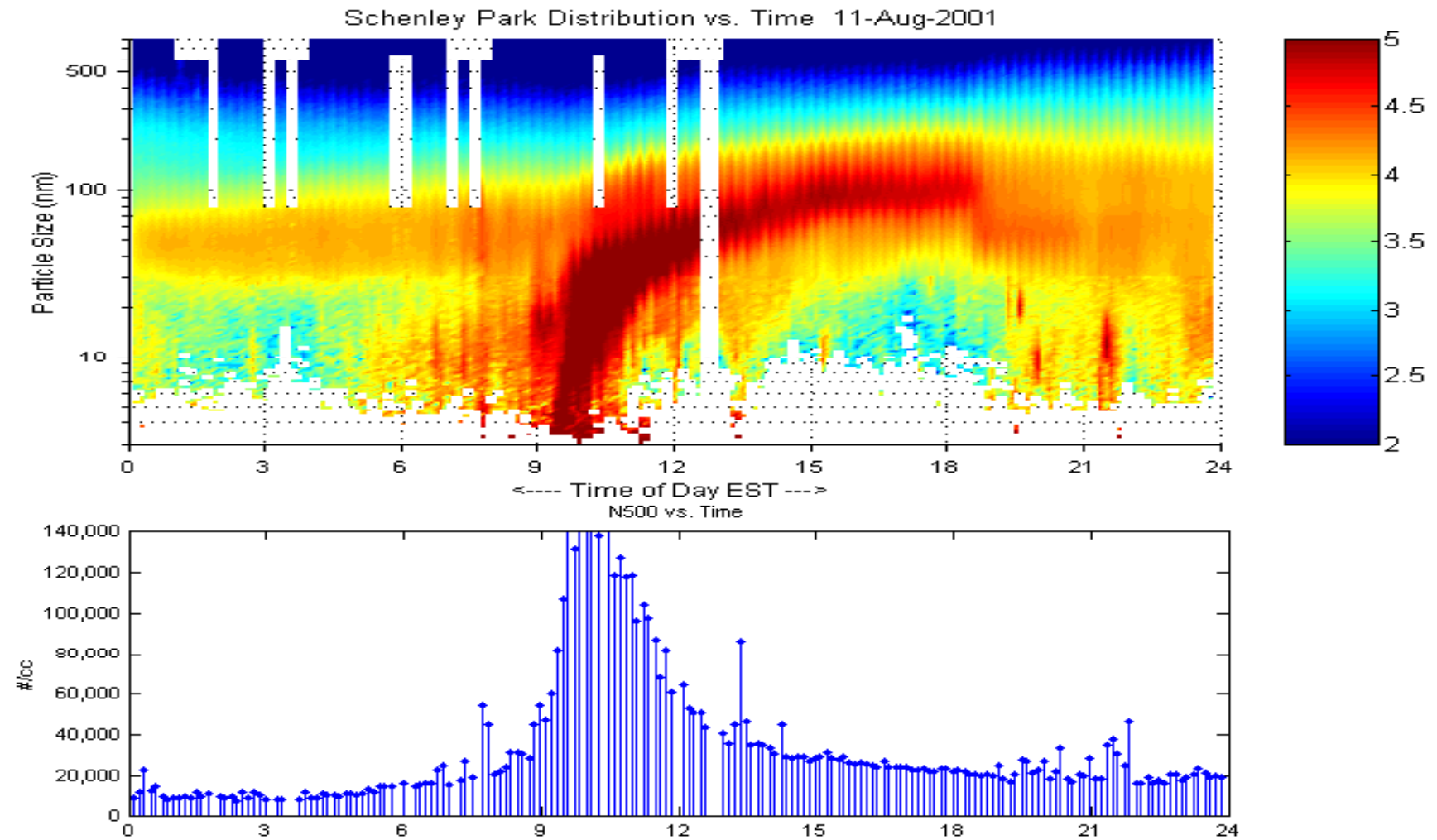


Size distribution in and around Zürich (day, night):

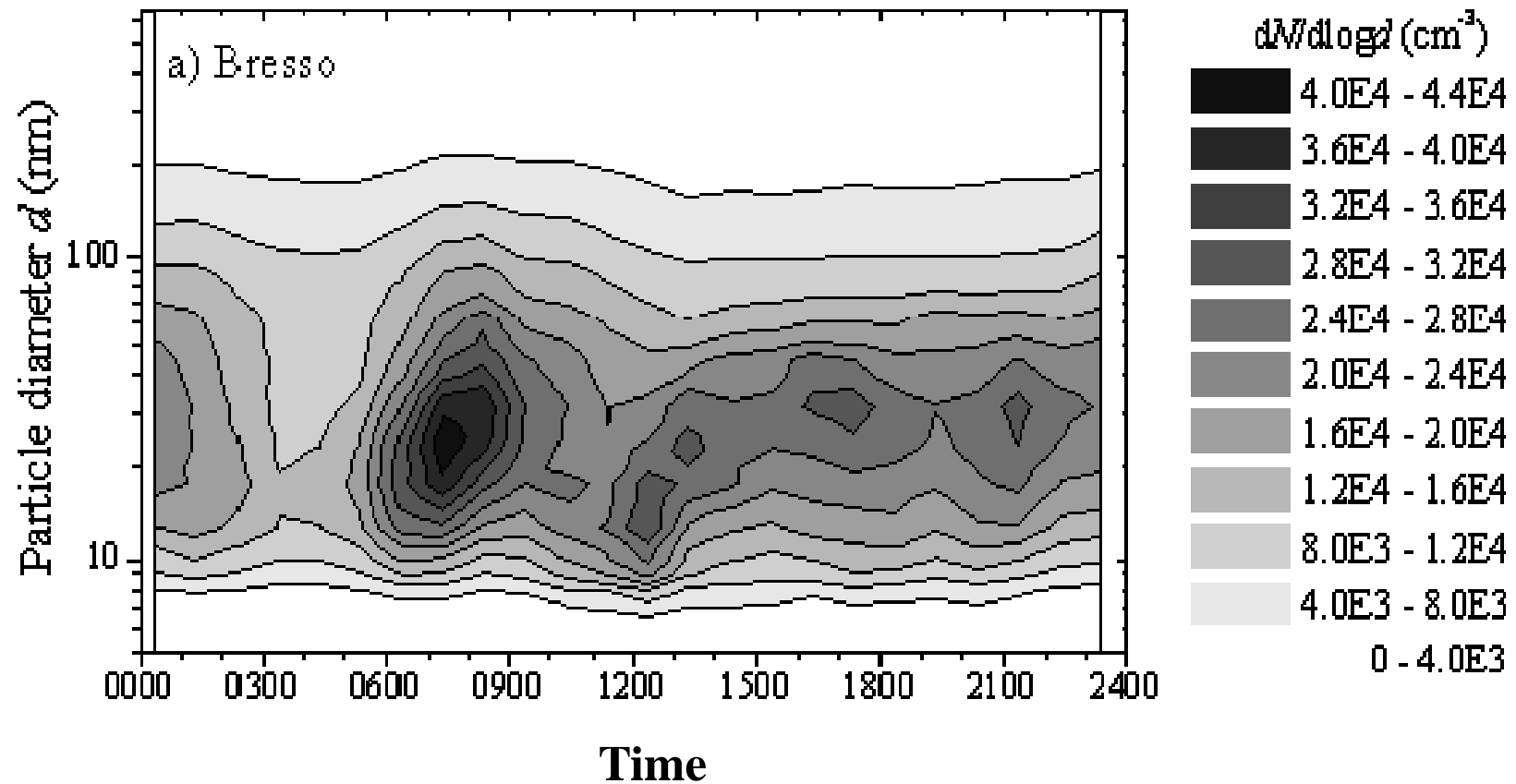
smallest particles are 10 times more abundant in the city compared to the country side and 100 times more abundant during the day than in the night



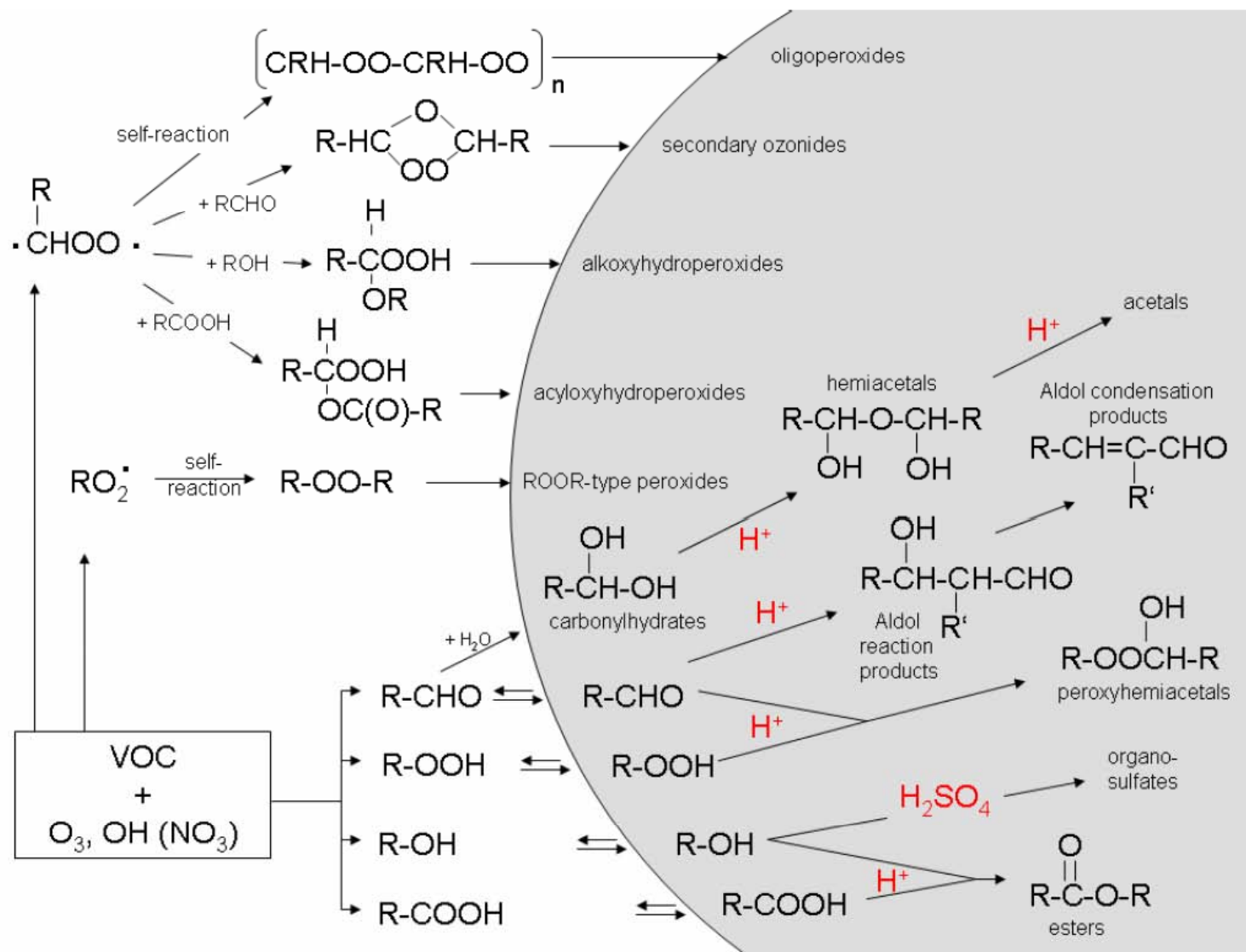
Nucleation and Growth in Pittsburgh (August 11, 2001)



Size distributions in Milan: Evidence for primary and secondary particle formation



Secondary organic aerosol production



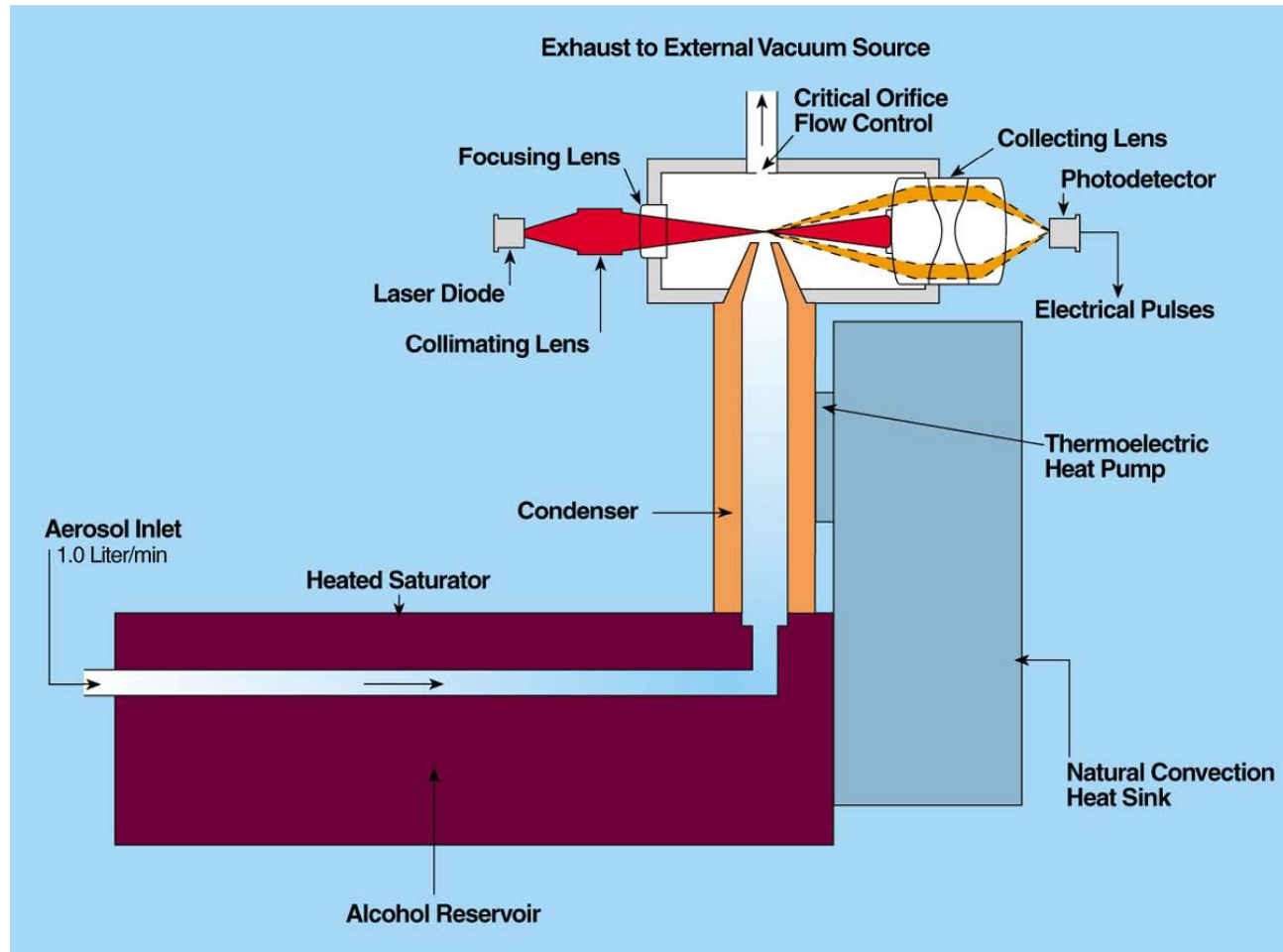
Terminology: Primary versus secondary

- **Primary particles: directly emitted to the atmosphere**
- **Secondary particles: formed in the atmosphere by condensation (nucleation and growth)
after chemical transformation**
- **How about oxidized primary particles ?
→ aged primary (not secondary as Fuzzi et al. 2006 suggested)**
- **How about primary particles that evaporate on dilution and condense after oxidation (Robinson et al., 2007) ?
→ secondary**

Measurement Techniques

- Number
- Number size distribution
- Mass
- Optical properties
- Aerosol composition (off-line / on-line)

Condensation Particle Counter (CPC)

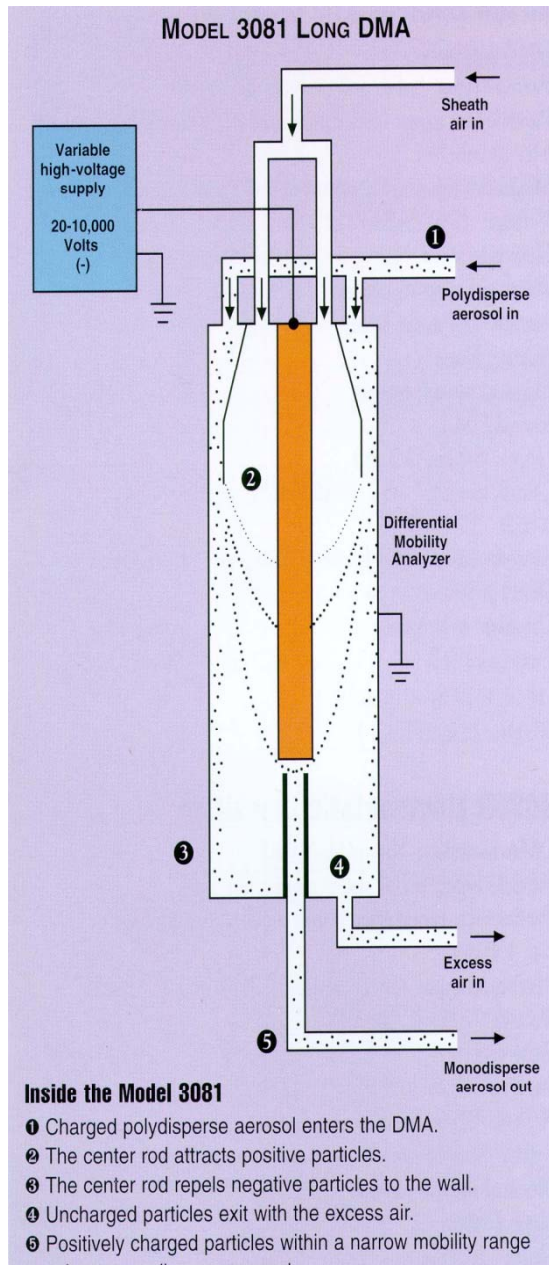


Example: TSI CPC 3010

Lowest detectable diameter: $D = 10 \text{ nm}$

Maximum particle concentration: 10^4 cm^{-3}

Measuring the electrical mobility with a Differential Mobility Analyzers (DMA)



Measurable sizes: $D=3-150$ nm or $20-900$ nm
A scan is possible within 60-300 seconds

Principle:

- Defined electrical charging of the particles with radiocative source
- The aerosol flows laminarily through cylindric condensator
- An electrical field force the particles depending on their electrical mobility to move toward the inner electrode.
- Particles of a specific mobility ($b=v_p/E$) are sucked through a gap at the inner electrode and are detected (typically by a CPC) afterwards.

$$b_{mech} = \frac{\ln(r_{out}/r_{in})}{2\pi \cdot h} \cdot \frac{Q}{U \cdot ne} \quad b(D_p) = \frac{C_c(D_p)}{3\pi\eta \cdot D_p}$$

Q : total gas flow through DMA;

h, r_{in}, r_{out} : height, and inner and outer diameter of DMA cylinder;

U : applied voltage;

e : elementary charge, $1.602e-19$ As;

n : number of elementary charges on aerosol particle.

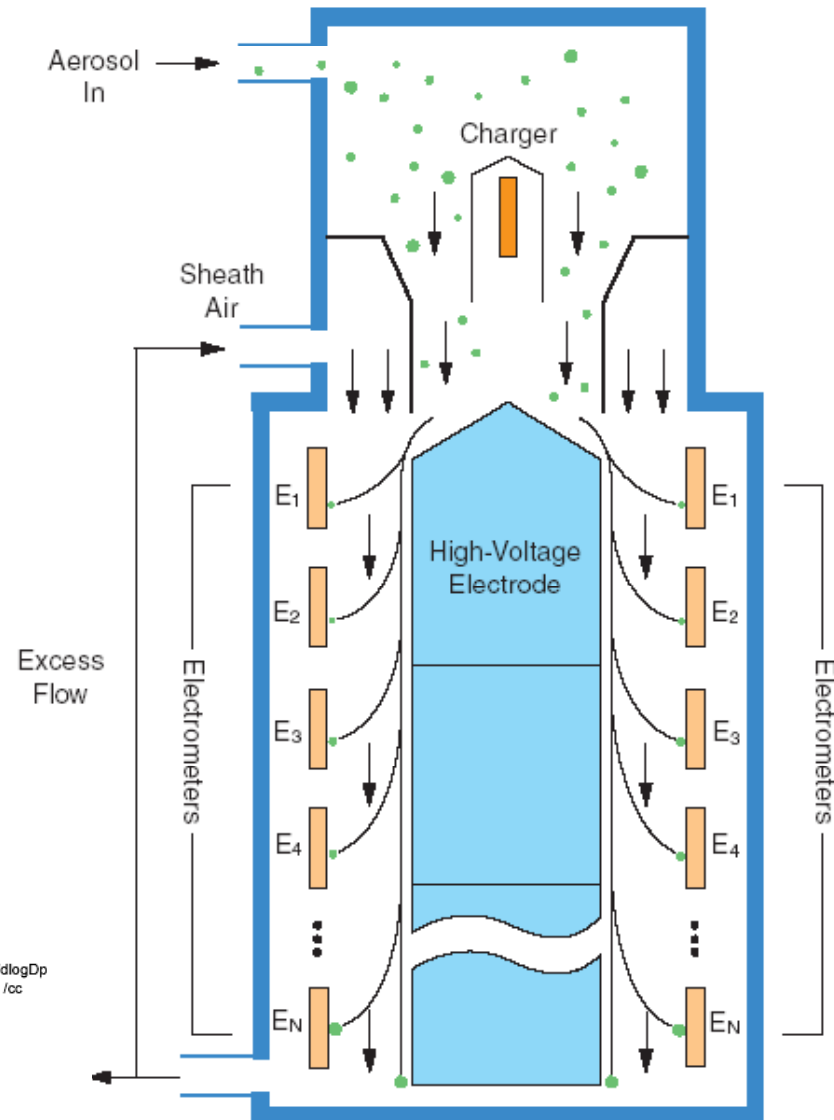
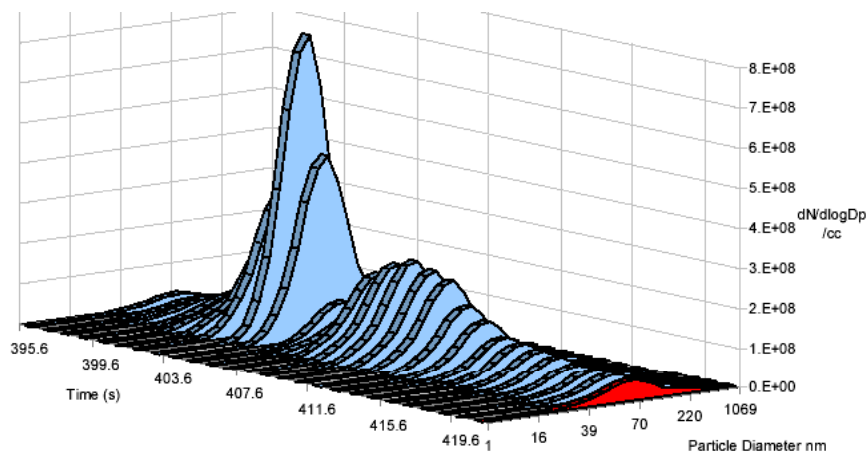
η : viscosity of gas, air $\sim 1.81e-5$ Ns/m²;

Fast Analyzers:

