Aging Processes of Soot Particles in the Atmosphere

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Soot particles are emitted by all kinds of incomplete combustion processes and consist of a mixture of elemental and organic carbon (EC and OC). Besides the soot mode at a particle diameter of about 100 nm a second mode is clearly seen in traffic-influenced areas, with a diameter around 20 to 30 nm (Weingartner *et al.*, 1997a, Bukowiecki *et al.*, 2002). These particles are formed by condensation of semivolatile exhaust components and therefore disappear to a large extent in a thermal desorber (Baltensperger *et al.*, 2002). Coagulation results in a rapid decrease of the number concentration of these condensation particles (typically 1 hour, Bukowiecki *et al.*, 2002), while the soot particles have much longer life times. Atmospheric aging processes result in a significant change of the chemistry of these soot particles.

The hygroscopic properties of aerosols play a crucial role in climate impact, air quality, acid deposition, biochemical cycles, visibility reduction, and the formation of clouds and precipitation. Hygroscopicity measurements are a suitable means to detect the degree of this chemical transformation, since most of these aging processes lead to an enhanced water solubility of the particles. At high relative humidity (RH) water is often the dominant component of the ambient aerosol. If an aerosol particle is transferred from low to high RH, its diameter may change by up to a factor of 3. This ability to absorb water strongly depends on the particle “dry” size, shape and chemical composition, and hence the age.

The response of aerosol particles on changes in RH are commonly mesaured by means of a so-called Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) (Weingartner *et al.*, 2002). This instrument is suited for a nearly artefact free measurement of the hygroscopic growth factor D/D_o defined as the ratio of the humidified diameter D to the dry diameter D_o.

The H-TDMA was operated during different extensive field campaigns conducted during different seasons at the high alpine site Jungfraujoch. During most of the time, the station was located in the free troposphere, and the shape of the humidified H-TDMA size spectra were preferentially characterized by a narrow monomodal growth distribution (see Figure 1). This implies that the particles in the observed size range were to a large extent internally mixed, as regards their hygroscopic and chemical properties. This is in contrast to the behavior of continental polluted aerosols where the particles generally separate into a less- and more-hygroscopic group, i.e. an external mixture of freshly emitted combustion particles (less hygroscopic) and a background aerosol (more hygroscopic). It can also be seen that the hygroscopic modes at the Jungfraujoch have a significantly higher hygroscopicity than the modes at Milano, indicating that atmospheric aging processes lead to a substantial increase in particle hygroscopicity.

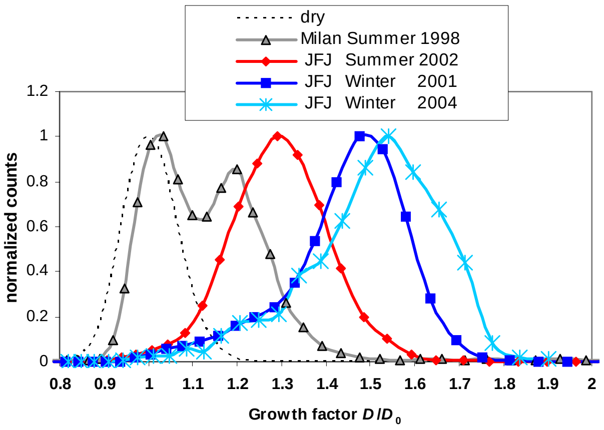

Figure 1: Typical examples of measured hygroscopic growth distribution at RH = 85% in Milan and at the Jungfraujoch showing that the free tropospheric aerosol particles experience a significantly higher hygroscopicity than the aerosol at an urban site. The dotted line is the distribution of the originally dry, monodisperse aerosol particles with a modal diameter of $D_o = 100$ *nm (data from Weingartner et al., 2002 and Baltensperger et al., 2002).*

Directly after their emission, soot particles are hydrophobic, i.e., both EC and OC are water insoluble, and the particles grow only little upon exposure to high RH (Weingartner *et al.*, 1997b). After aging, i.e., at a remote site such as the Jungfraujoch, the carbonaceous material is internally mixed with a high fraction of water soluble material (typically 80 to 90%), which results in a monomodal distribution of the growth factor. Typically 50% of the organic carbon of this aged aerosol is water soluble (Krivacsy *et al.*, 2001).

Processes that contribute to this increased growth factor are: (1) coagulation with water soluble particles, (2) (photo)-chemical degradation of the aerosol particle surface, (3) gas to particle conversion (heterogeneous nucleation), (4) adsorption and reaction of gaseous molecules and (5) cloud processing.

Coagulation is not very efficient in changing the chemical characteristics of the soot particles. Much more efficient is the condensation of condensable molecules such as secondary organic aerosol produced by photochemical oxidation of gaseous precursors (Saathoff *et al.*, 2002). This condensation significantly changes also the optical properties of the soot particles, since a layer of scattering material greatly enhances the absorption efficiency of the soot (Schnaiter *et al.*, 2002). Absorption and reaction of gaseous molecules may also result in significant changes of the chemistry of the soot particles, even though this process is usually limited to the surface of the particles. This is exemplified by the reaction of NO_2 and diesel soot (Gutzwiller *et al.*, 2002 and references therein). (Photo)- chemical degradation may be exemplified by the rapid decrease of polycyclic aromatic hydrocarbons on the surface of soot particles by reaction with NO_2 or OH, or with ozone (Pöschl *et al.*, 2001). Finally, cloud processes are also an efficient process in adding water soluble material to the aerosol particles, e.g. by SO_2 oxidation in the cloud droplets (Weingartner *et al.* 1999). However, for this process the particles require a certain size to be activated during cloud formation (Henning *et al.*, 2002).

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Atmospheric aging processes of soot particles

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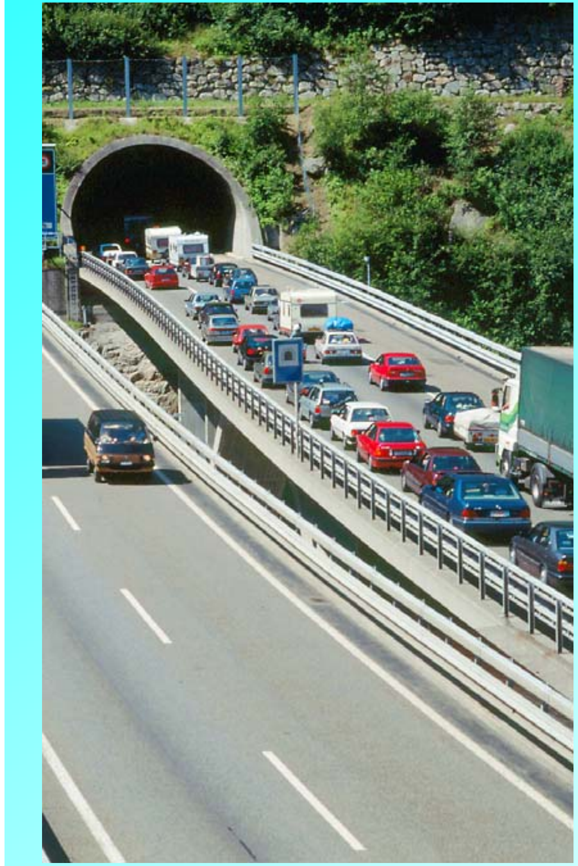
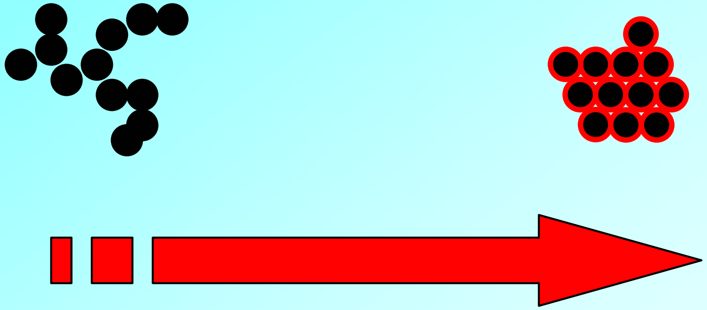