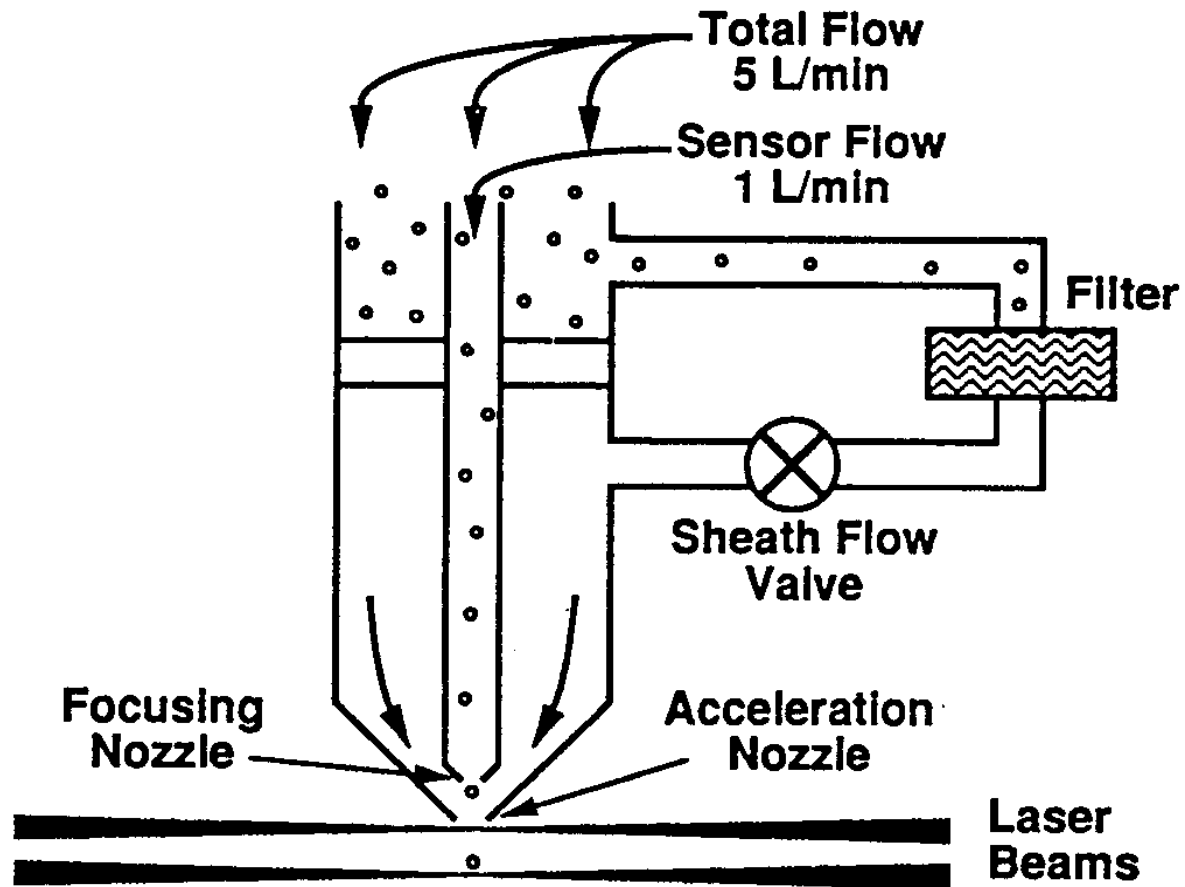
- EEPS Engine Exhaust Particle Spectrometer. Scan time typ. 2 sec.
- FPS Fast Particle Spectrometer (similar to EEPS)
- FMPS Fast Mobility Particle Sizer (ambient air version of EEPS)

Engine Exhaust Particle Sizer Spectrometer (EEPS, TSI)

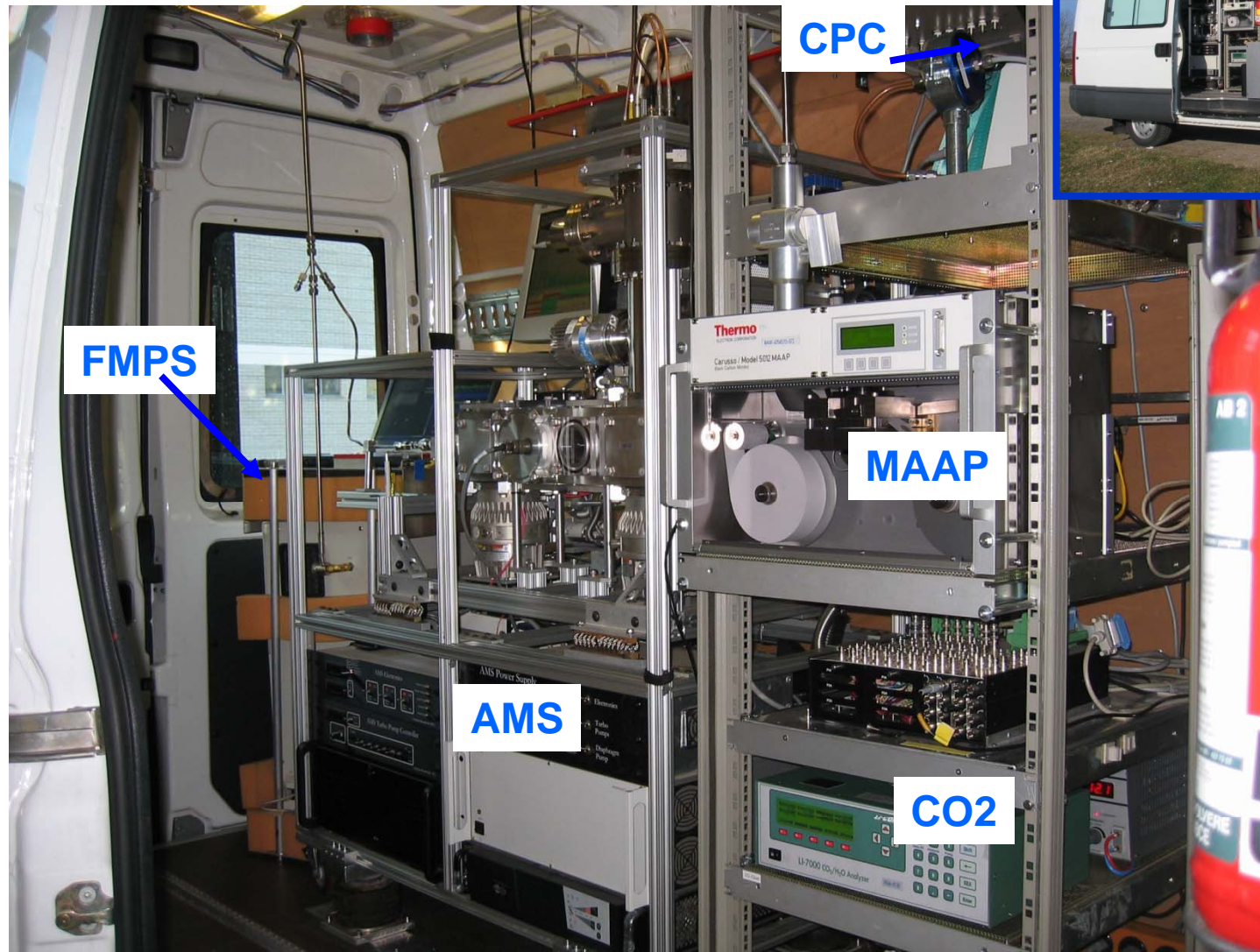
Fast Particle Spectrometer (DMS500, Cambustion)



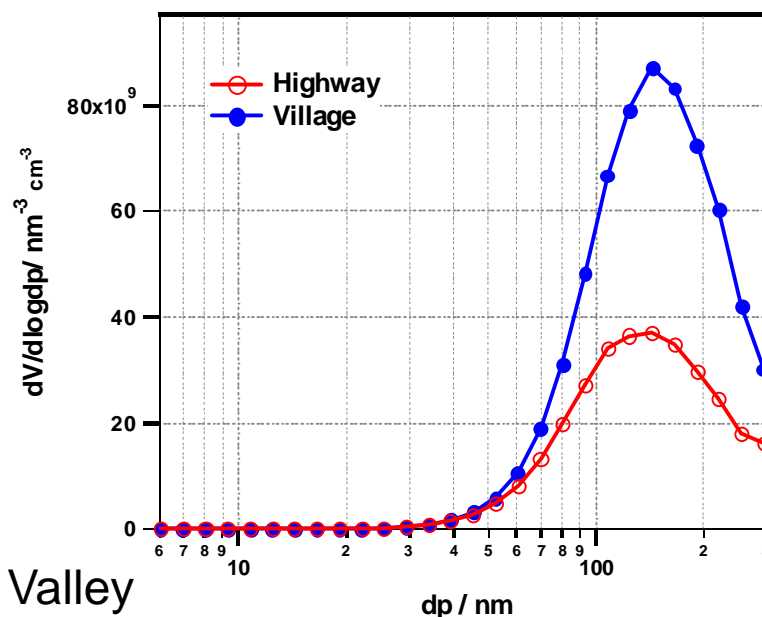
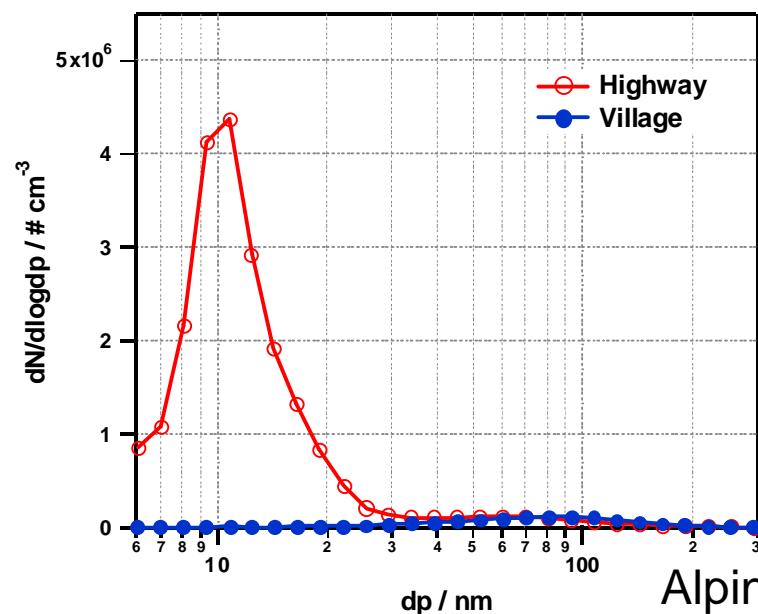
Aerodynamic particle sizer



The PSI mobile laboratory



Aerosol size distribution (5.6-560 nm) in an Alpine valley



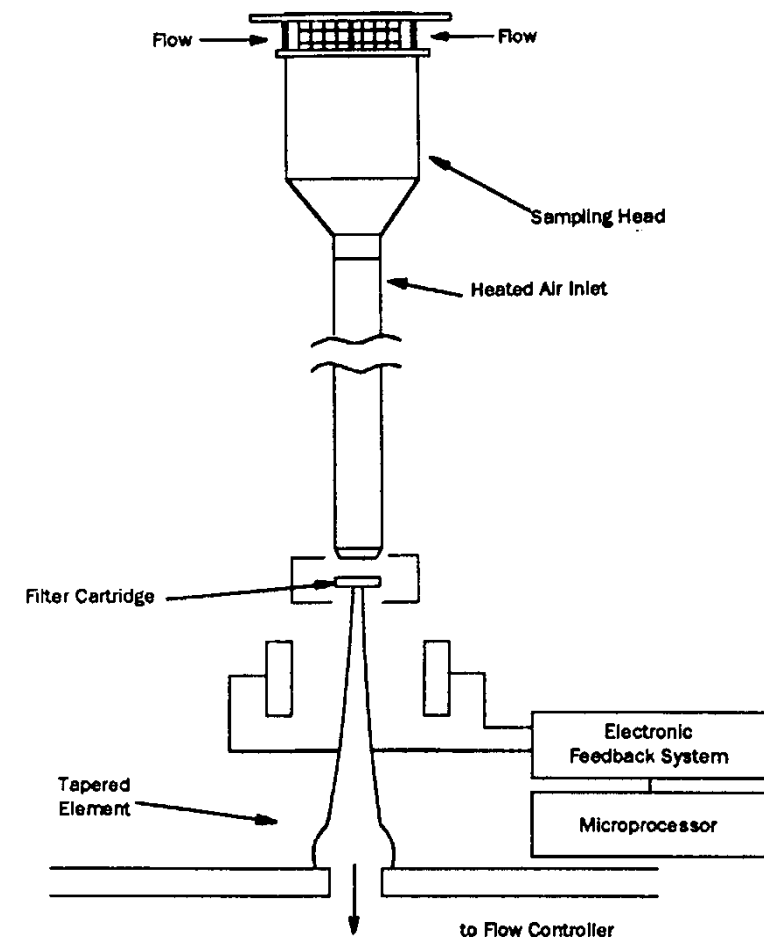
Alpine Valley
Riviera 2005 Winter

- **Consistent picture : Nanoparticle concentrations <30 nanometers very high on highway**
- **In villages : much lower nanoparticle concentrations, in case of high wood burning contribution, higher volume concentration**

Particulate mass

- Filters and gravimetric analysis
- On-line : e.g. Betameters, TEOM

Tapered element oscillating
microbalance (TEOM)





Optical instruments e.g. light absorption by aethalometer

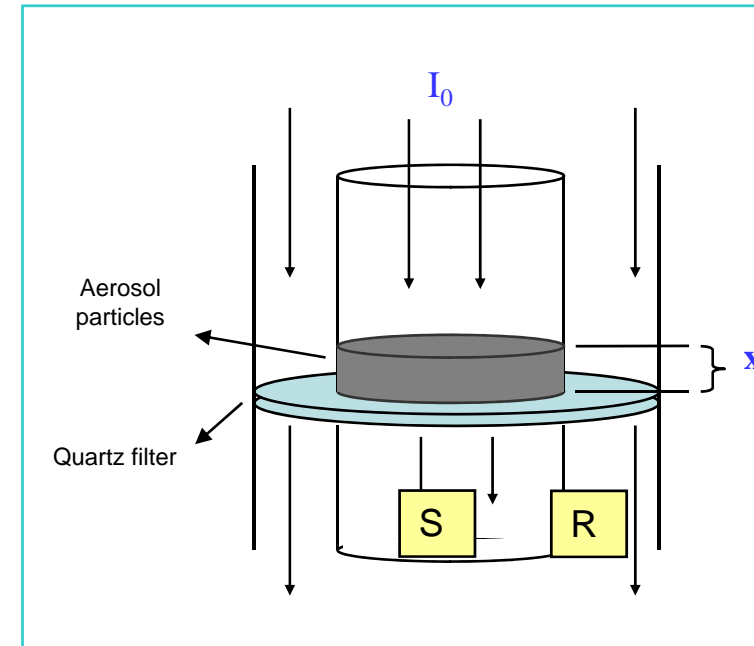


“Lambert-Beer’s Law” $I = I_0 e^{-b_{abs} \cdot x}$

“Optical attenuation” $ATN = 100 \times \ln\left(\frac{I_0}{I}\right) = 100 \times \ln\left(\frac{I_r}{I_s}\right)$

For the time interval $\Delta t = t_2 - t_1$:

$$\Delta ATN = \ln\left(\frac{I_r(t_2)}{I_s(t_2)}\right) - \ln\left(\frac{I_r(t_1)}{I_s(t_1)}\right)$$



The attenuation coefficient (filtered aerosol)

The absorption coefficient (airborne aerosol)

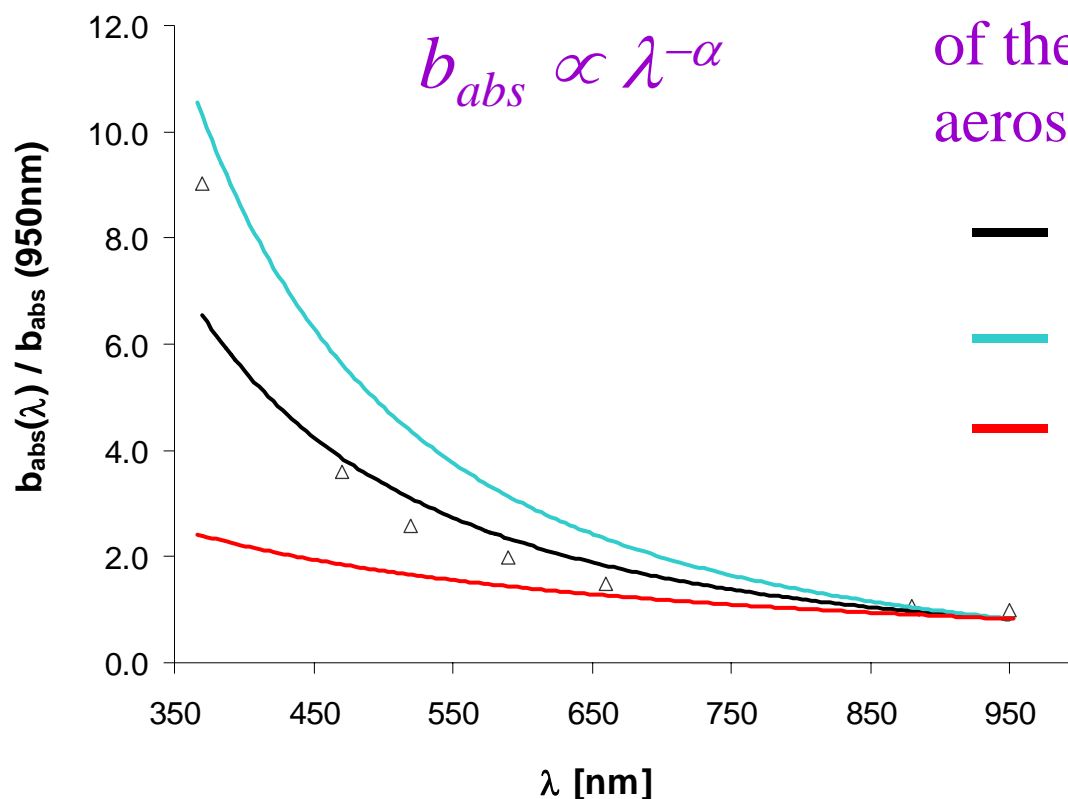
$$b_{ATN} = \frac{A}{Q} \frac{\Delta ATN}{\Delta t}$$

—————>
Correction needed, e.g.

b_{abs}

- Weingartner et al., 2003
- Arnott et al., 2005

Absorption exponent α : a measure of the spectral variation in aerosol light absorption



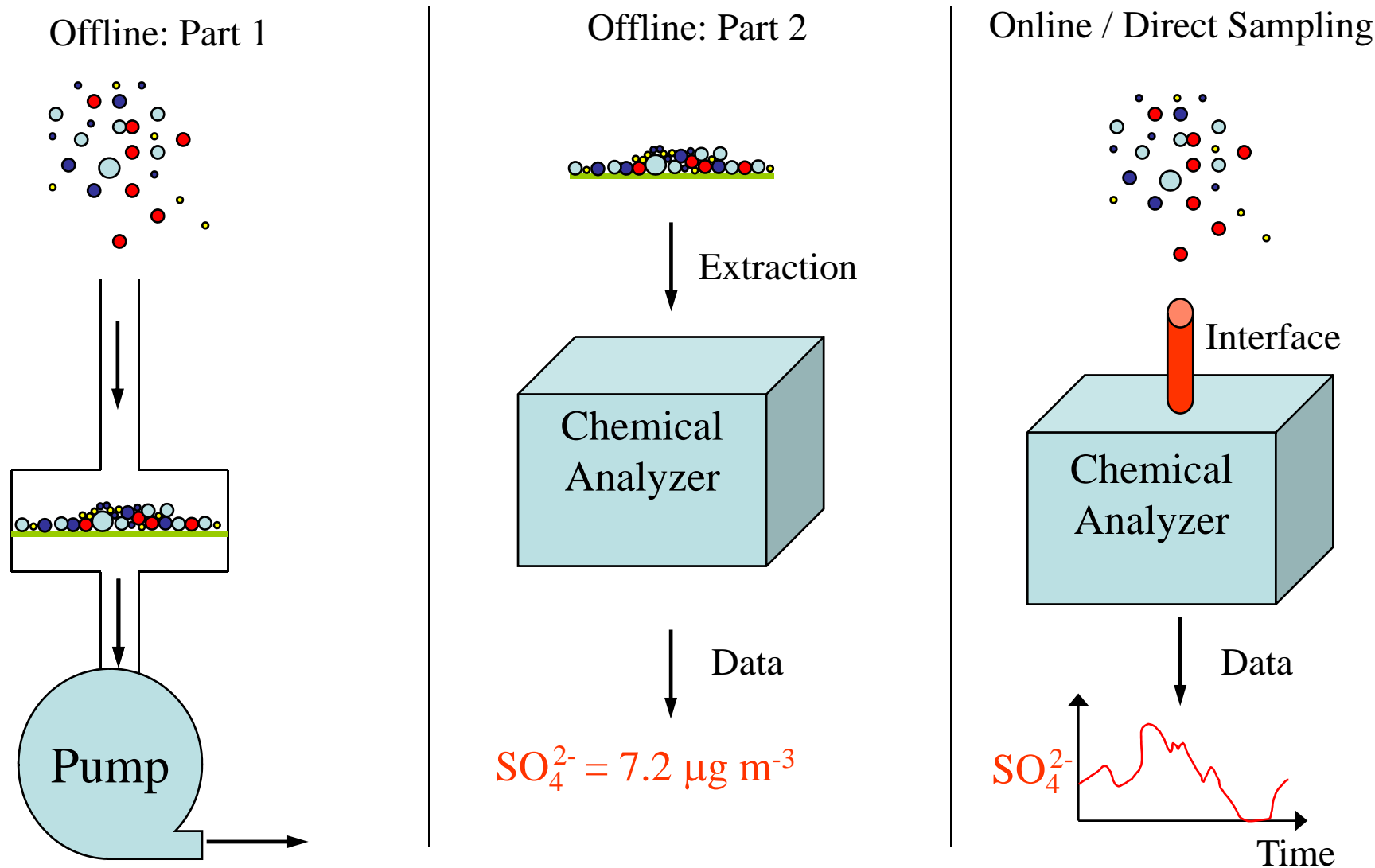
- Example power law fit ($\lambda^{-2.0}$)
- Wood burning^a $\lambda^{-1.8 \text{ to } -2.2}$
- Traffic, diesel soot^{a,b} $\lambda^{-1.0 \text{ to } -1.1}$

^a Kirchstetter *et al.* 2004

^b Schnaiter *et al.* 2003 & 2005

Enhanced UV-absorption due to the presence of wood smoke

Aerosol Chemical Analysis



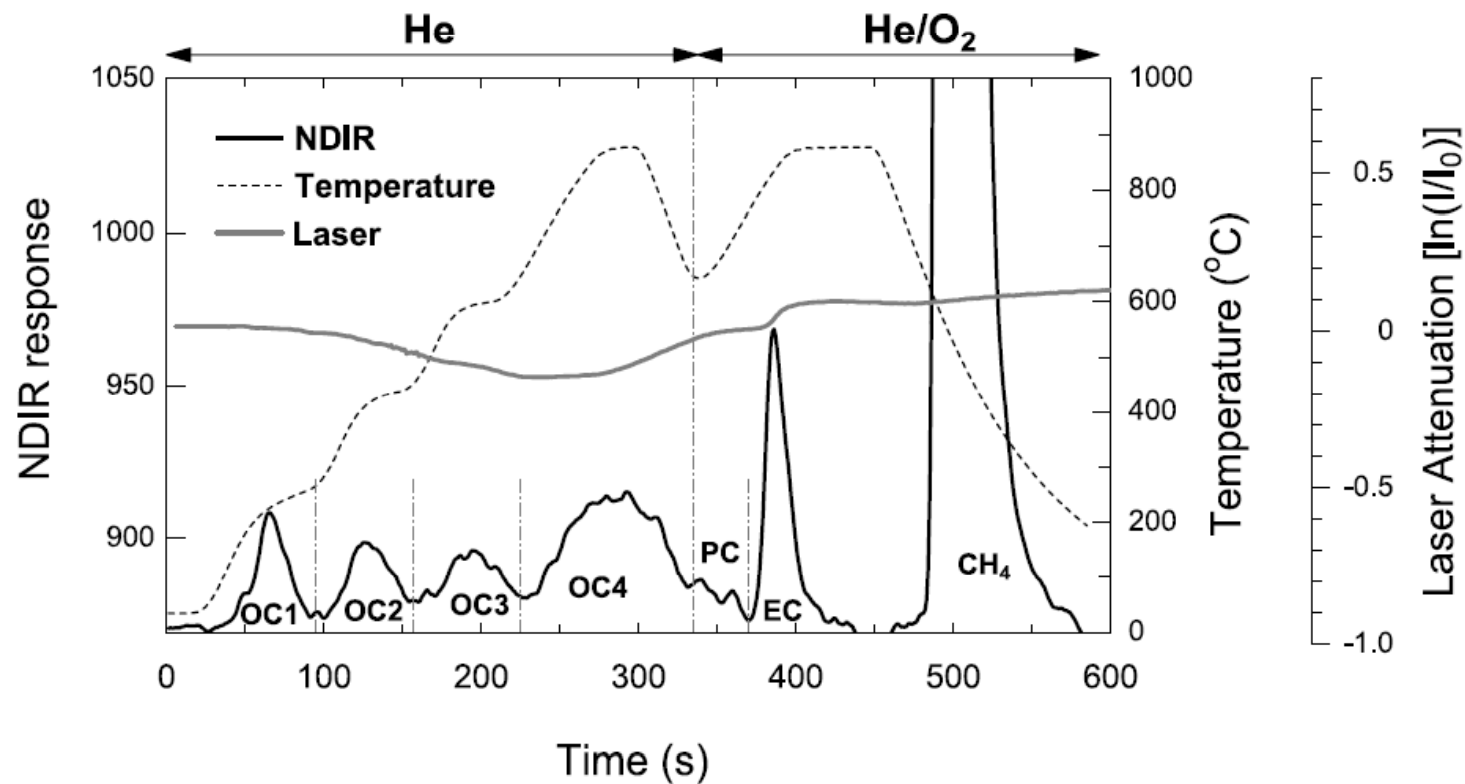
Slide courtesy of Jose-Luis Jimenez

Examples of off-line analysis

- Ion chromatography (NH_4 , NO_3 , SO_4 , organic acids)
- X-ray fluorescence, Particle Induced x-ray emission (PIXE), Inter Coupled Plasma mass spectrometry (ICP-MS), Neutron activation, Atomic Absorption Spectroscopy (AAS) (elemental analysis: K, S, Pb, Zn, ..)
- GC- / LC-MS (organic compounds: e.g. marker compounds hopanes, levoglucosan,)
- IR / UV / proton-NMR- spectroscopy : functional groups
- Mass spectrometry in general : isotope analysis, oligomers and more