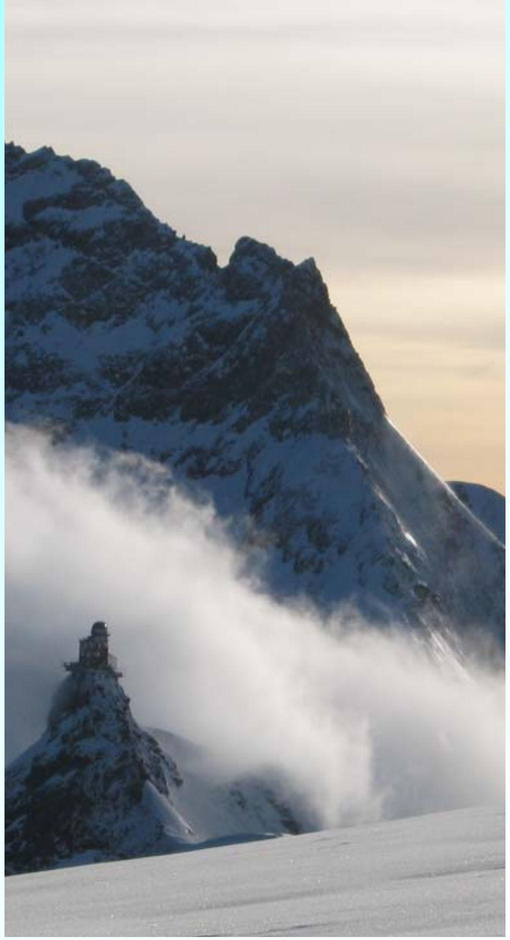
Close to the source



Freshly emitted soot particles

Background aerosol

Which transformation processes change the particles physical and chemical properties?



High-alpine research station Jungfraujoch 3580 m asl

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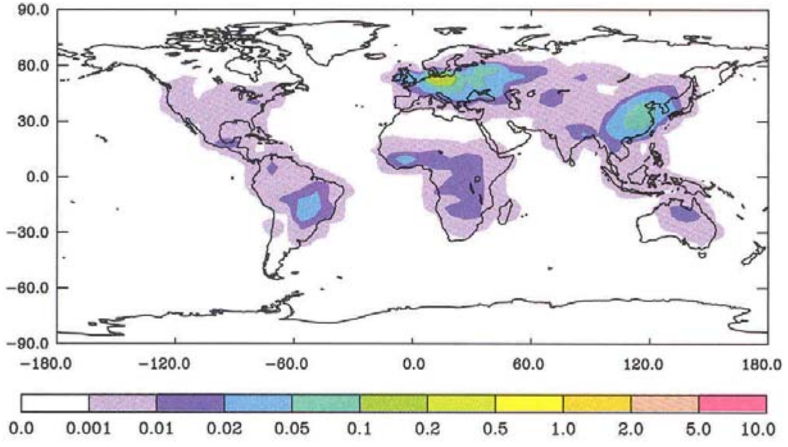
Motivation

- The global emissions of carbonaceous particles from anthropogenic sources (BC) are estimated at 11–17 Tg / y (~50% biomass burning, 50% fossil fuel) (www.ipcc.ch)



BC source strength in kg km^{-2} hr^{-1}

- The size distribution of soot particles peaks in the accumulation size range, therefore dry deposition velocities are small and soot particles can attain long lifetimes and be transported over long distances. They are mainly removed by wet deposition.

- Soot particles are an important constituent of the atmospheric aerosol, since they

  affect human health

  and scatter and absorb light

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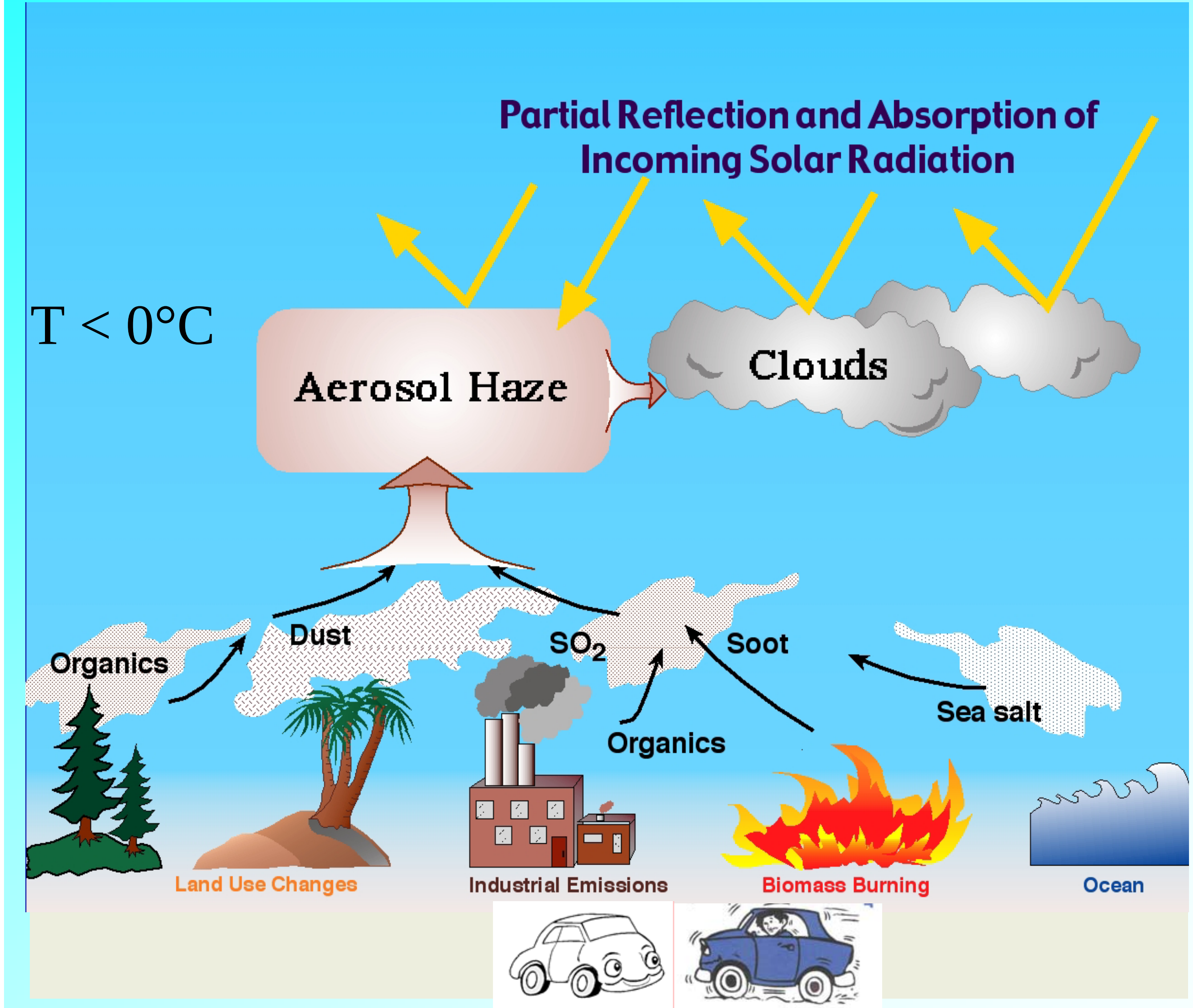
Radiative Forcing by Tropospheric Aerosols