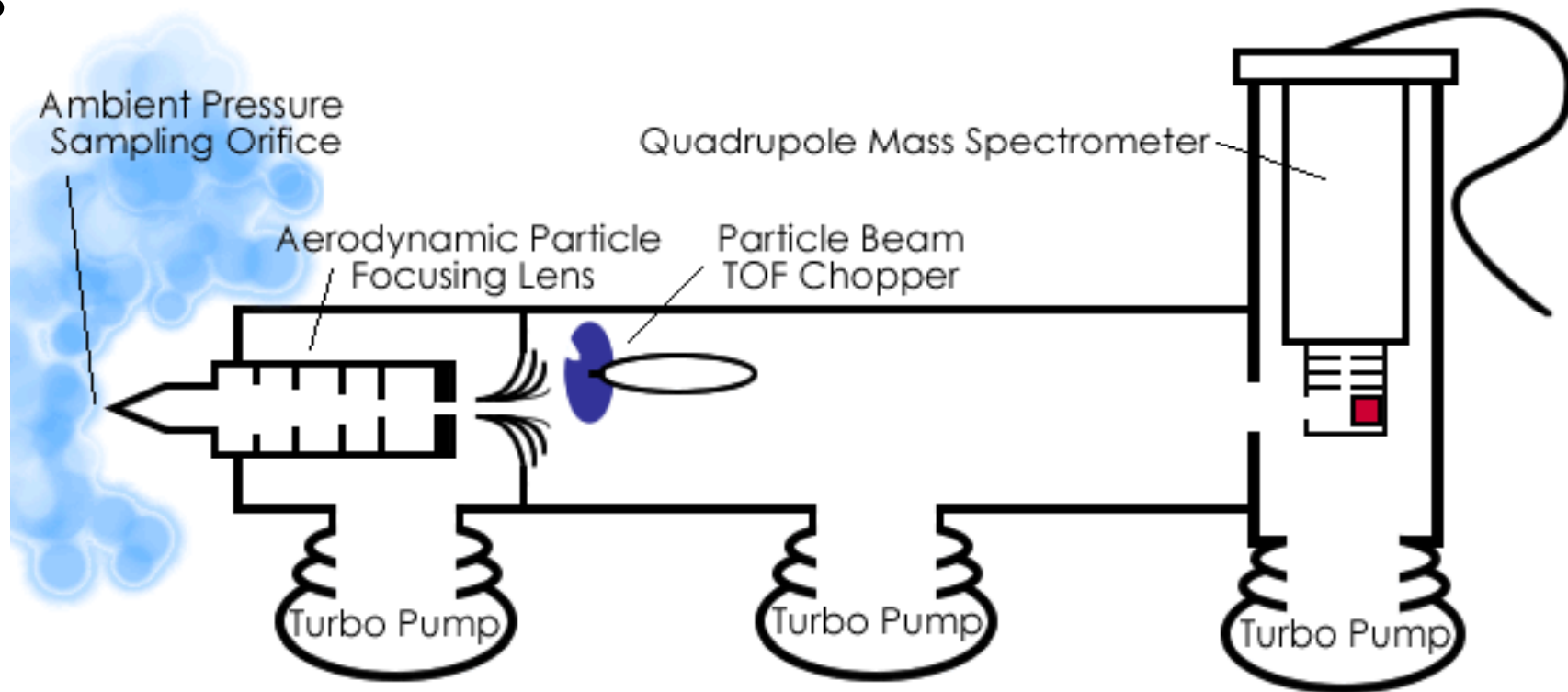
On-Line Analysis

- Semi-online: EC-OC (separation of black/elemental carbon from organic carbon)

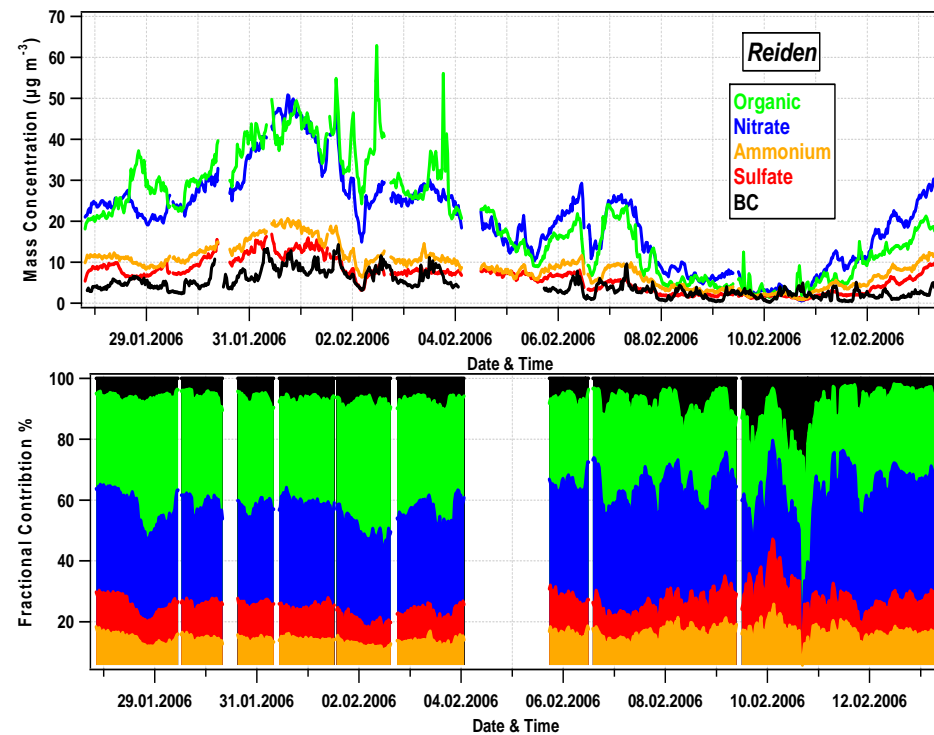
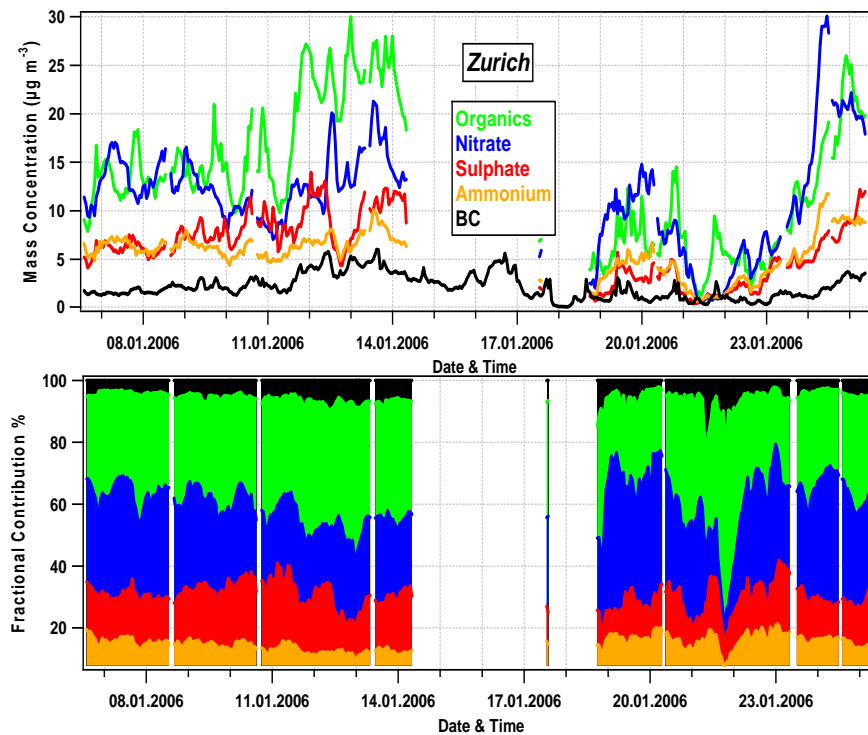


On-line analysis

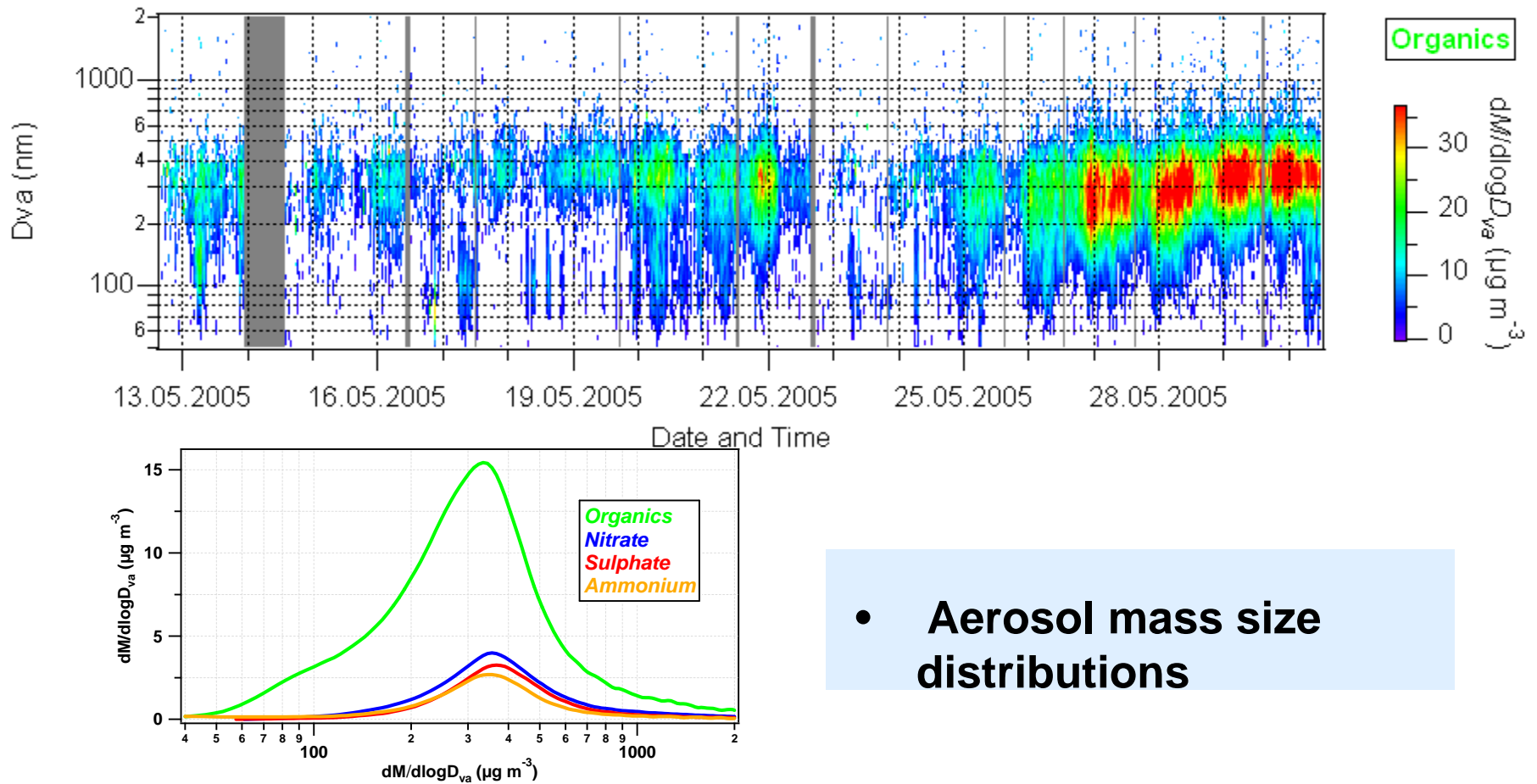
- ATOF-MS
- Aerodyne Aerosol mass spectrometer
-



Example of Aerosol mass spectrometer measurements together with some black carbon measurements by an Aethalometer

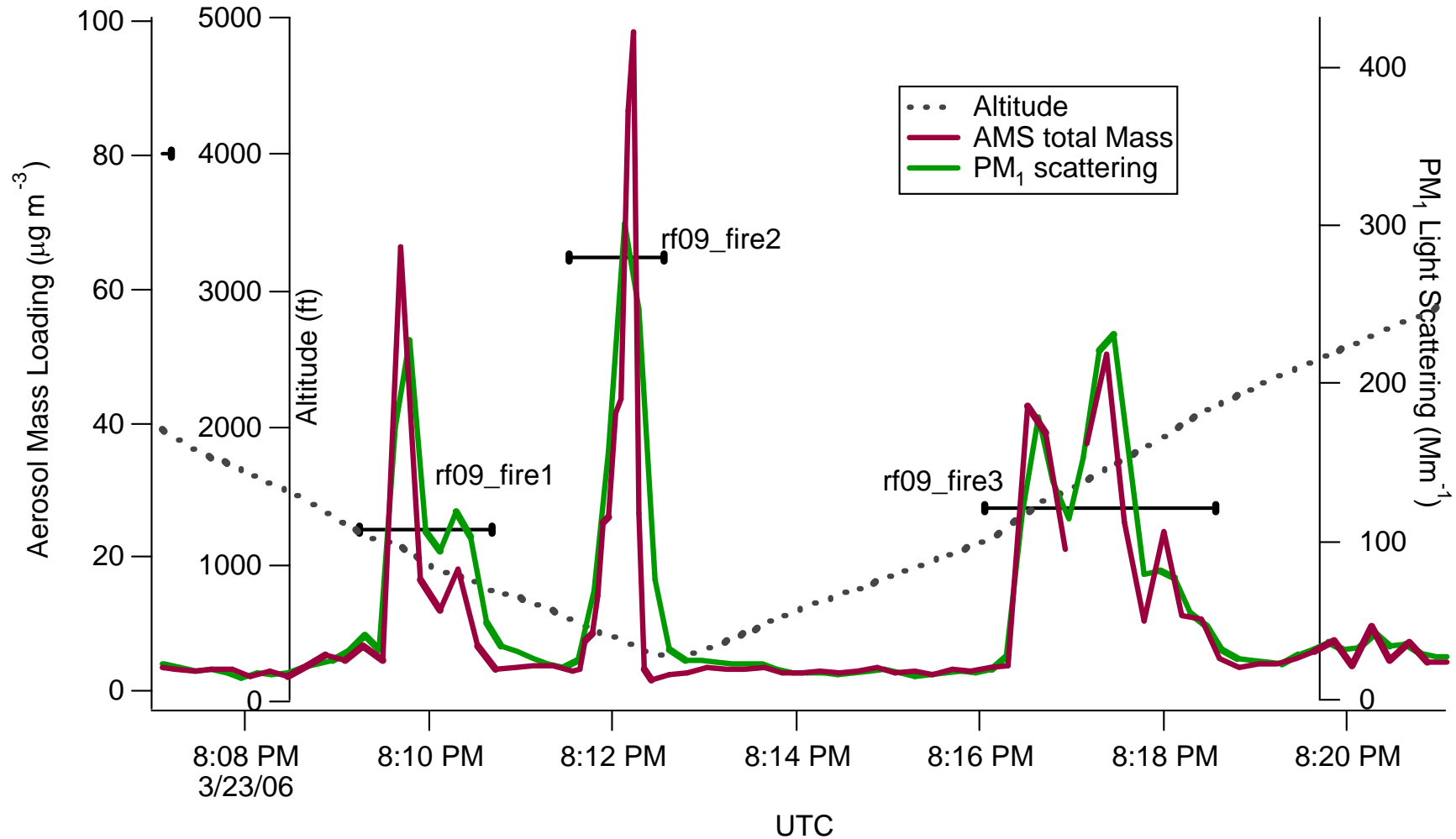


Time resolution: minutes down to 6 seconds at low detection limits

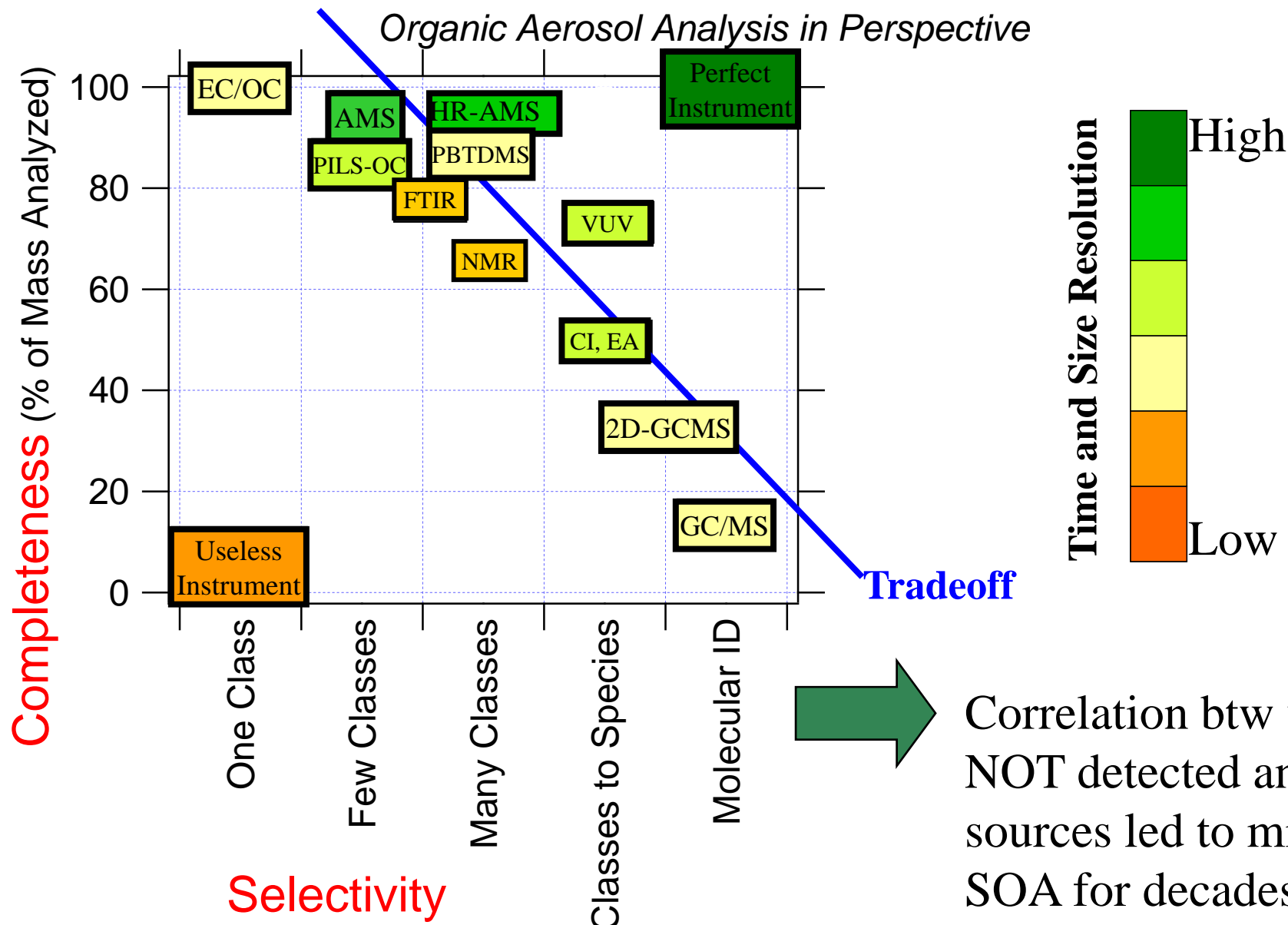


- **Aerosol mass size distributions**

Time Resolution Example - Fire Plumes from aircraft

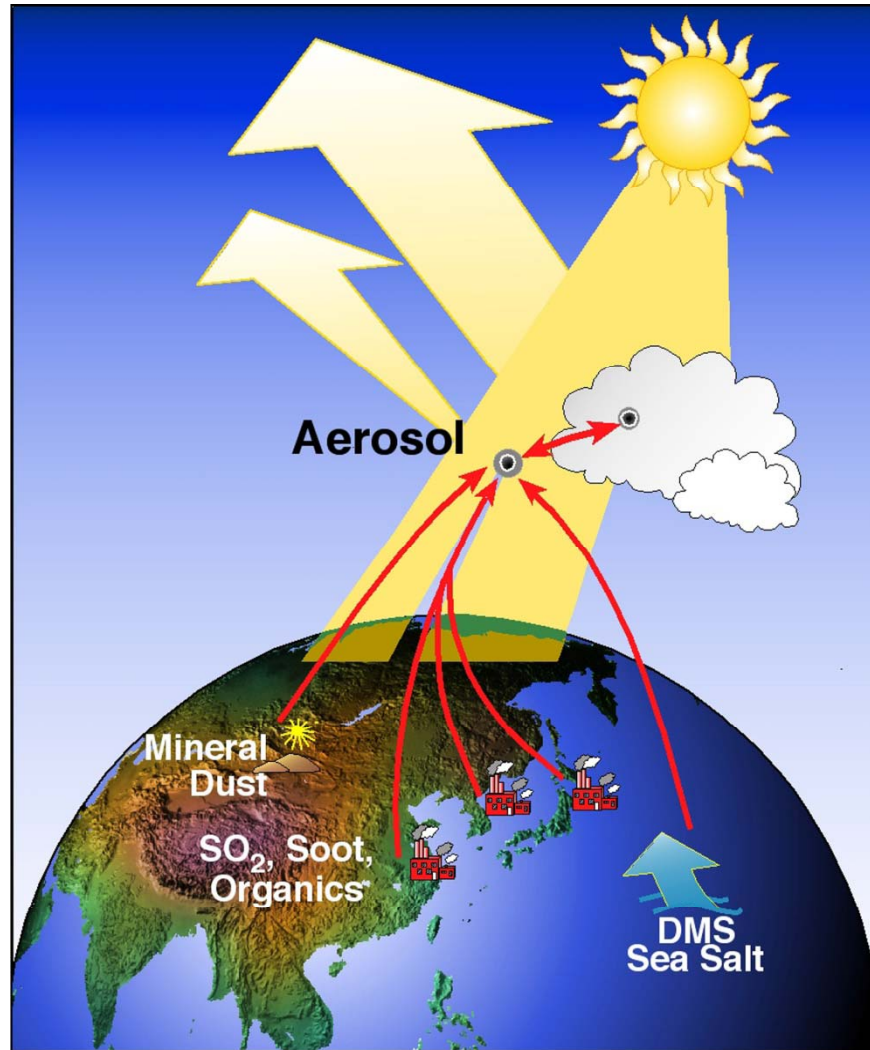


3 Fires in the Yucatan Peninsula - MILAGRO field campaign



Slide courtesy of Jose-Luis Jimenez

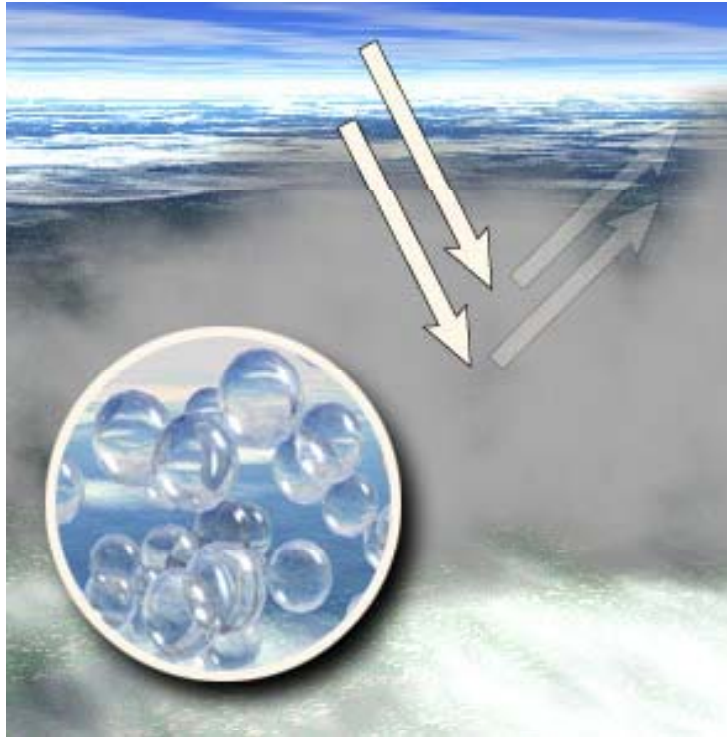
Direct and indirect aerosol effect on climate



Direct effect:
Scattering and absorption of incoming sunlight by aerosol particles

Indirect effect:
The number concentration of cloud condensation nuclei (CCN) influences the cloud droplet size and thereby changes the cloud albedo and lifetime

Indirect aerosol effect



Large droplets
→ Weak reflection

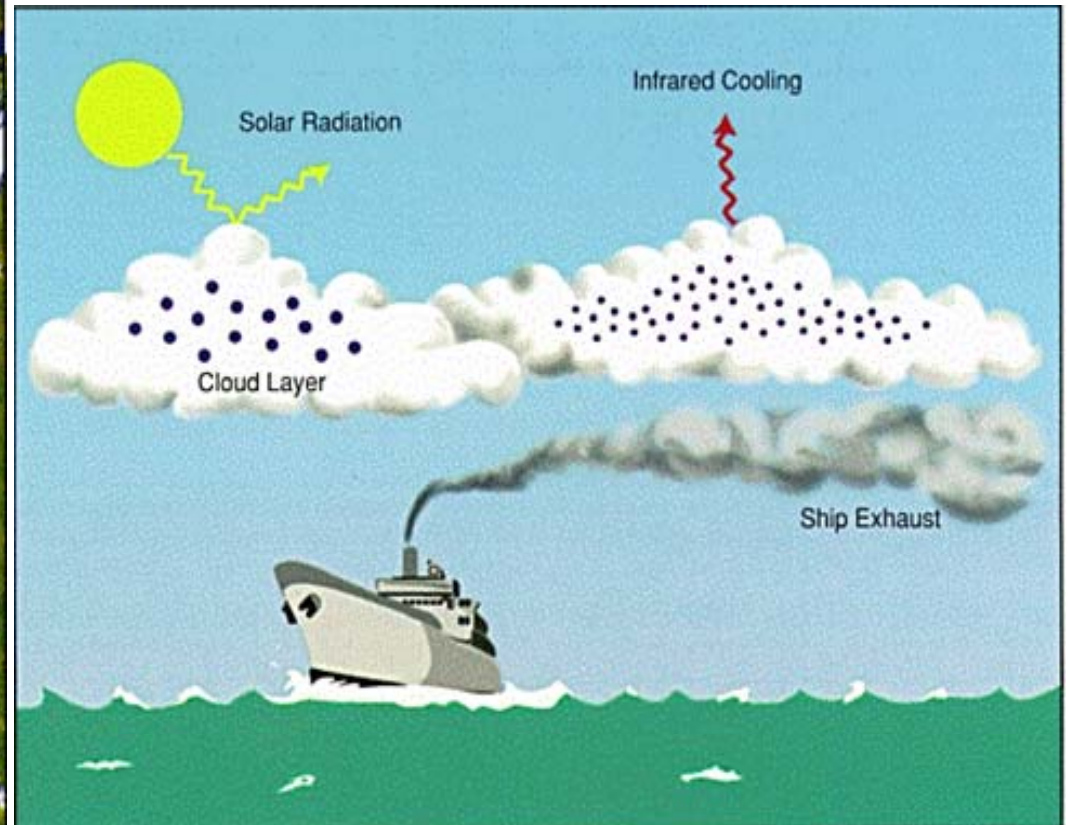
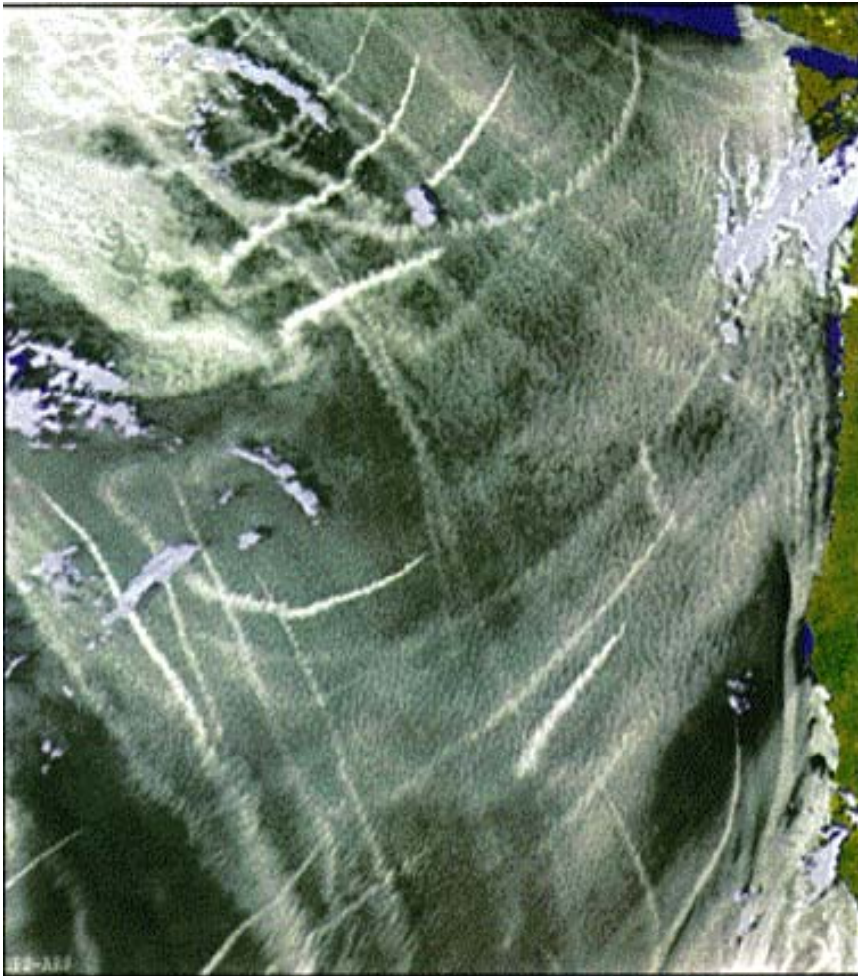


Small droplets
→ Strong reflection

Indirect effect

Number of CCN influences the droplet number and size (Twomey-Effect) and thereby the cloud albedo and lifetime.

'Ship tracks' visualise the indirect effect



Satellitenaufnahme (Wellenlänge: 3.7 μm)

Indirect aerosol effects

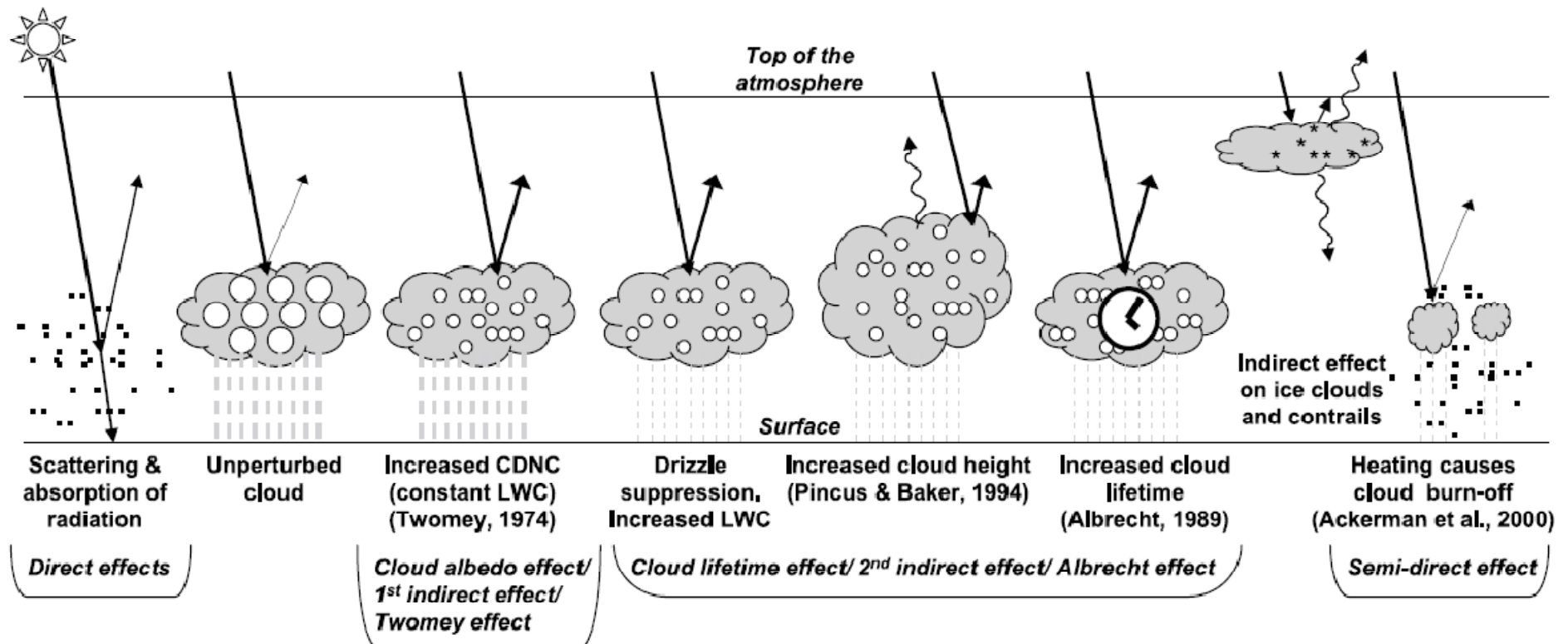
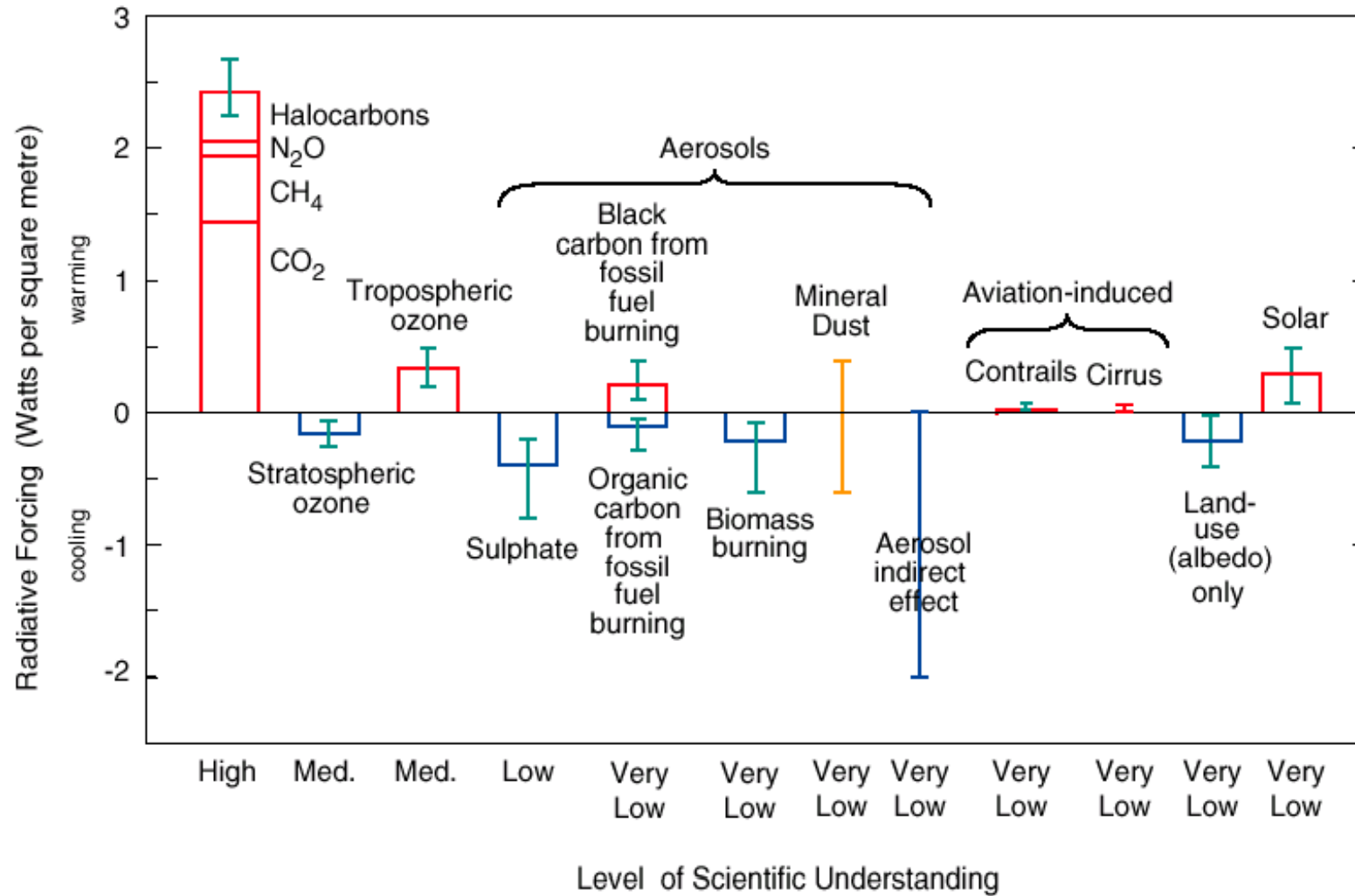
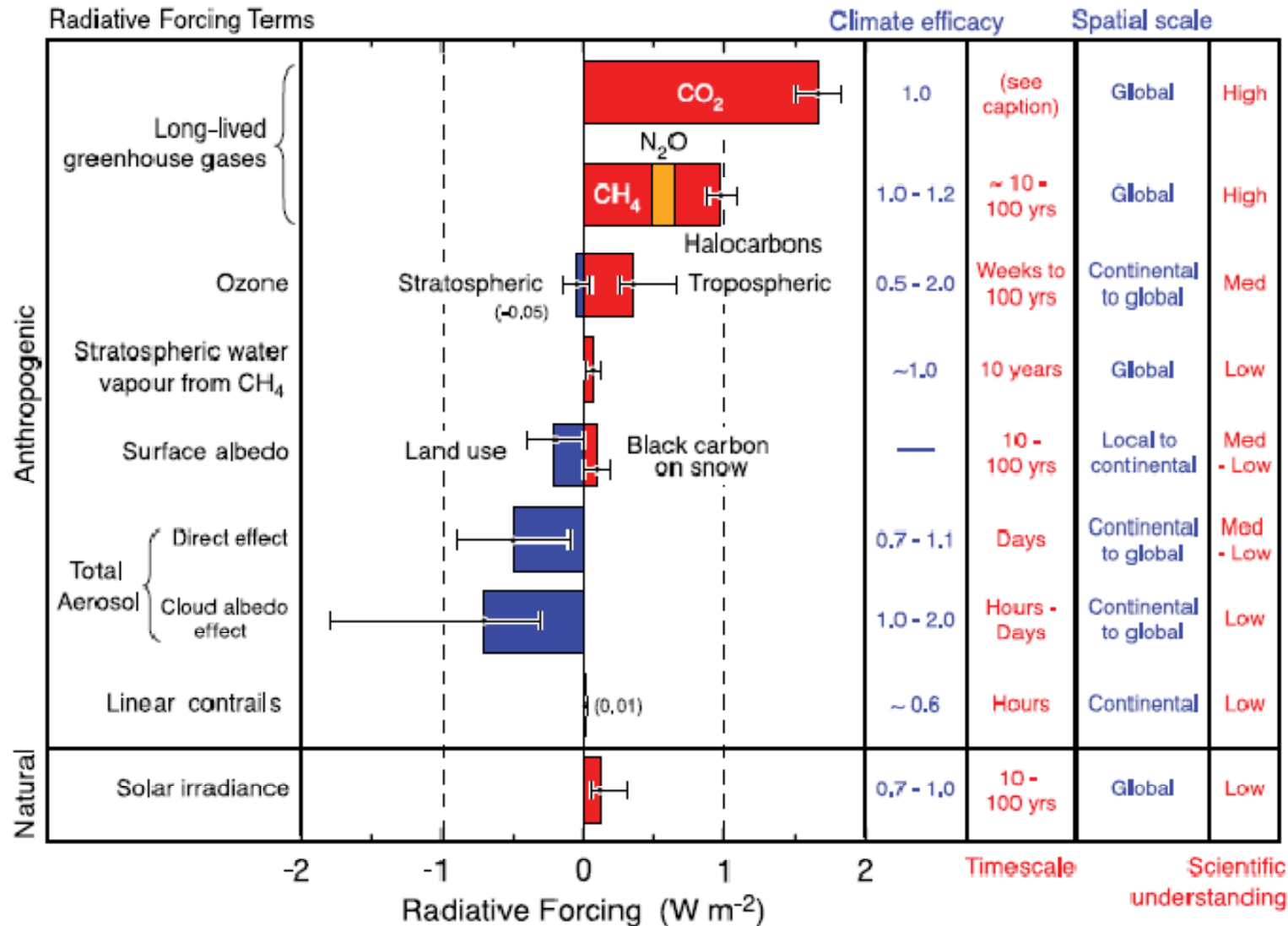


Figure 2.10. Schematic diagram showing the various radiative mechanisms associated with cloud effects that have been identified as significant in relation to aerosols (modified from Haywood and Boucher, 2000). The small black dots represent aerosol particles; the larger open circles cloud droplets. Straight lines represent the incident and reflected solar radiation, and wavy lines represent terrestrial radiation. The filled white circles indicate cloud droplet number concentration (CDNC). The unperturbed cloud contains larger cloud drops as only natural aerosols are available as cloud condensation nuclei, while the perturbed cloud contains a greater number of smaller cloud drops as both natural and anthropogenic aerosols are available as cloud condensation nuclei (CCN). The vertical grey dashes represent rainfall, and LWC refers to the liquid water content.

Climate forcing 2000 relative to 1750



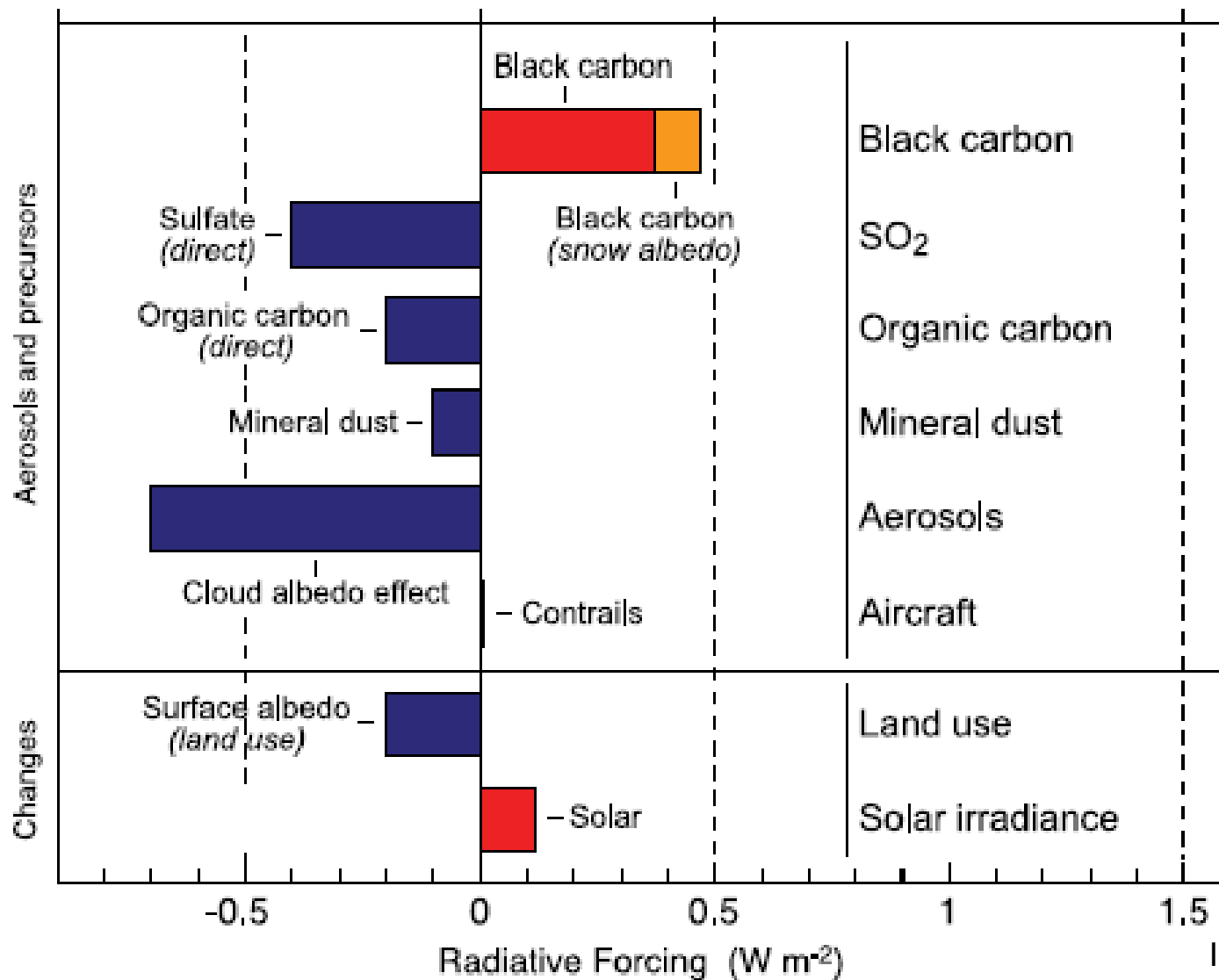
Radiative forcing of climate between 1750 and 2005