T < 0°C

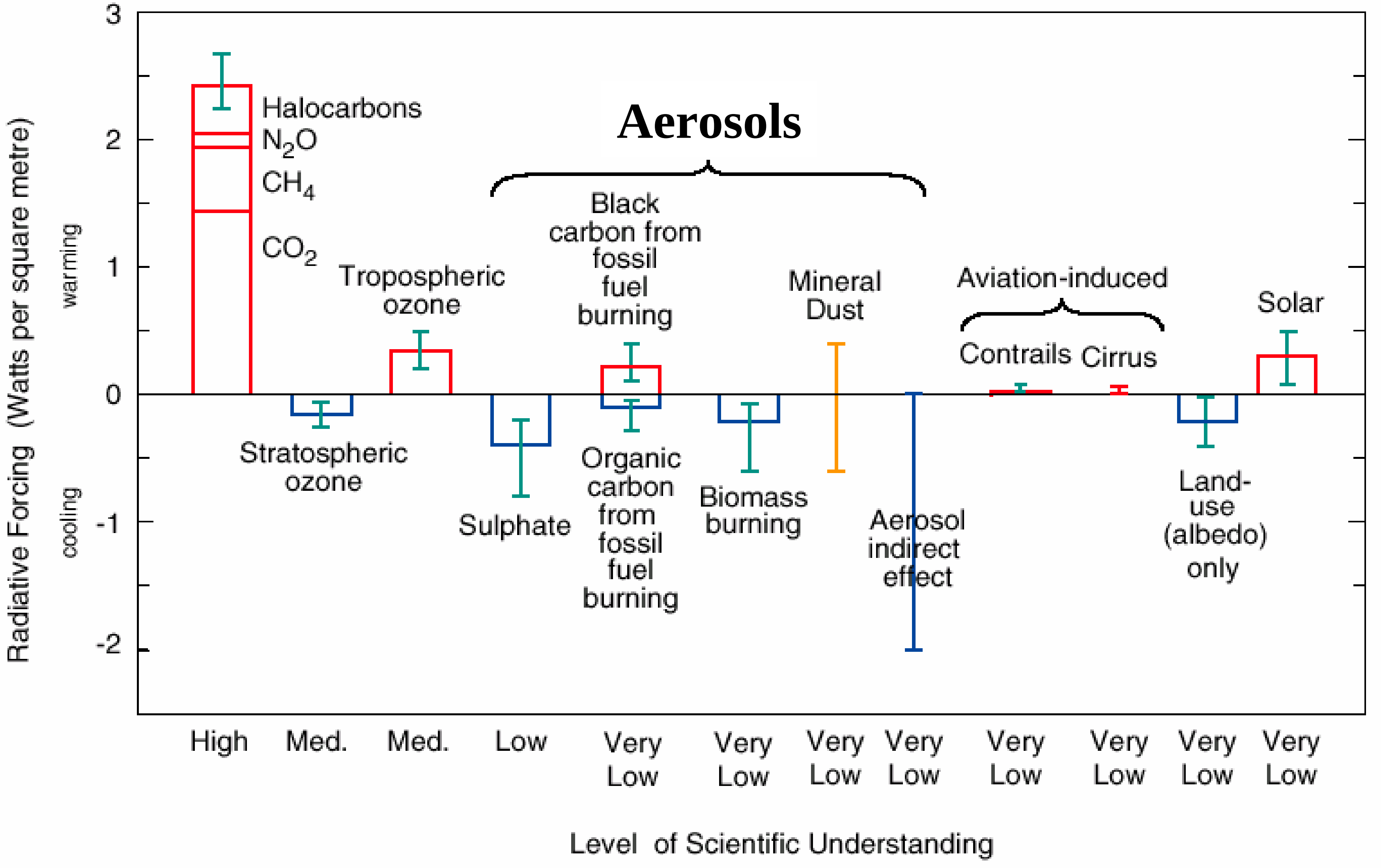
Direct Effect

Scattering and Absorption of incoming sunlight by aerosol particles

Indirect Effect

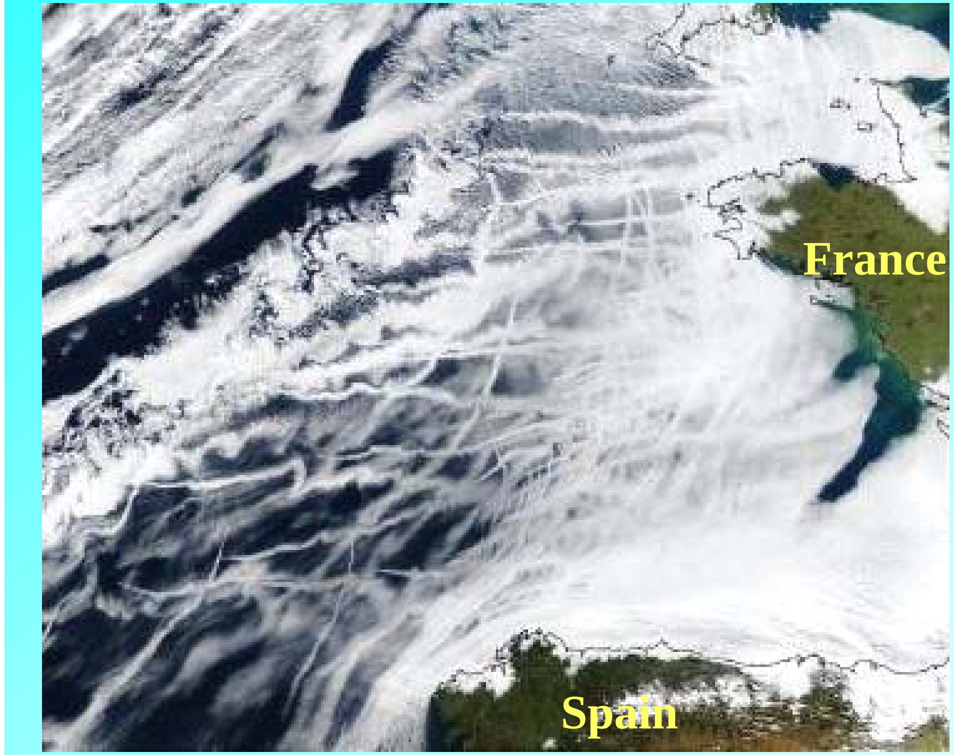
The number of CCNs influences the cloud droplet size and thereby changes the cloud albedo and lifetime