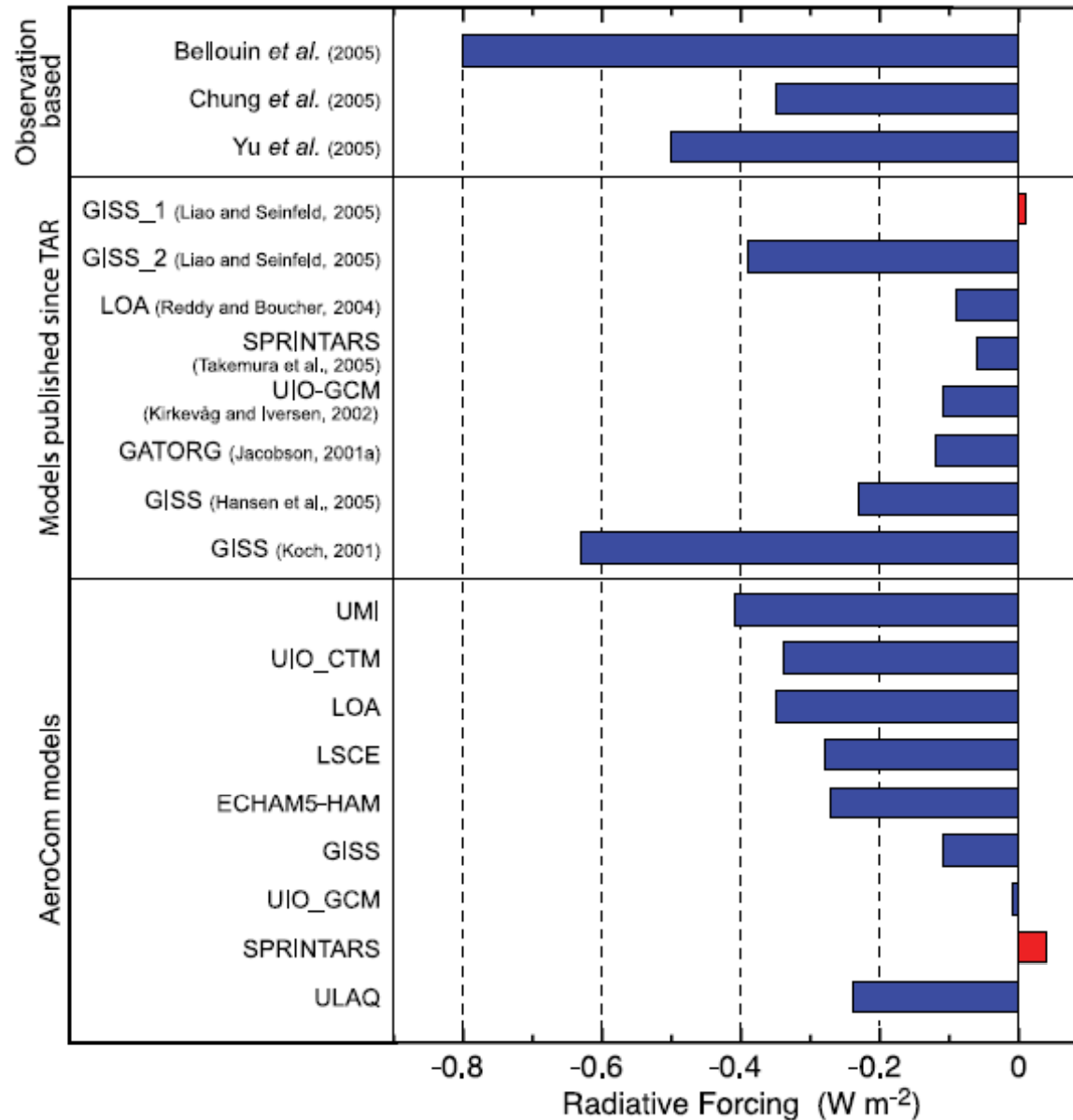
IPCC (2007)

No CO₂ time scale is given, as its removal from the atmosphere involves a range of processes that can span long time scales :

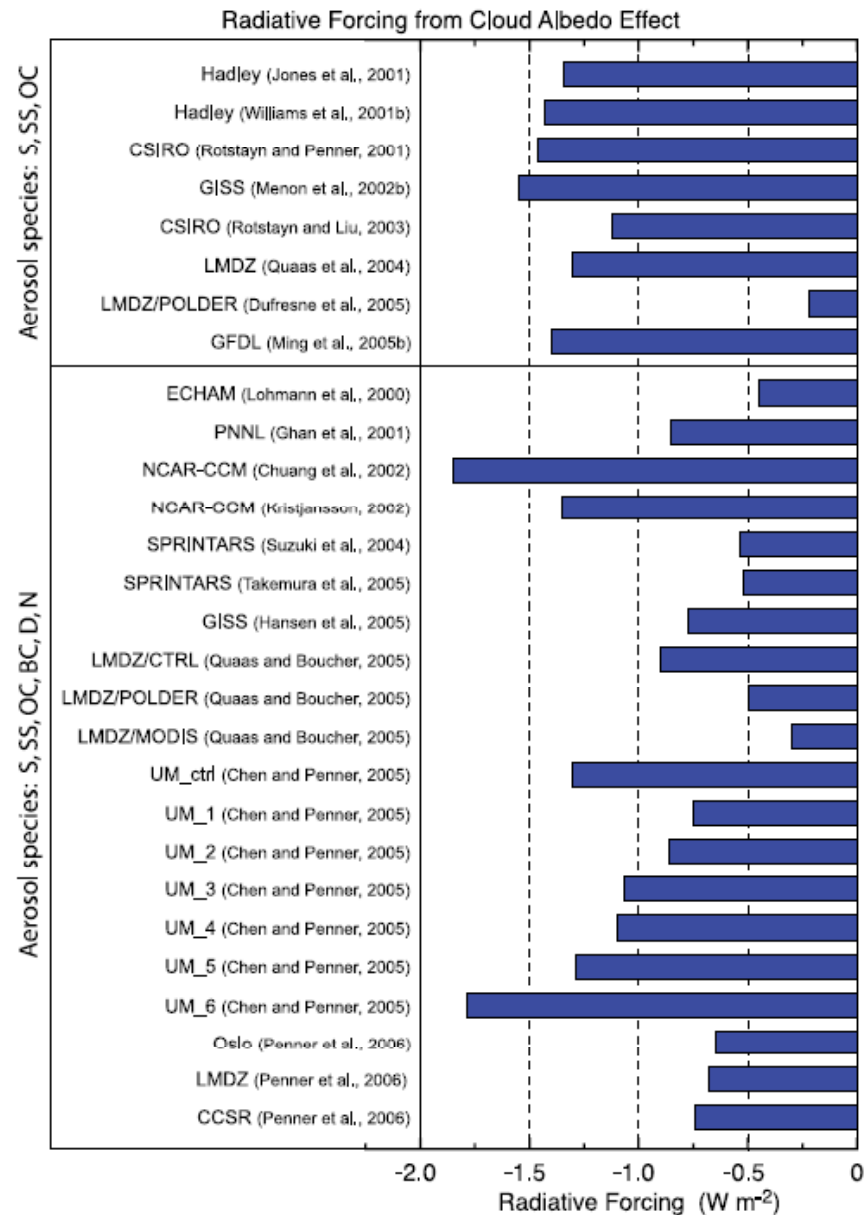
Radiative forcing of climate between 1750 and 2005 for different aerosol components



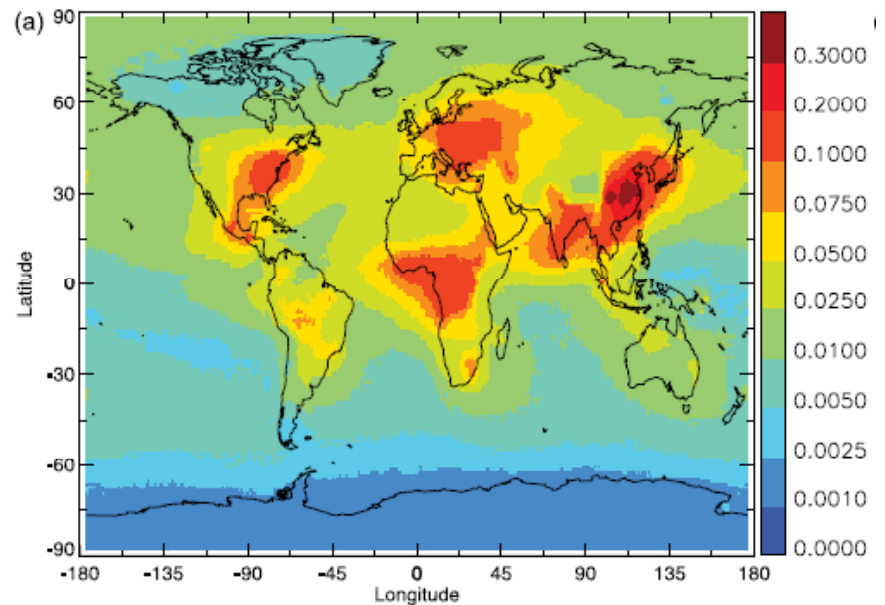
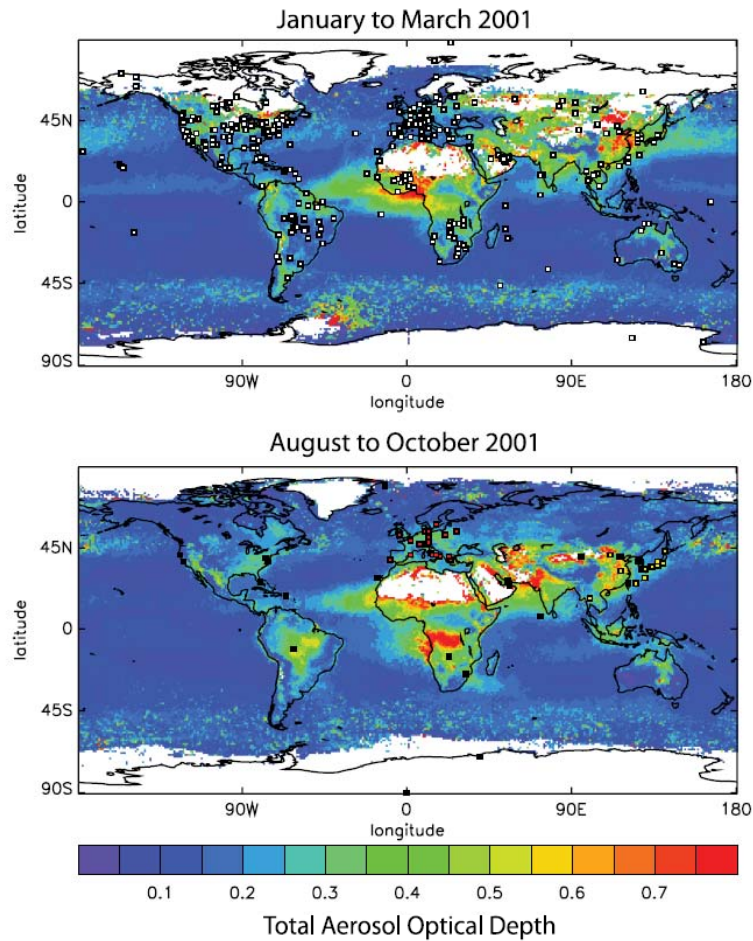
Aerosol direct radiative forcing – Comparison of different models



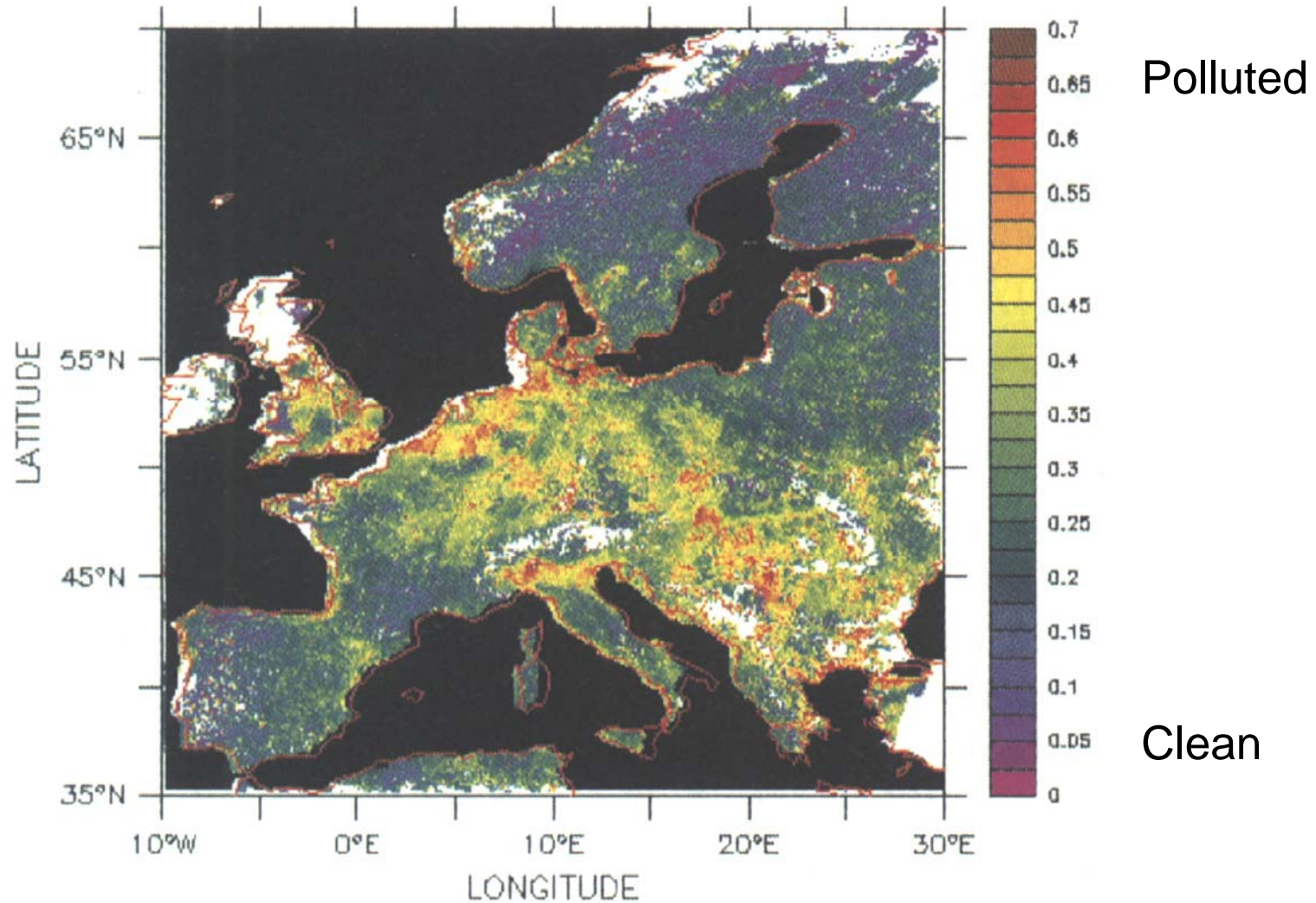
Radiative forcing due to the cloud albedo effect – Comparison of different models



Total Aerosol Optical Depth (MODIS satellite) modelling

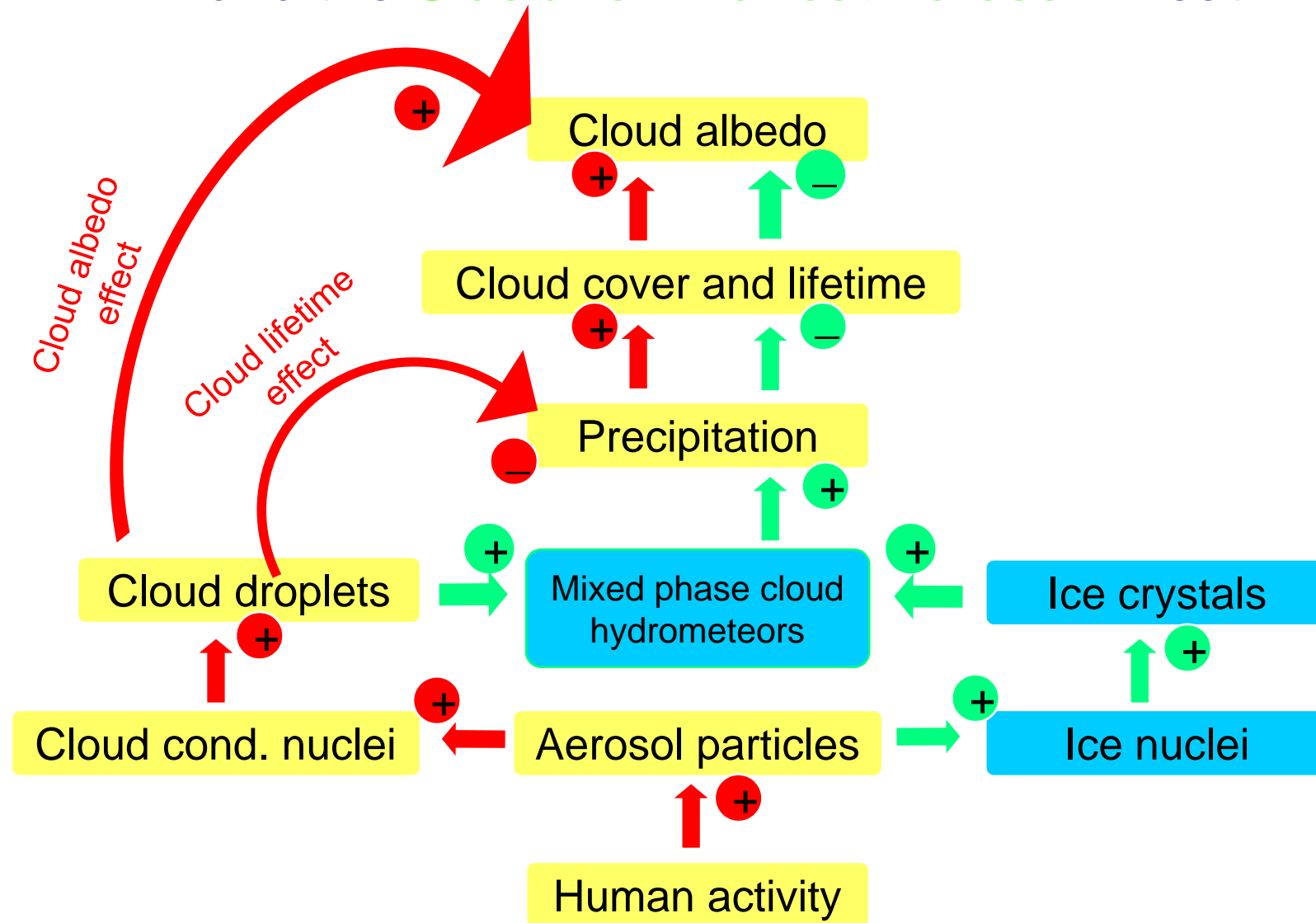


Satellite retrieved AOD over Europe: Aerosols show high spatial variability

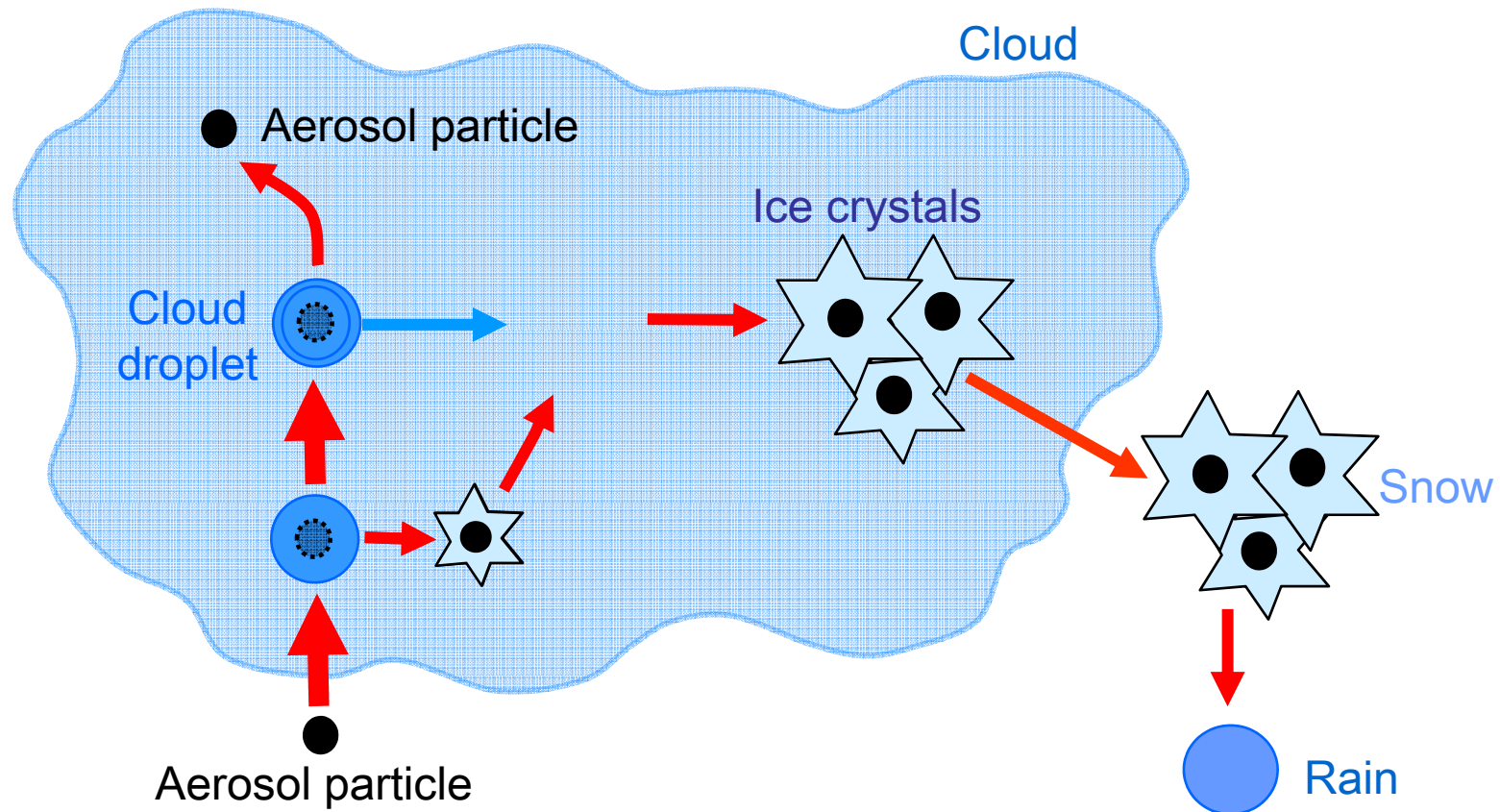


Robles Gonzales et al., GRL 27, 955 (2000)

Pathways of the Traditional *Warm Indirect Aerosol Effect* and the *Glaciation Indirect Aerosol Effect*



Evolution of particles in cloud: Bergeron-Findeisen process



Saturation Vapor Pressure (SVP) difference: $SVP(\text{ice}) < SVP(\text{liquid})$
 \Rightarrow Flux of water vapor from liquid droplets to ice crystals

The WBF mechanism converts many small supercooled drops to only few, large ice crystals, thus changing cloud radiative properties and enhancing precipitation.

Aerosols and Health

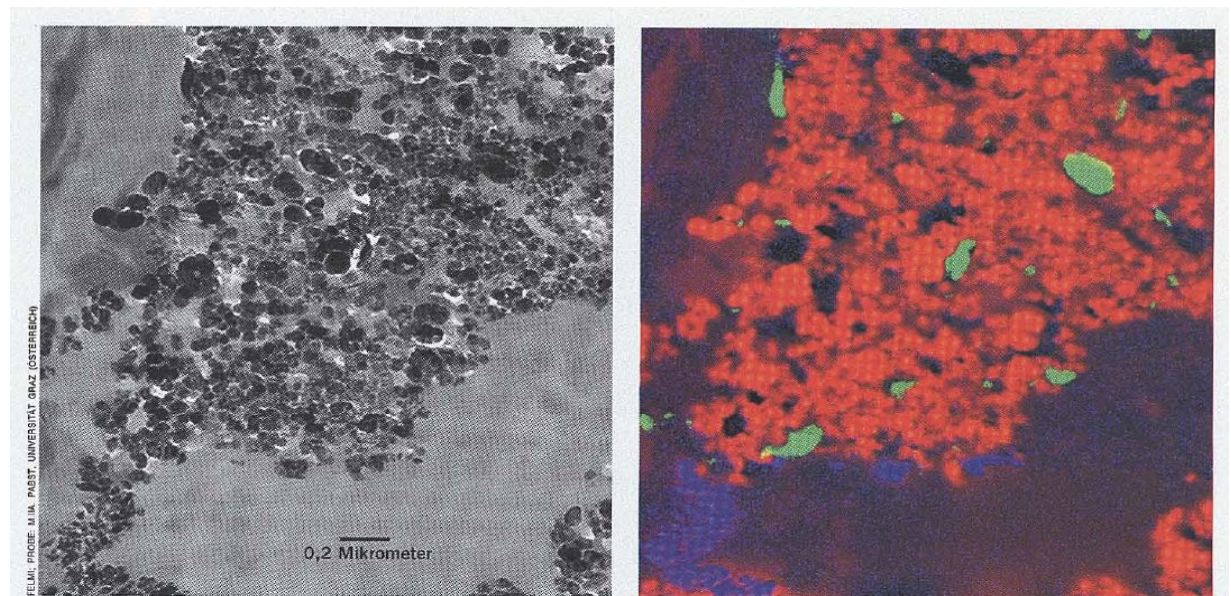
Diesel particles



- a health hazard

Source: www.ecocouncil.dk

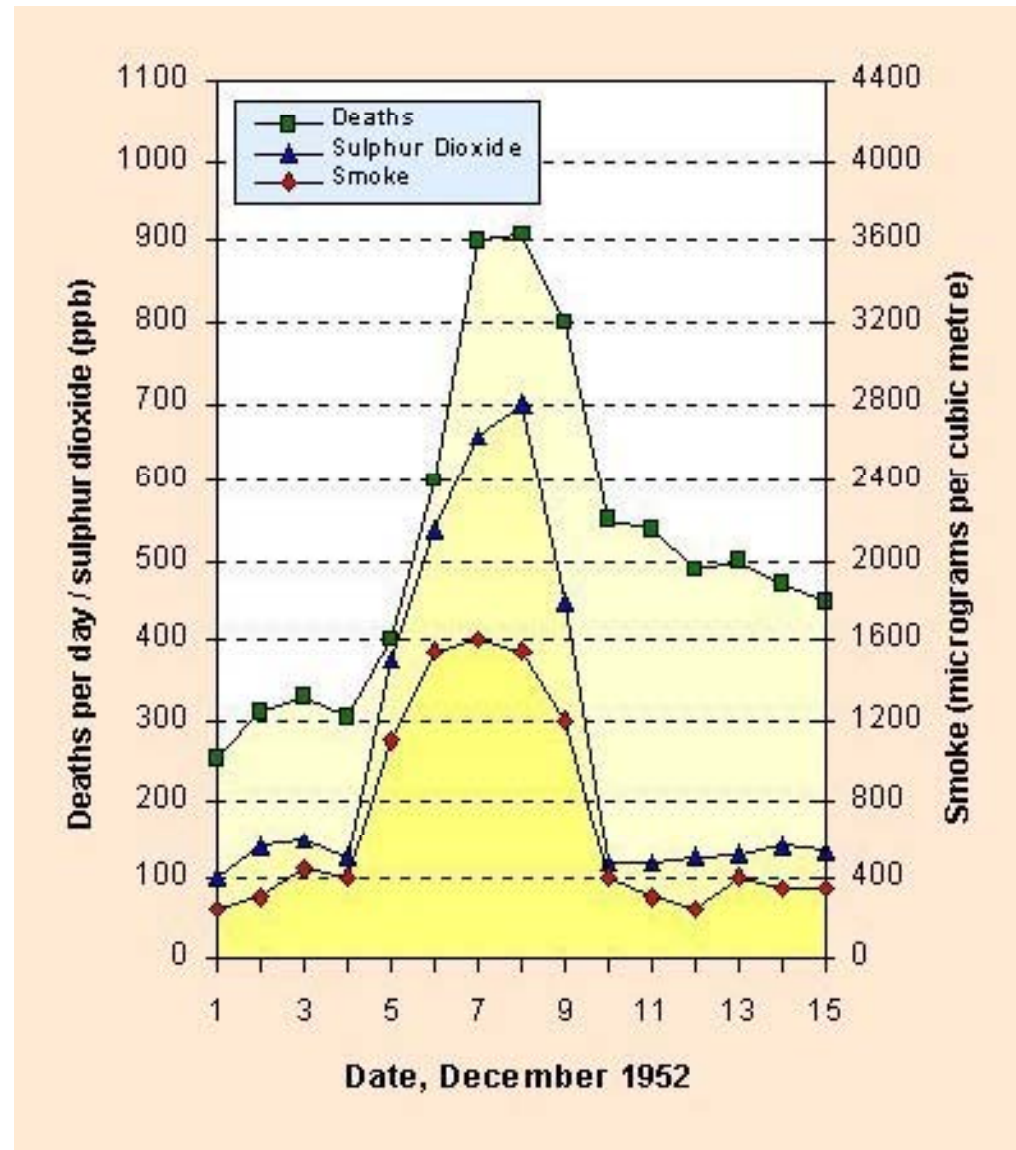
Aerosols is not a recent problem:
The lung of 'Ötzi'



black: soot

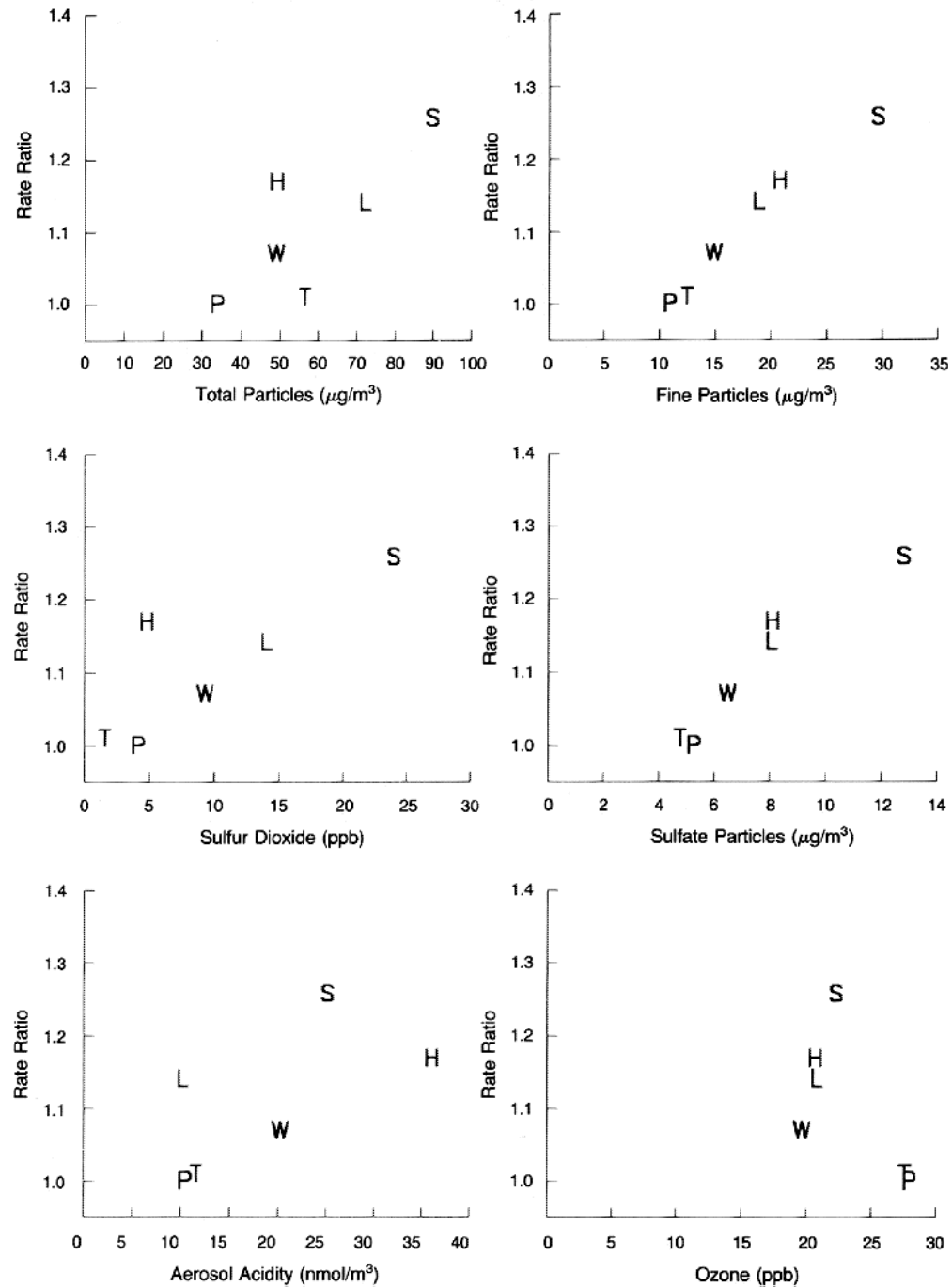
red: soot

Air pollution and mortality during London winter smog in 1952.



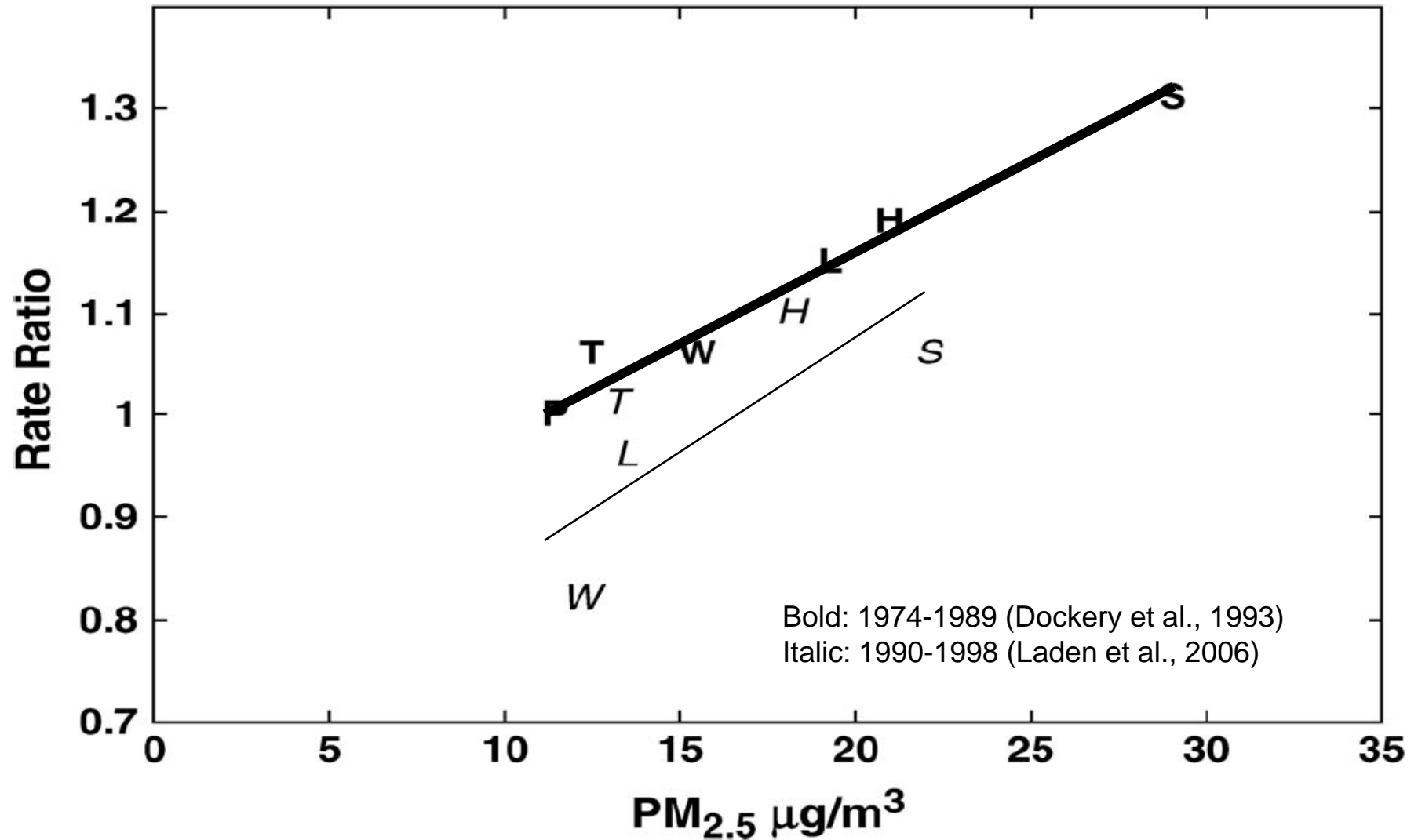
Adapted from Wilkins (1954)

Increased mortality correlates best with PM2.5 (fine particles)



Dockery et al. (1993)

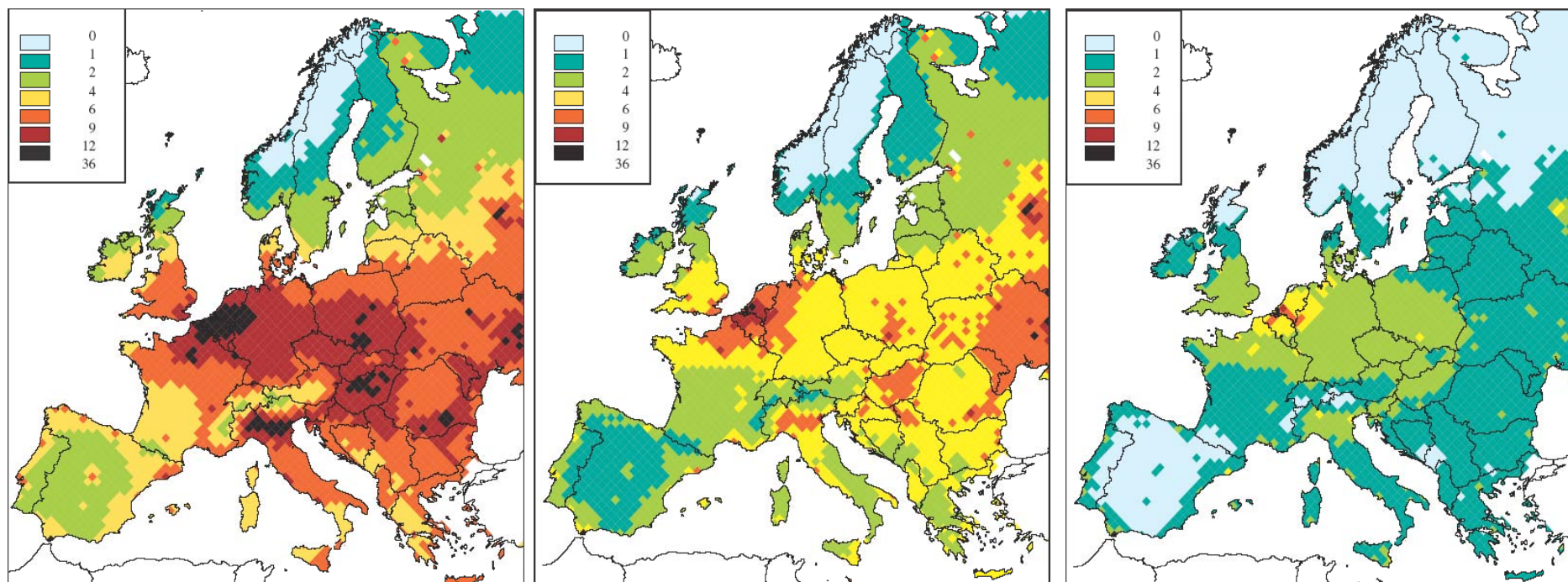
Epidemiology: clear relationship between PM_{2.5} (or PM₁₀) and mortality



Different health effects of PM10

- Well established: Of all air pollutants, PM10 (and even more so PM2.5) show best correlation with increased mortality
- Increase of mortality with increase of PM10 by 10 $\mu\text{g}/\text{m}^3$ (Laden et al., 2000):
 - Traffic: 3.4%
 - Coal combustion: 1.1%
 - Mineral dust: ~0%
- ➔ Influence of
 - Chemical composition (metals, radicals, organic compounds, acidity)
 - Biological constituents (allergens, endotoxin)
 - Morphology (effect of asbestos)
 - Size distribution: smaller particles have greater surface area per unit mass
 - Number concentration
 - ...
- Mechanism not well known yet

Loss in life expectancy attributable to anthropogenic PM2.5 [months]



2000

2020

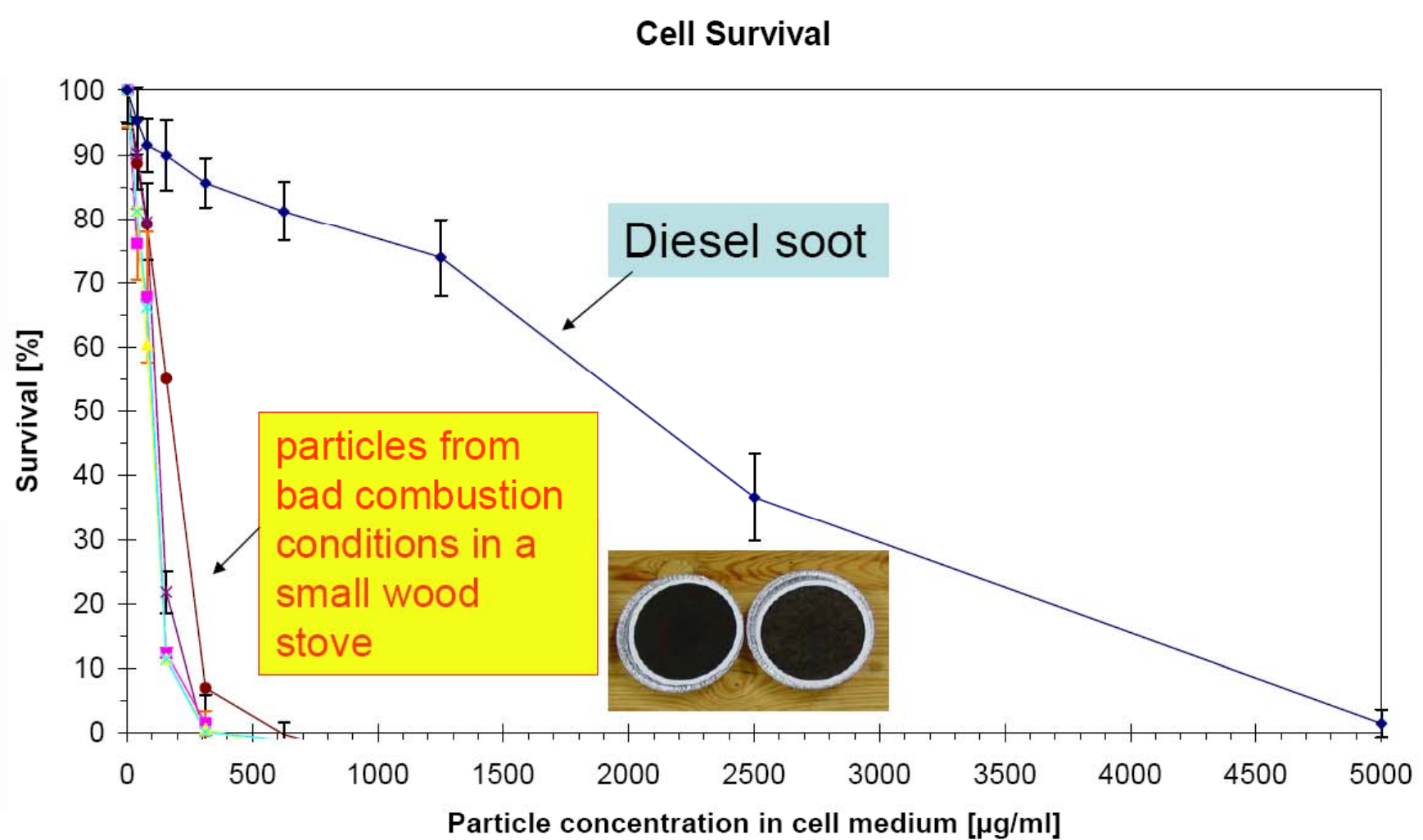
2020

Current legislation

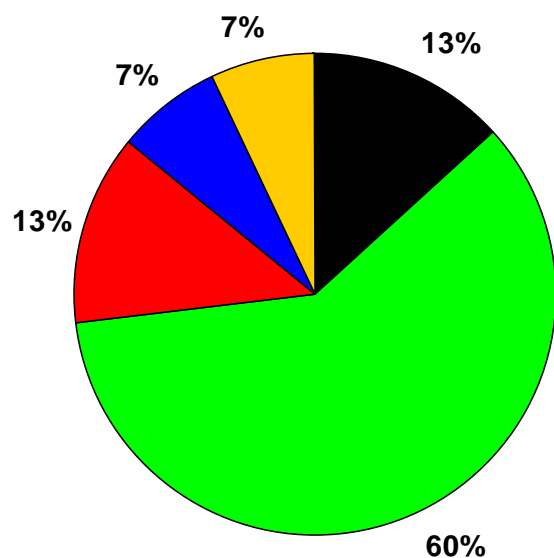
MTFR

Loss in average statistical life expectancy due to identified anthropogenic PM2.5
Calculations for 1997 meteorology
Provisional estimates with generic assumption on urban increment of PM

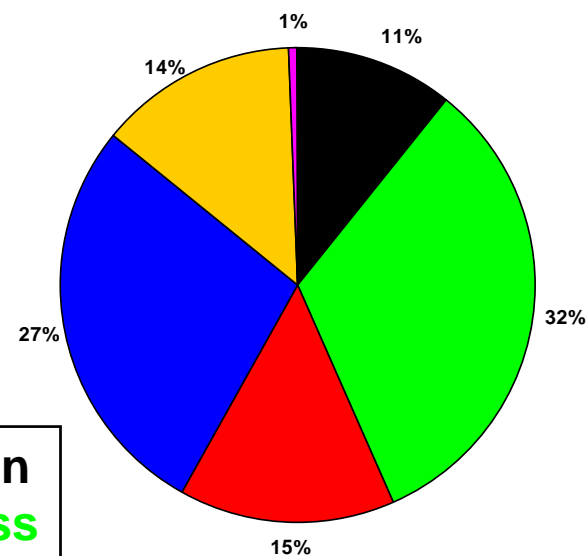
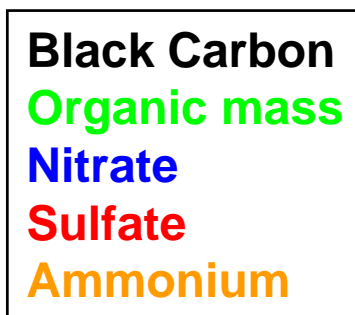
Cytotoxicity of wood smoke from bad combustion: N. Klippel, Verenum



Average composition in Zürich in summer and winter

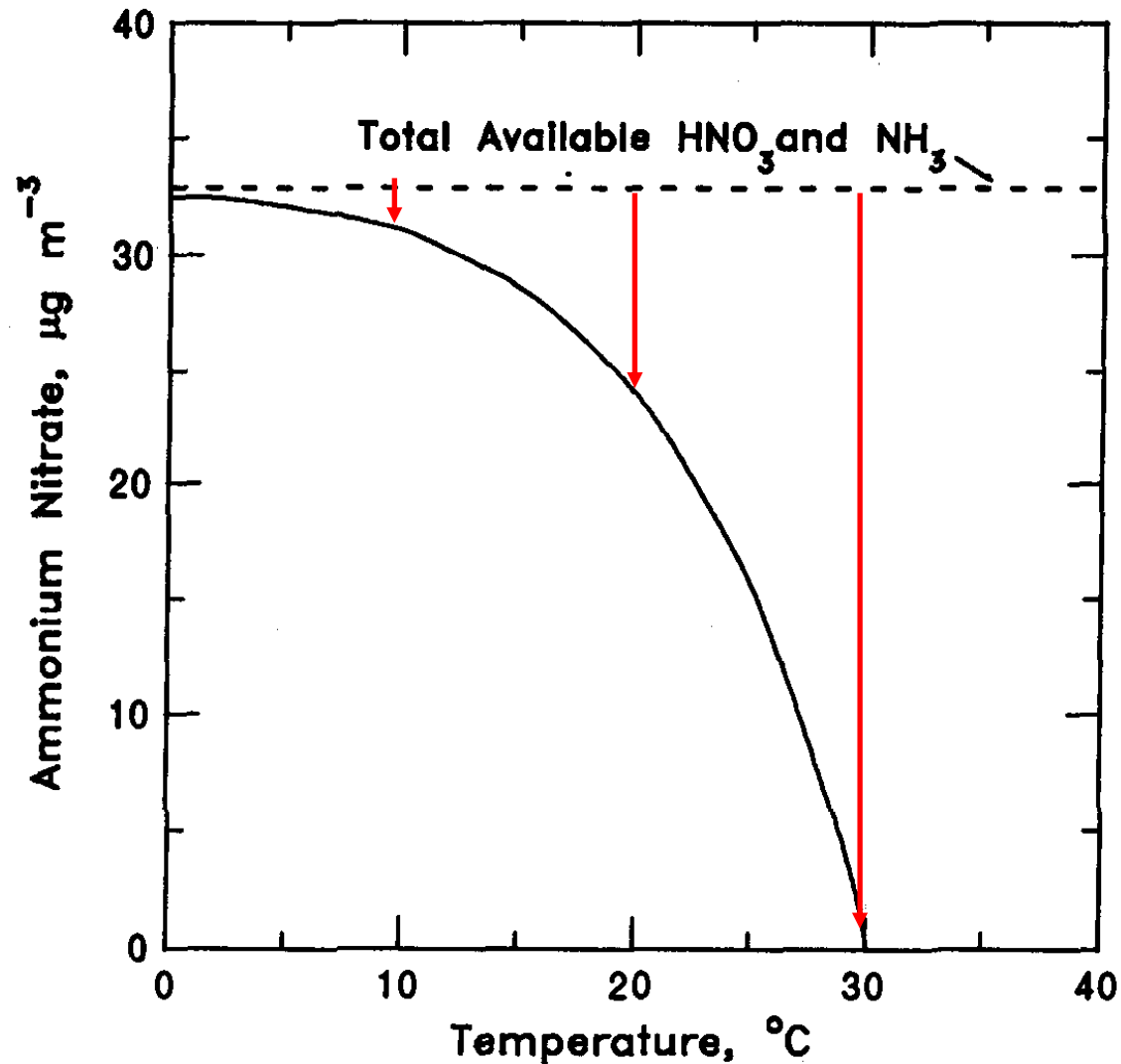


Zürich (July)