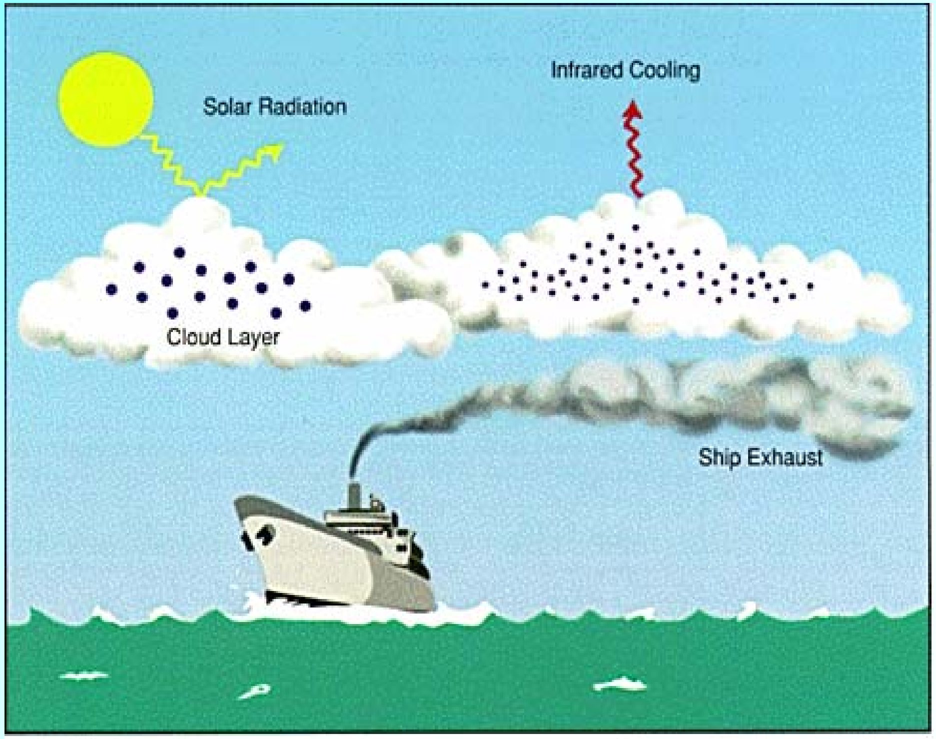
The global mean radiative forcing of greenhouse gases and aerosols for the year 2000, relative to 1750



Source: www.ipcc.ch

Indirect effect of carbonaceous particles: Ship tracks

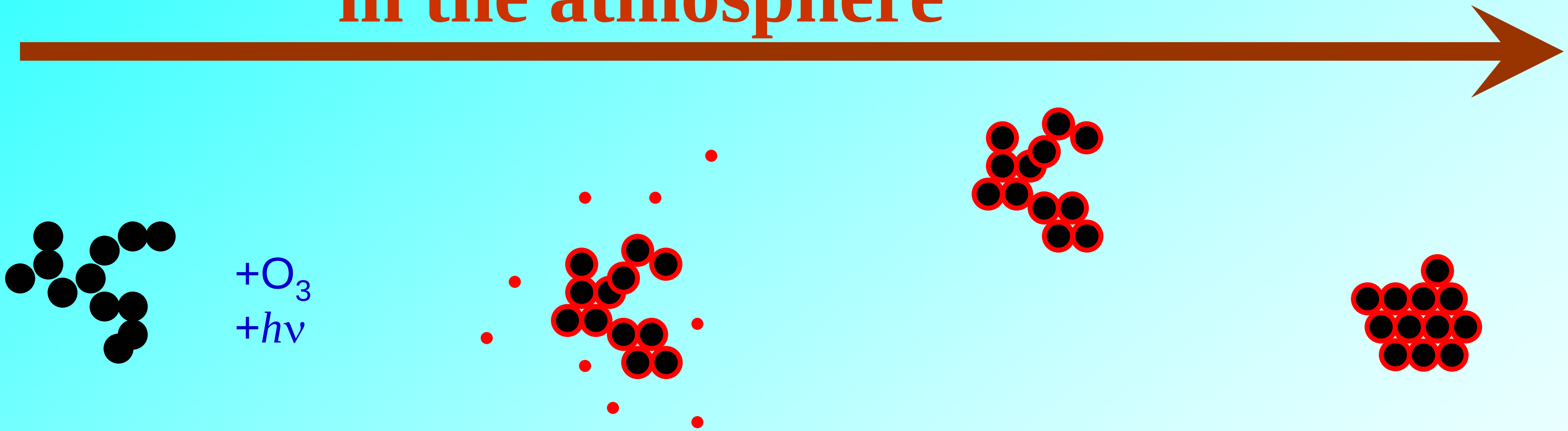




Ship tracks on the East Atlantic

Aerosol particles emitted by ships (soot particles with a high sulfur content) act as CCN and form clouds and enhance cloud reflectivity

Aging processes of soot particles in the atmosphere

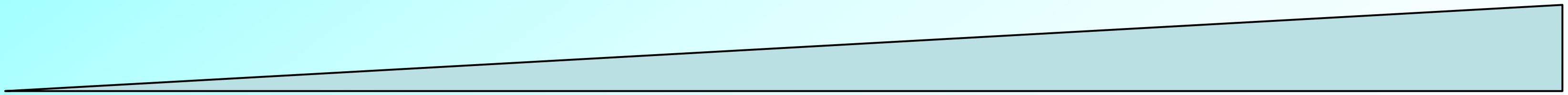


(Photo)-chemical degradation of the aerosol particle surface

Gas to particle conversion (heterogeneous condensation)