Zürich (January)

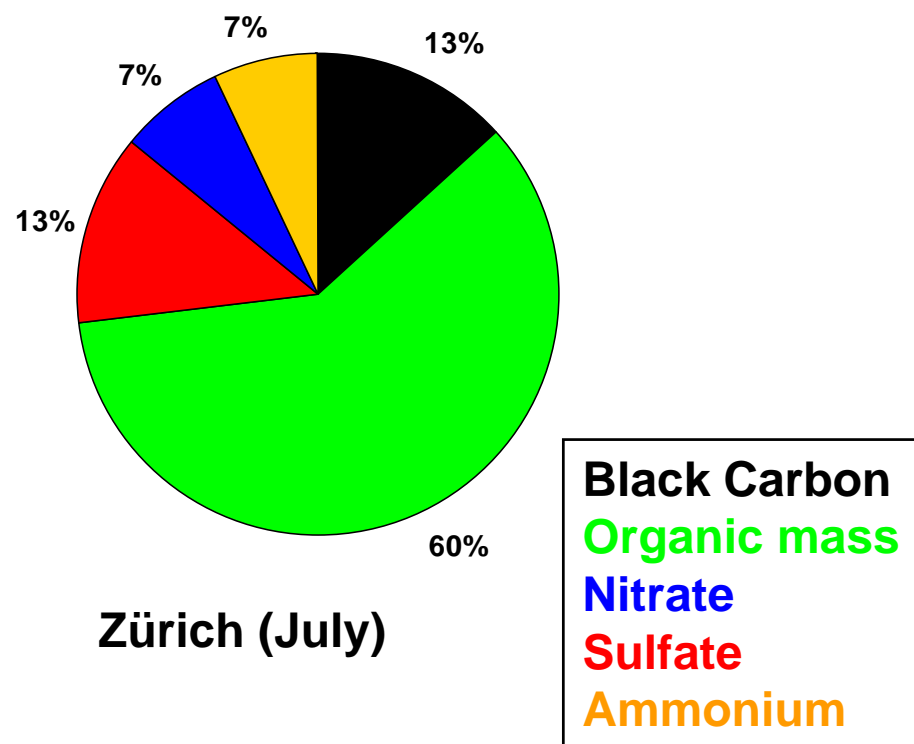
Concentration of solid ammonium nitrate as a function of temperature



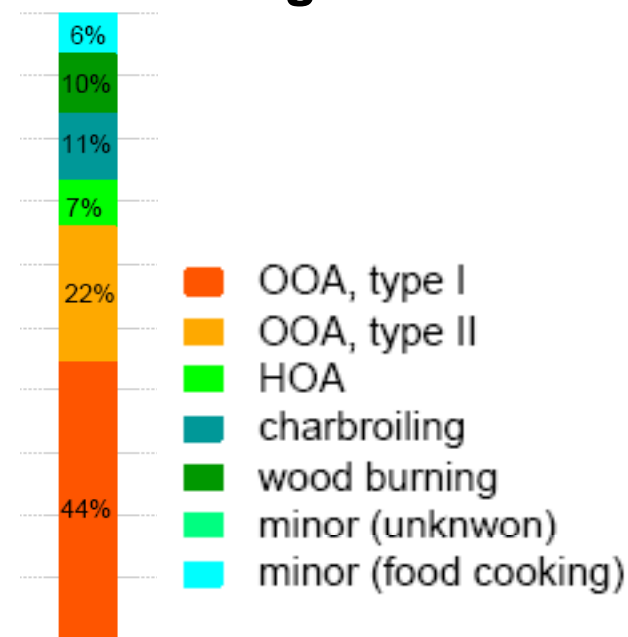
$7 \mu\text{g/m}^3 \text{NH}_3$
 $26.5 \mu\text{g/m}^3 \text{HNO}_3$
 $\text{RH} = 30\%$

↓ Gas phase conc.

Chemical composition in Zürich summer and Positive Matrix Factorization of the organic matter



Organic mass

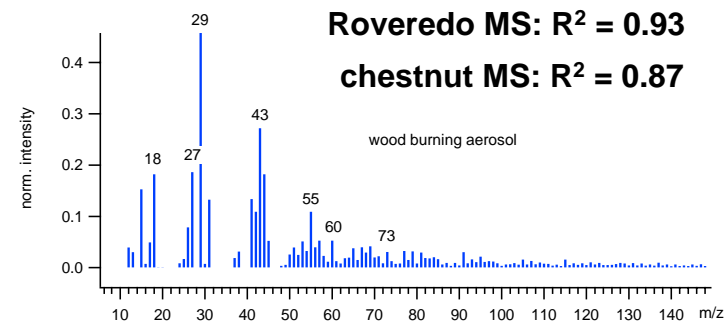
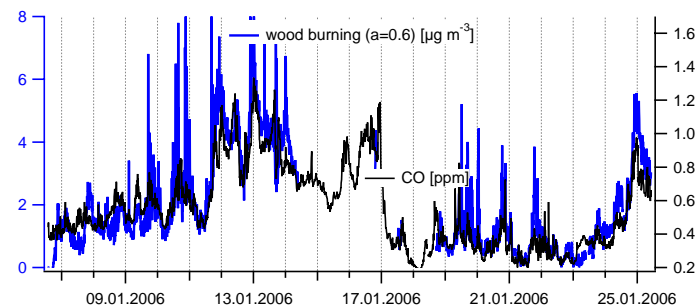


OOA: Secondary organic aerosol

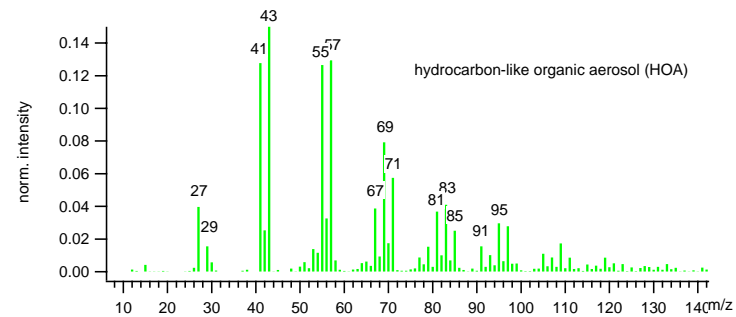
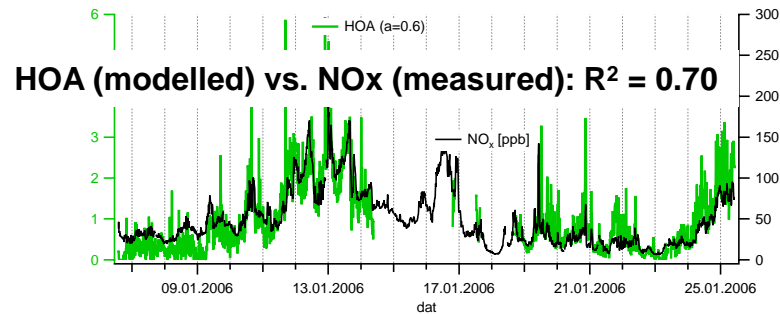
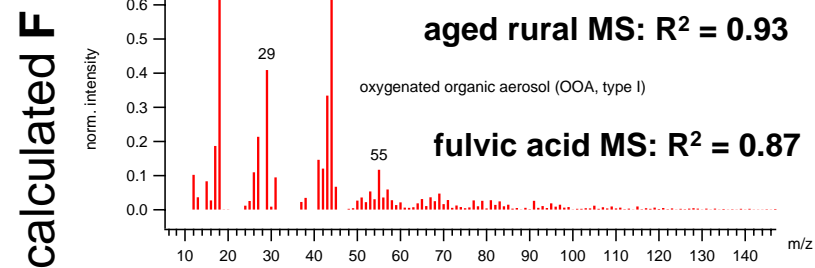
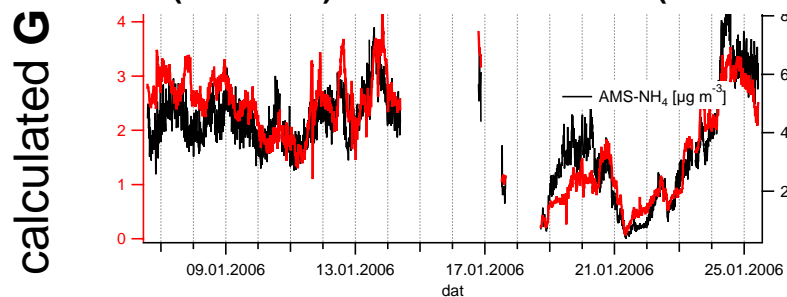
HOA: mostly traffic

Plausibility of solution including 3 factors

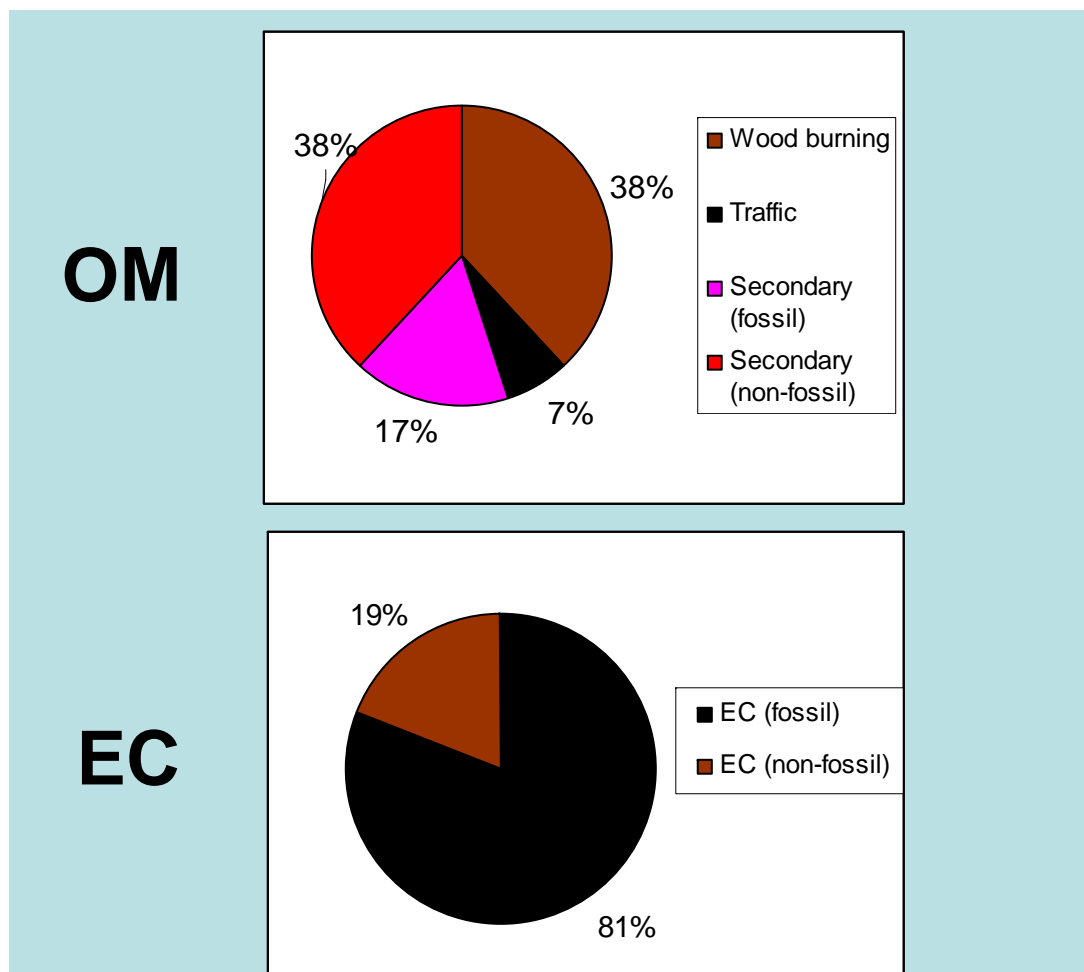
wood burning (modelled) vs CO (measured): $R^2 = 0.78$



OOA (modelled) vs. AMS-ammonium (measured) $R^2 = 0.72$



Carbon apportionment using ^{14}C analysis Estimation of fossil and non-fossil SOA contribution



Use of AMS analysis :

- wood burning 38%
- HOA 7%

Assumptions :

- only SOA, HOA and wood burning present
- $\text{OM/OC}=2$ for wood burning and SOA and $\text{OM/OC}=1.2$ for HOA

Smogchamber results of Carnegie Mellon

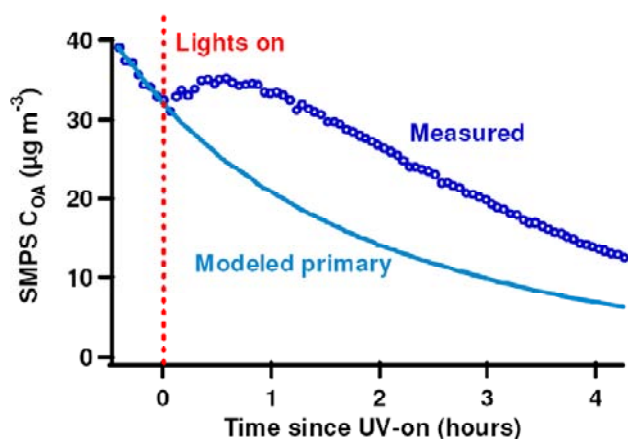


Figure 2 – Time series of aerosol mass (assuming $\rho = 1 \text{ g cc}^{-1}$) during an oxidation experiment and modeled primary mass assuming first order wall. Mass increases substantially when UV lights are turned on.

- **Smog chamber results indicate that wood burning emissions is doubled after only 2 hours of chemistry**

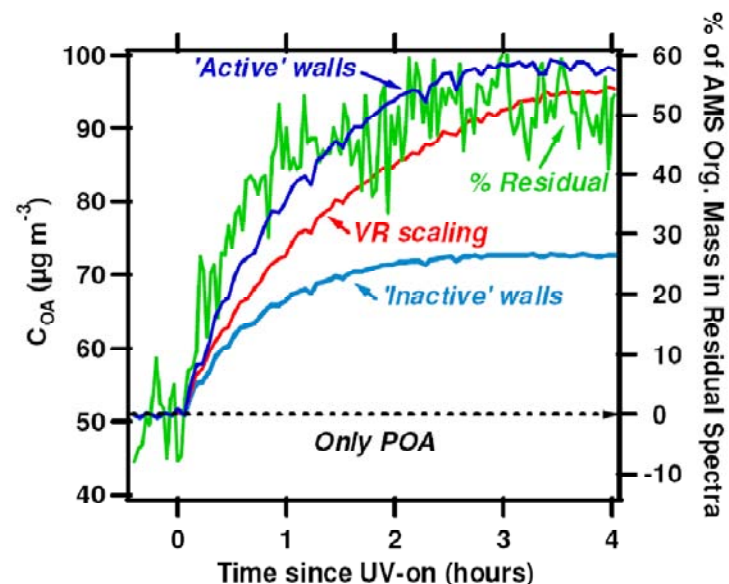
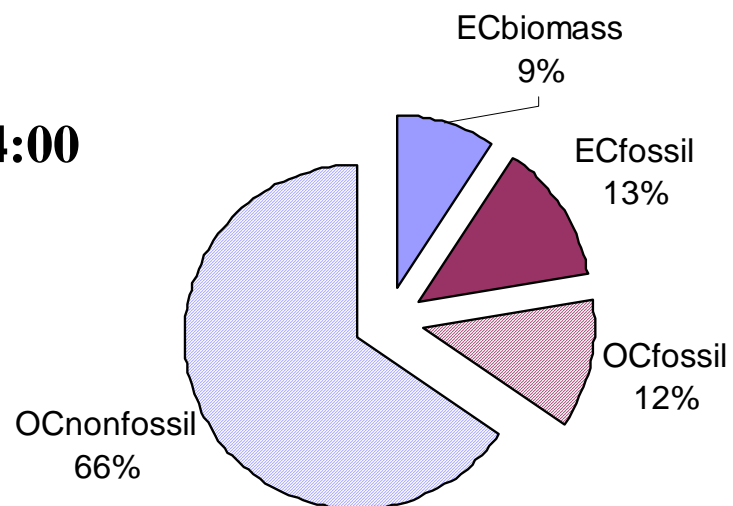


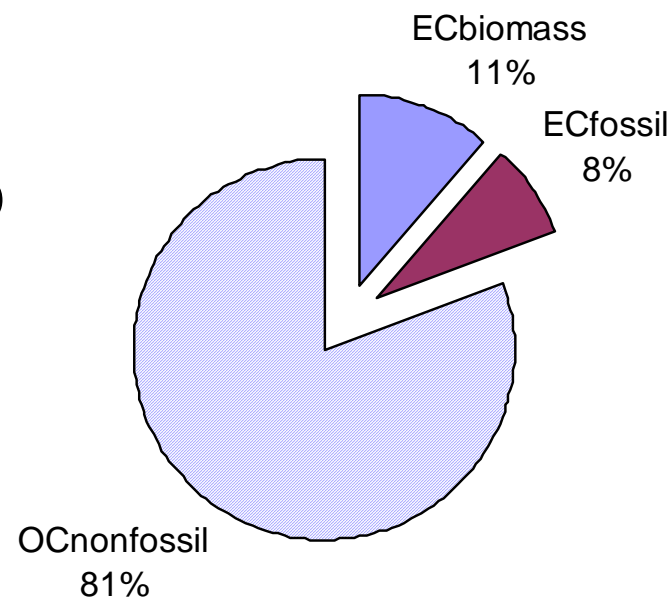
Figure 3 – Total aerosol mass (suspension + walls) during an experiment calculated with: 1) wall loss correction (with and without 'active' walls); 2) volume ratio. Also shown, against the right-hand axis, is the fractional contribution of the residual spectrum to the total AMS organic spectrum.

Roveredo in an Alpine valley, Januar 2005

06:00 – 14:00

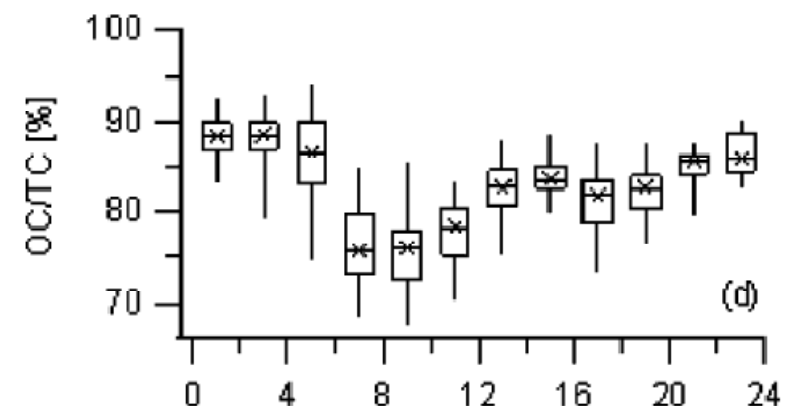
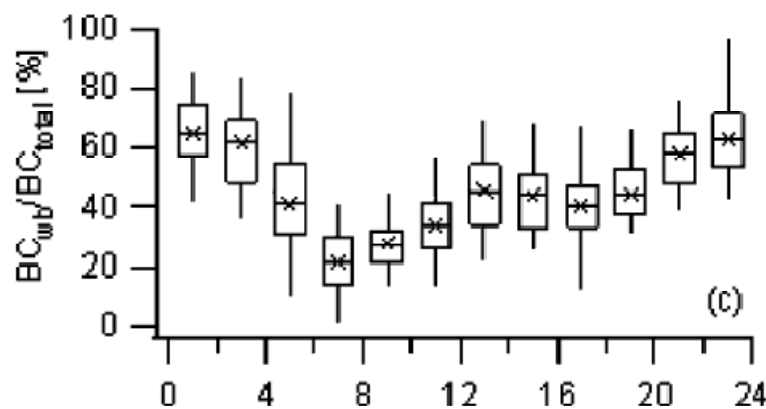
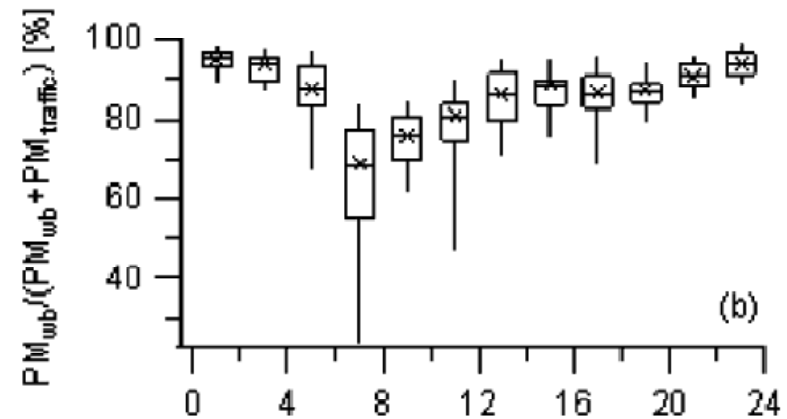
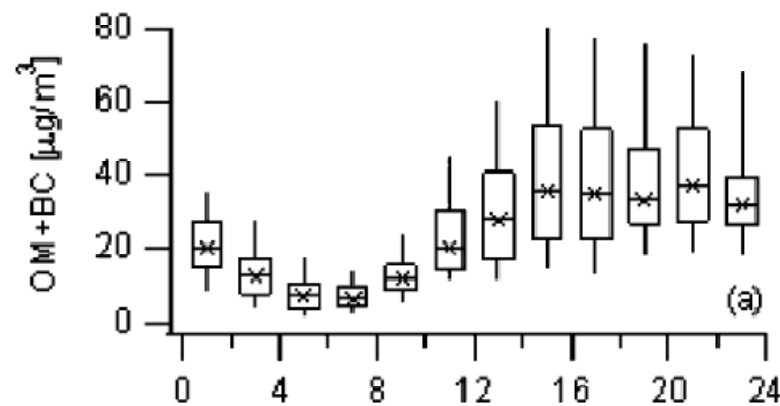


18:00 – 02:00



Szidat et al., GRL, 2007

Average diurnal cycle of the carbonaceous material, OC/EC and wood burning versus traffic contributions