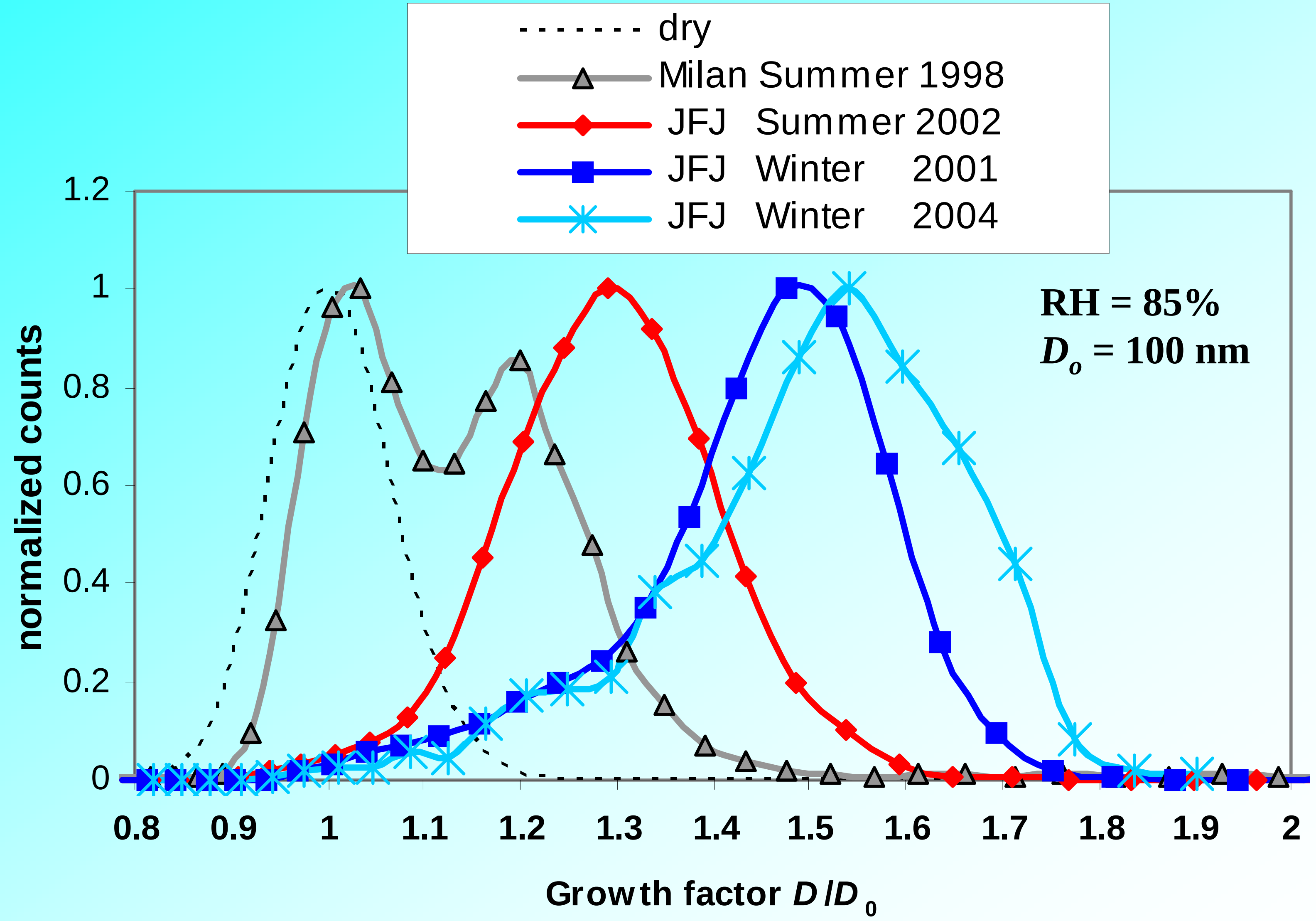
Coagulation with (dry) water soluble particles, e.g. $(NH_4)_2SO4$

Liquid phase reactions, immersion in solution droplets

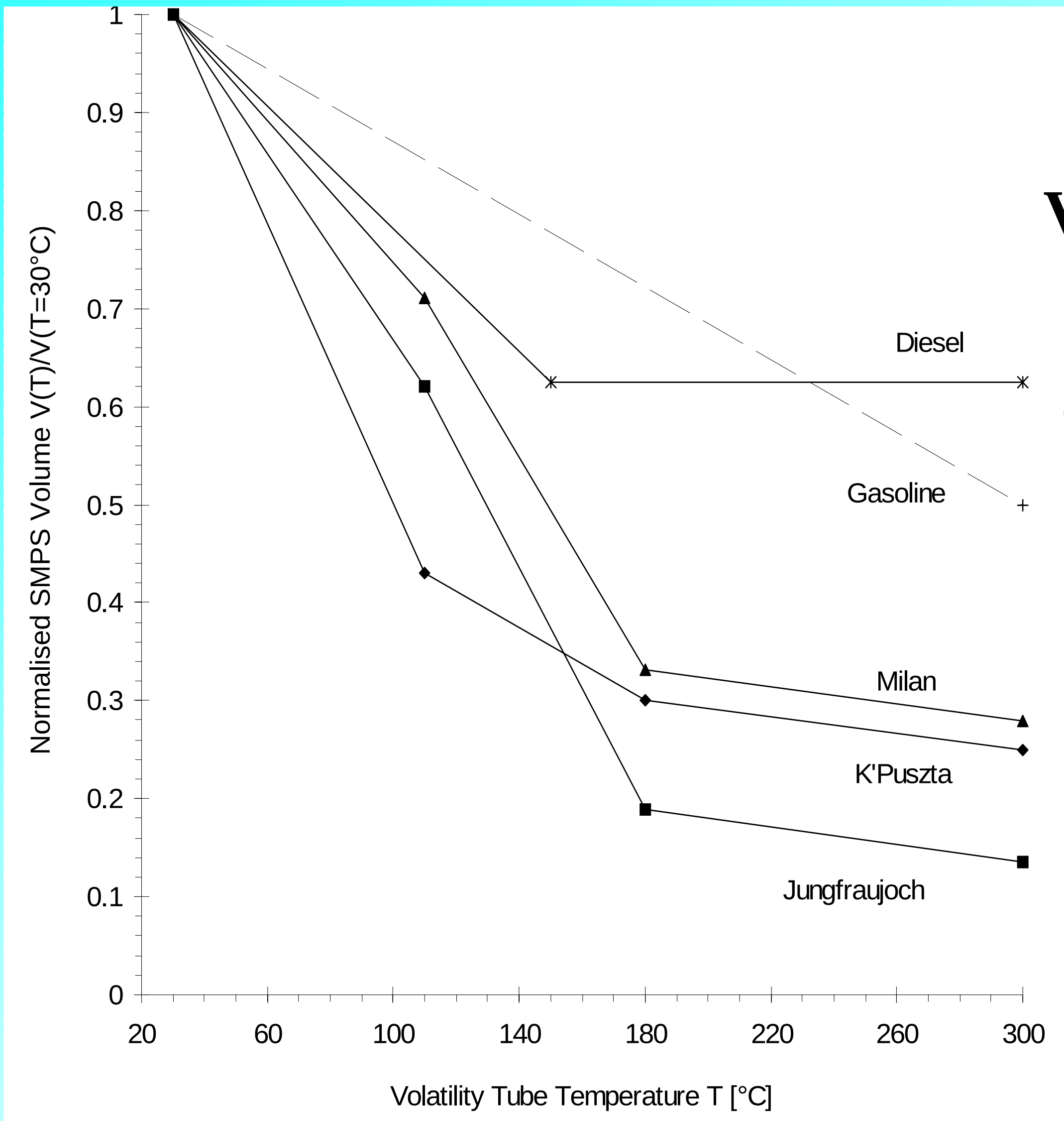


~2	**fractal like dimension, d_f**	**~3**
~1.01	**hygroscopicity,** D/D_o @ RH = 85%	> **1.4**
	light absorption efficiency	2-4 times higher

Hygroscopic Growth Factor of Aerosol Particles in Milano and at the Jungfraujoch



Aerosol volume experience a lower volatility close to the sources



Volatilization temperatures:

H_2SO_4 : ~90°C

Organics: 20 - ~400°C

$(NH_4)_2SO_4$ / NH_4HSO_4: 150°C

Soot: >300°C

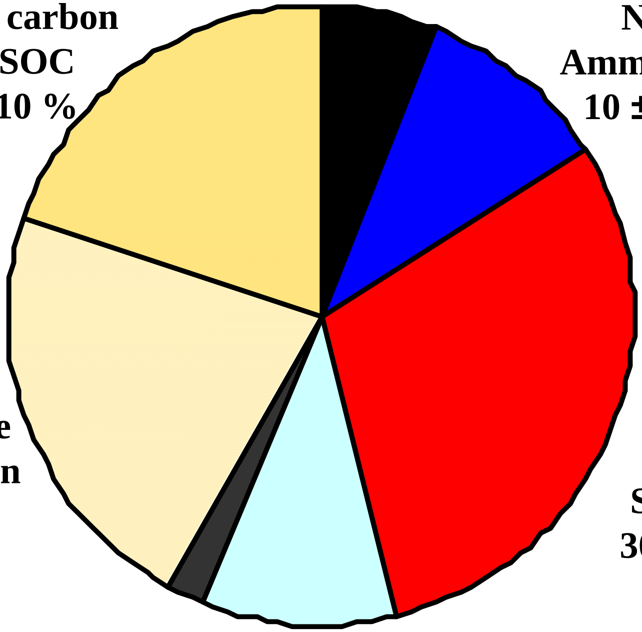
NaCl, Mineral dust: > 600°C

Burtscher et al., J. Aerosol Sci. (2001) 32, p427

Chemical composition of the Jungfraujoch aerosol during summer

Analyzed offline with IC, solid phase extraction combined with TOC Analyzer

Summer 1998, PM2.5, 8 High Vol Samples



Anthropogenic

EC
6 ± 1 %

Anthropogenic

NH_4
Ammonium
10 ± 4 %

SO_4
Sulphate
30 ± 13 %

Mainly anthropogenic
< 20% from natural sources

NO_3
Nitrate
10 ± 4 %

Mainly anthropogenic

other inorganic ions
2 ± 2 %

Water soluble organic carbon
WSOC
22 ± 6%

Water insoluble organic carbon
WINSOC
20 ± 10 %

Organic material: Predominatly from anthropogenic sources

Krivácsy et al. (2001)
J. Atmos. Chem, 39, p235

Absorption

What is the effect of coating on the absorption of carbonaceous particles?

PSI

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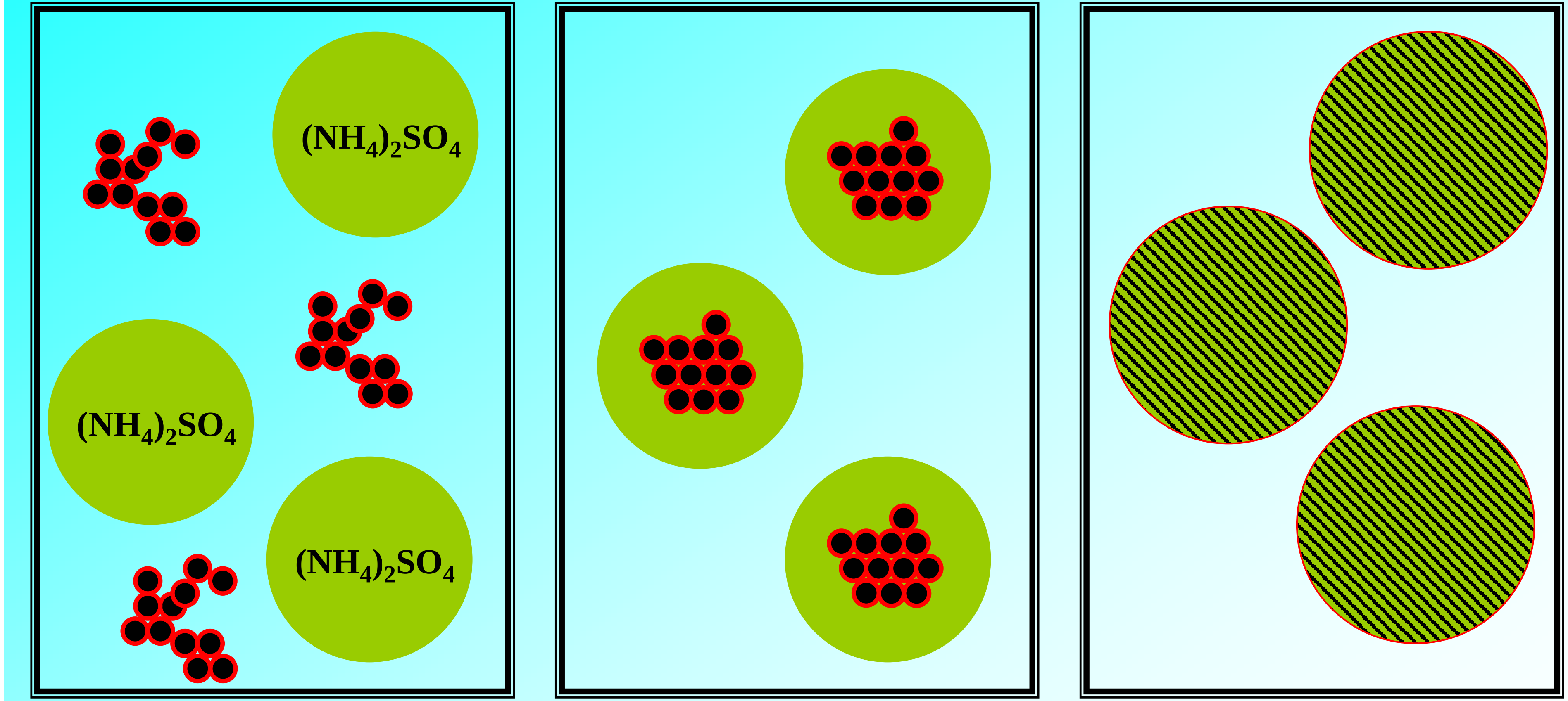
The mixing state is important!