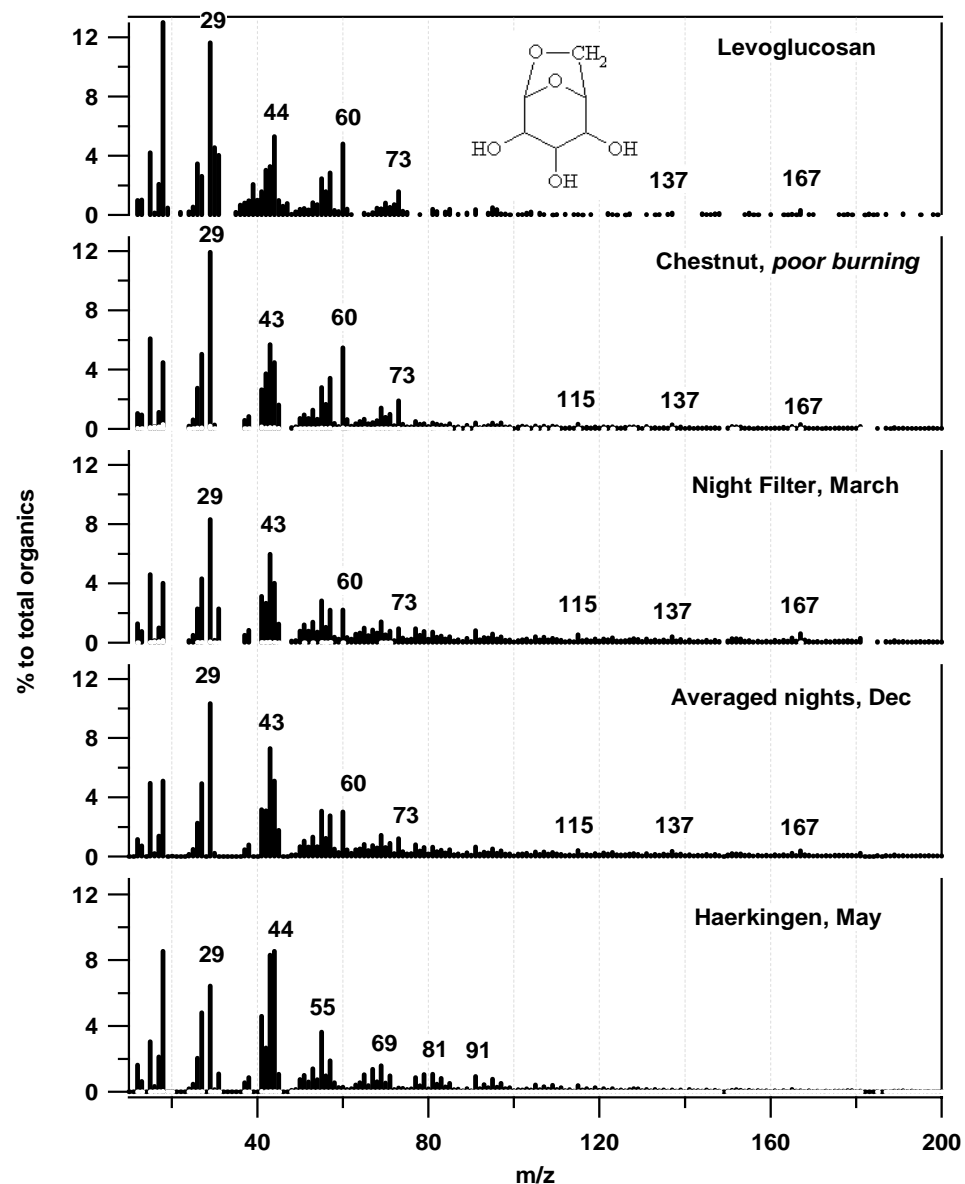
Levoglucosan

Wood burner (emissions) chestnut,
very inefficient burning

Night period in Roveredo in March,
more than 80% of OC non-fossil

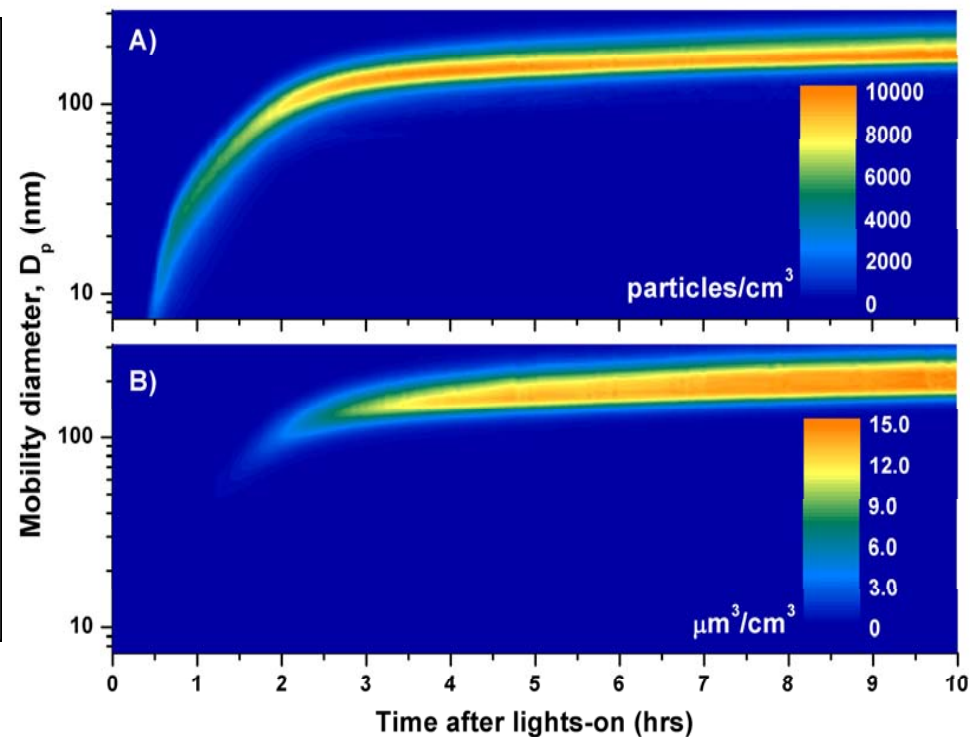
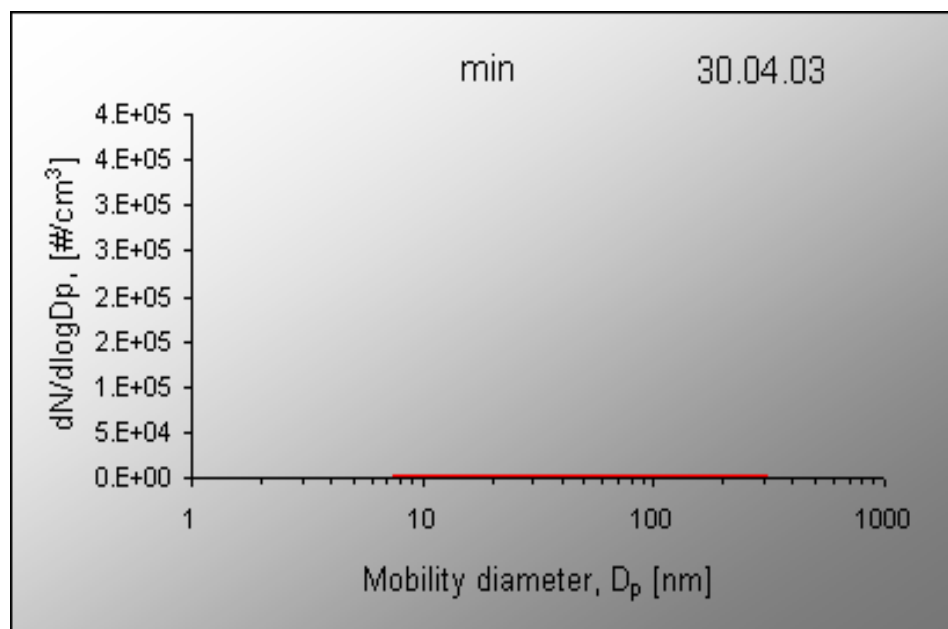
Average in Roveredo over the
whole December

Mass spectra from a Motorway site
in May

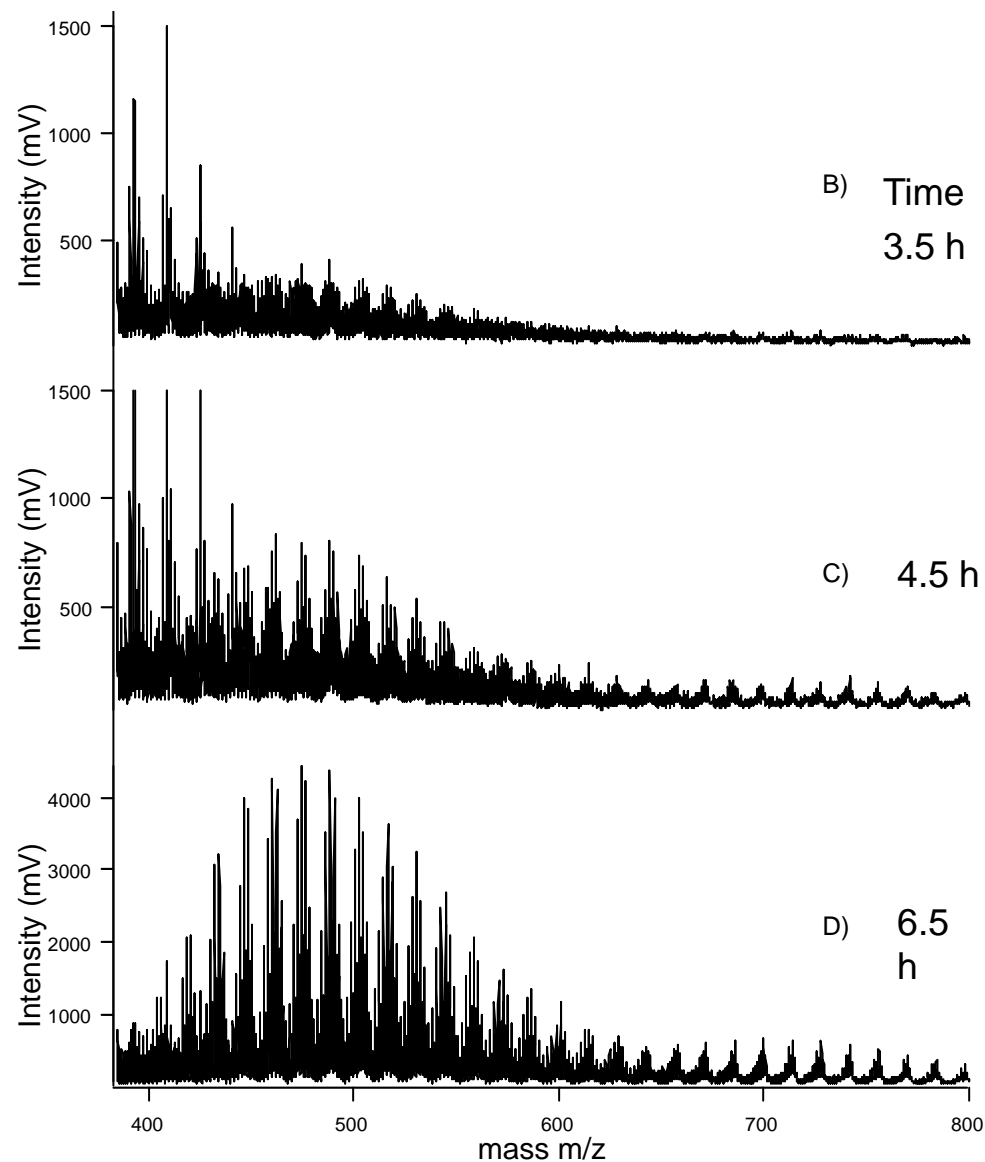


SOA formation from TMB (at 50% RH)

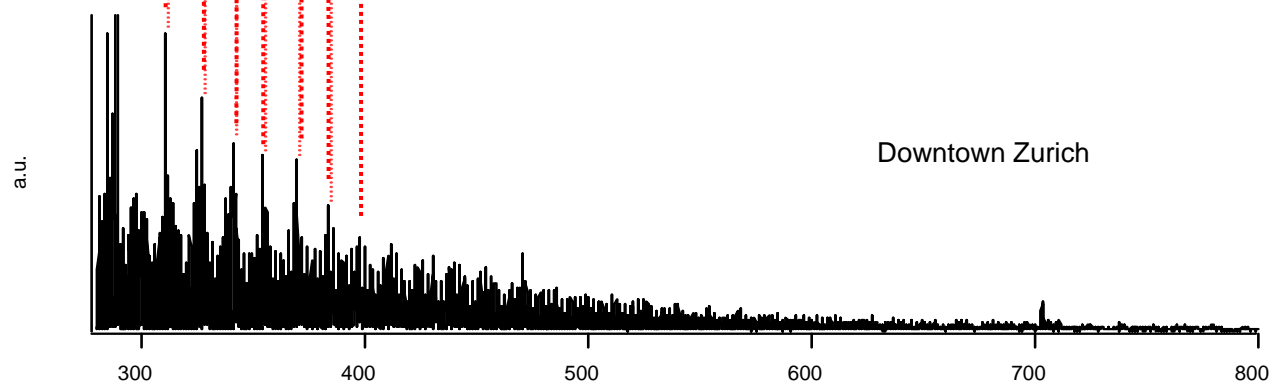
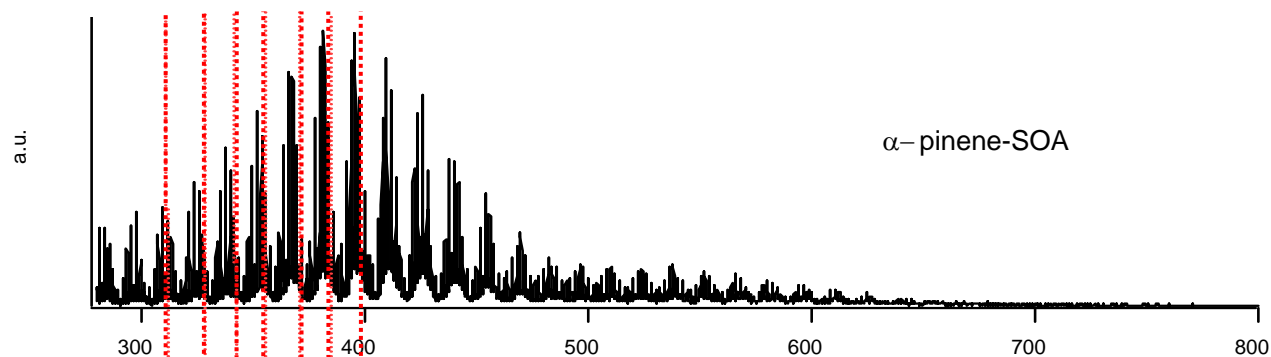
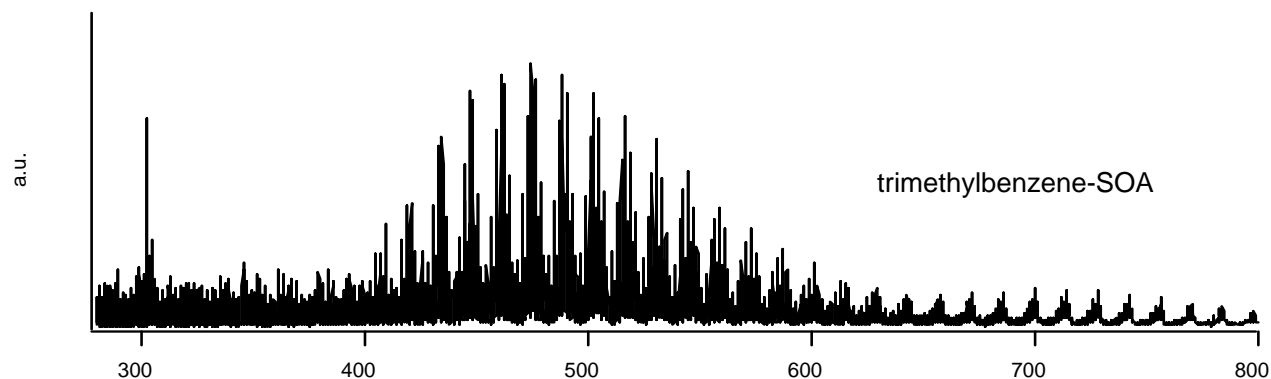
Trimethylbenzene + NO_x + light →→ Secondary Organic Aerosol



Observation of SOA oligomerization by Laser Desorption Ionization



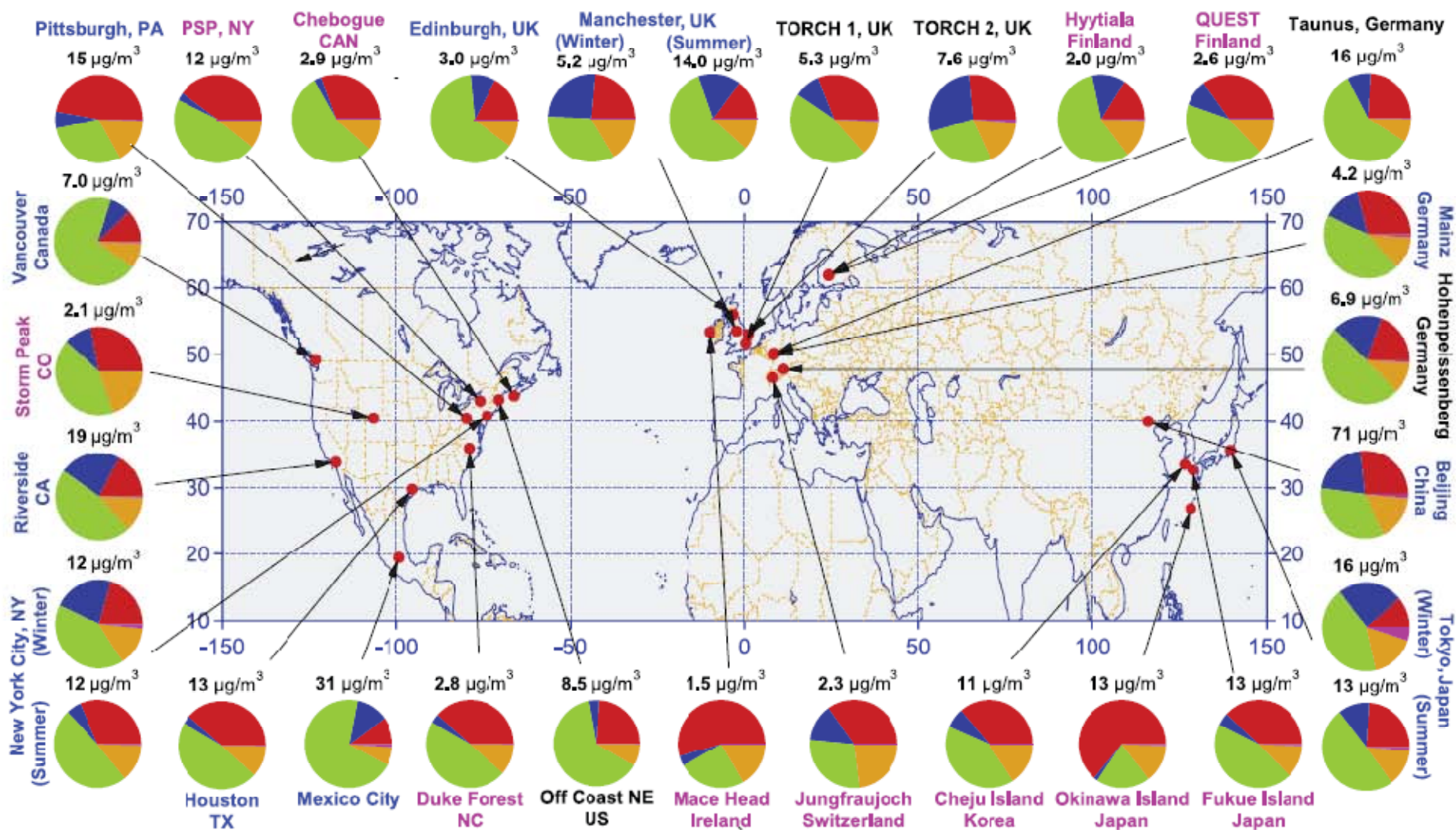
Comparison of smogchamber aerosols with ambient sample



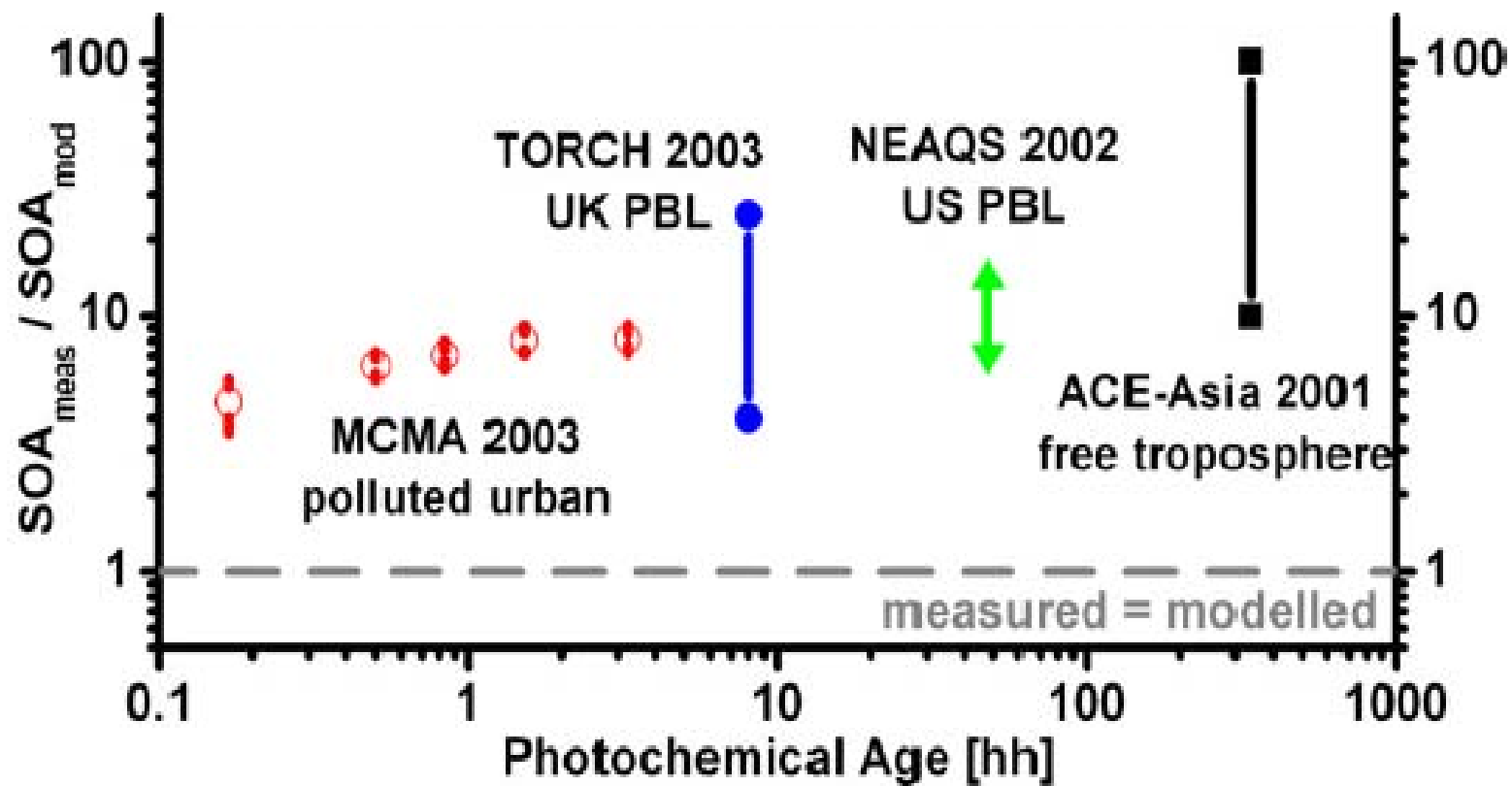
Pattern of Zurich points to α -pinene rather than TMB (or other anthrop. precursors)

Baltensperger et al.
Faraday Disc. (2005)

Worldwide AMS measurements of the chemical composition



Models underestimate SOA



SUMMARY

A significant progress was made in last years but many challenges remain:

- Better instrumentation (cheaper, smaller, more long-term, more specific, more precise, ...) is still needed
- Long-term chemical composition of aerosols is needed
- Secondary organic aerosol formation needs to be understood and implemented in models
- Health effects : more specific to size and chemical composition
- Climate : Indirect effects are not quantitatively understood