External Mixture

BC particles are separated from scattering particles

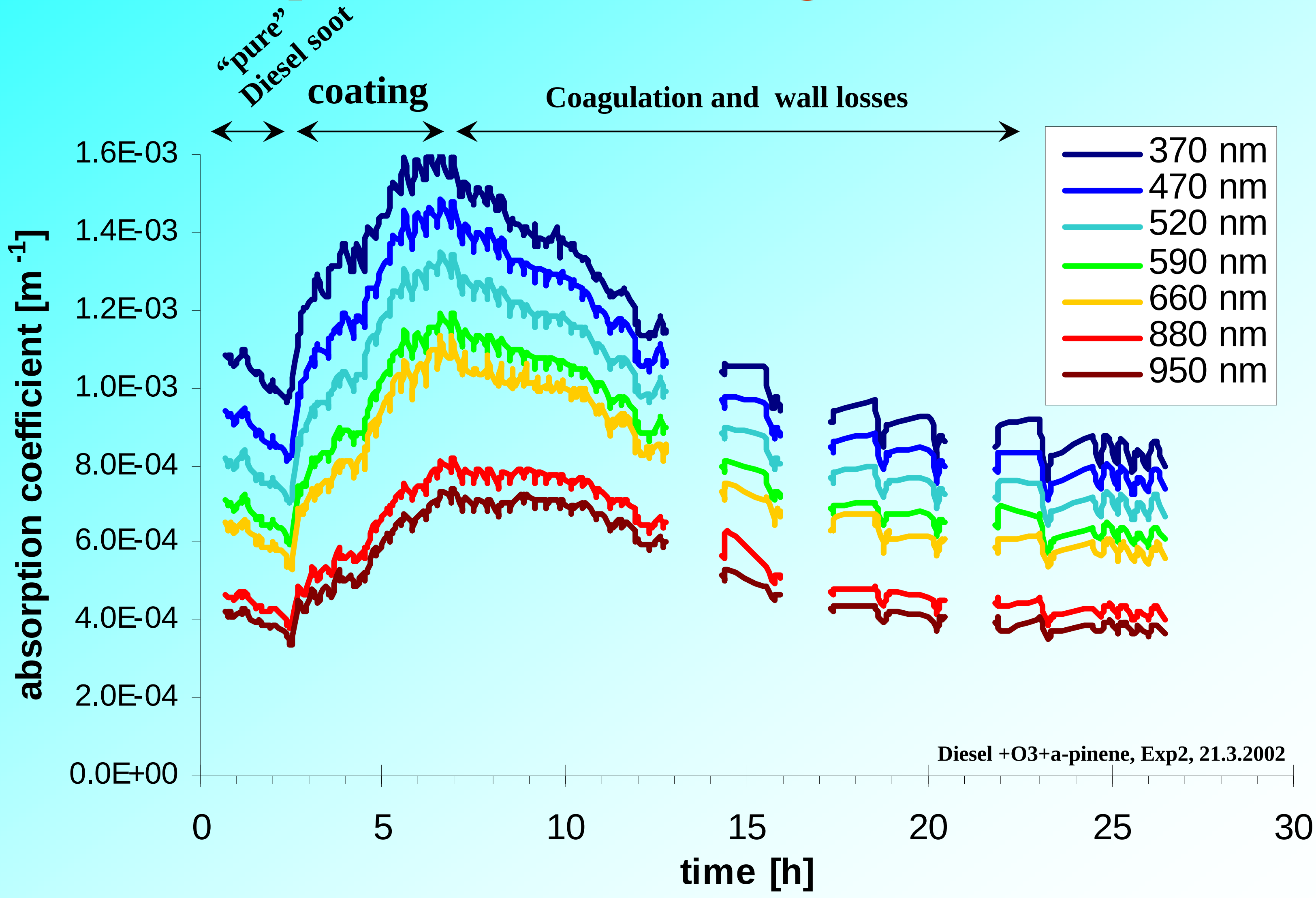
Coated Internal Mixture

BC particles are coated with a scattering material

Homogeneous Internal Mixture

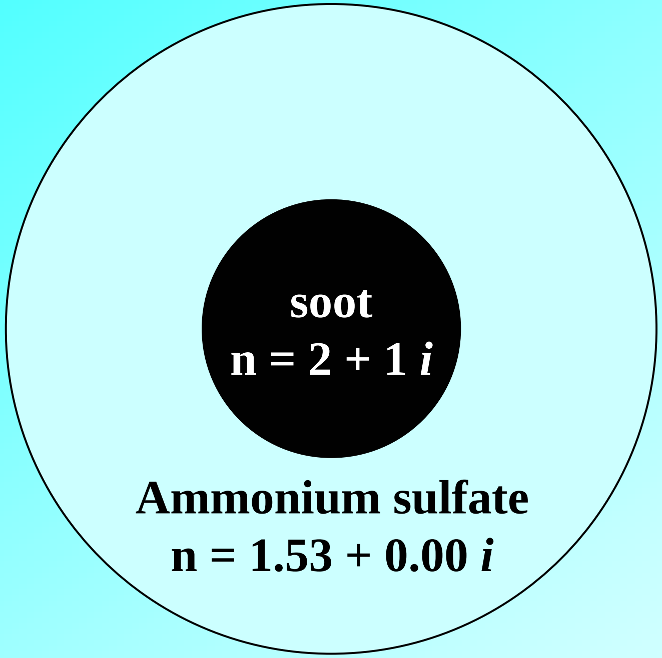
BC is mixed with scattering components throughout the particle

Enhancement of the absorption coefficient by coating Diesel soot particles with scattering material



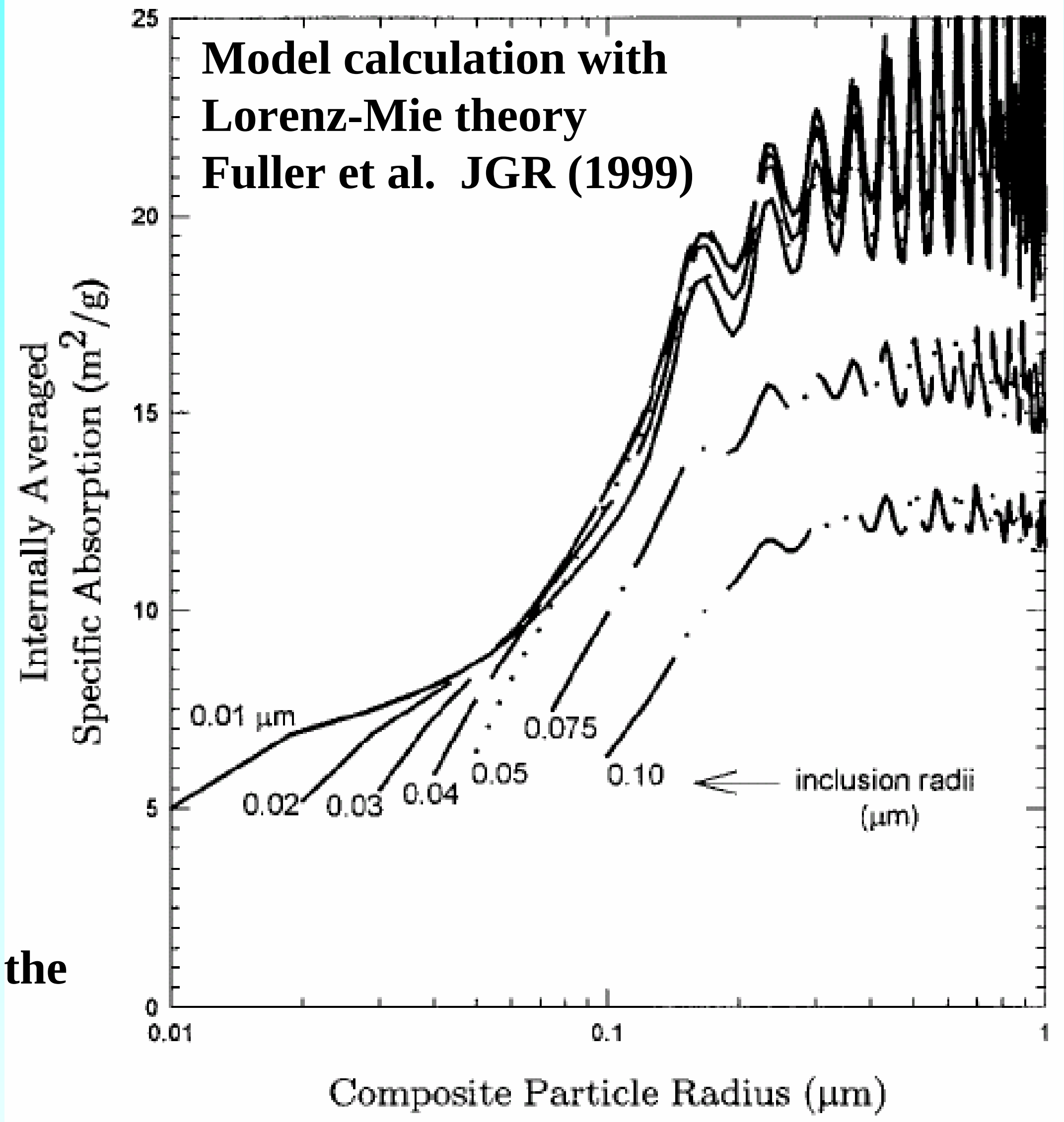
In collaboration with the AIDA crew, Forschungszentrum Karlsruhe

Encapsulating carbonaceous particles with scattering material results in enhanced absorption



soot
n = 2 + 1 *i*

Ammonium sulfate
n = 1.53 + 0.00 *i*



Model calculation with Lorenz-Mie theory
Fuller et al. JGR (1999)

Coating with ammonium sulfate:
up to a 4 times higher absorption for the mixed particle !

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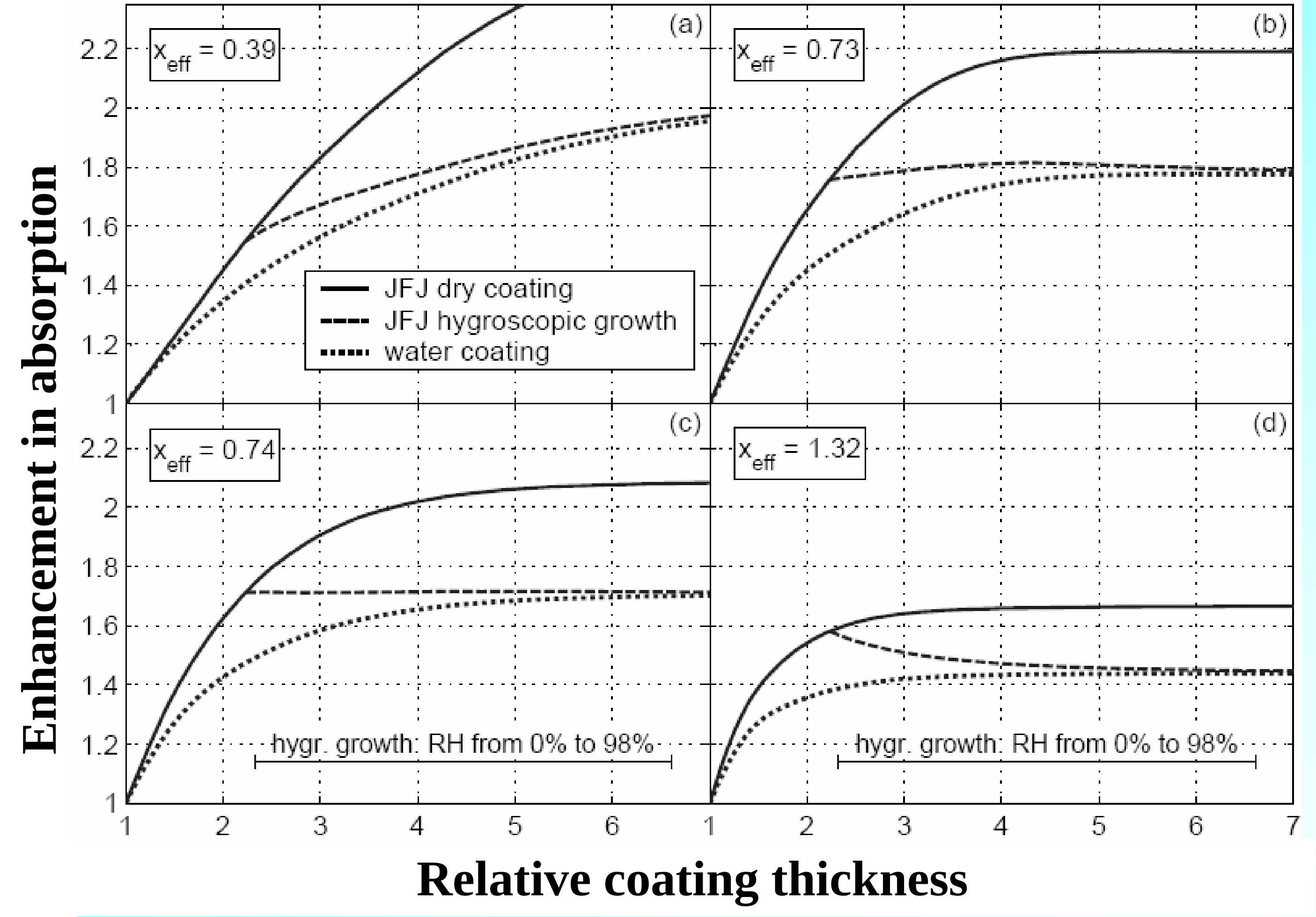
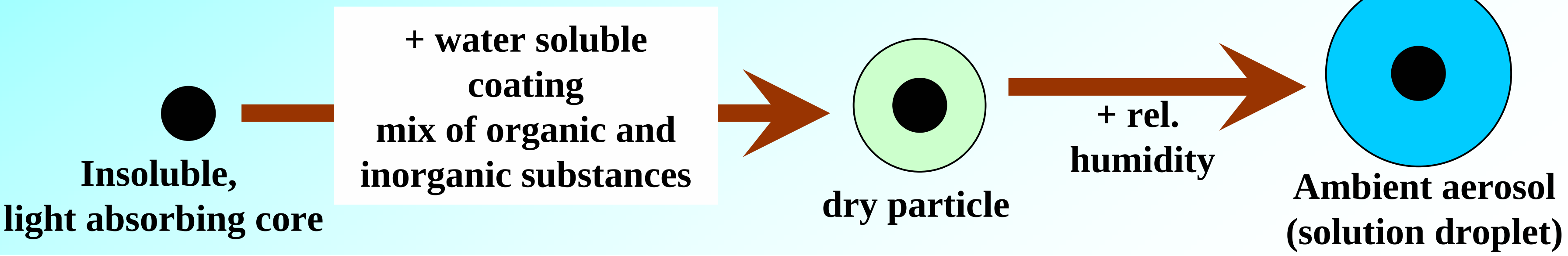
Model calculation for the conditions at the Jungfraujoch

(polydisperse size distribution and coating including the hygroscopic properties)



R. Nessler et al.,
Submitted to JAS
2004



Insolute,
light absorbing core

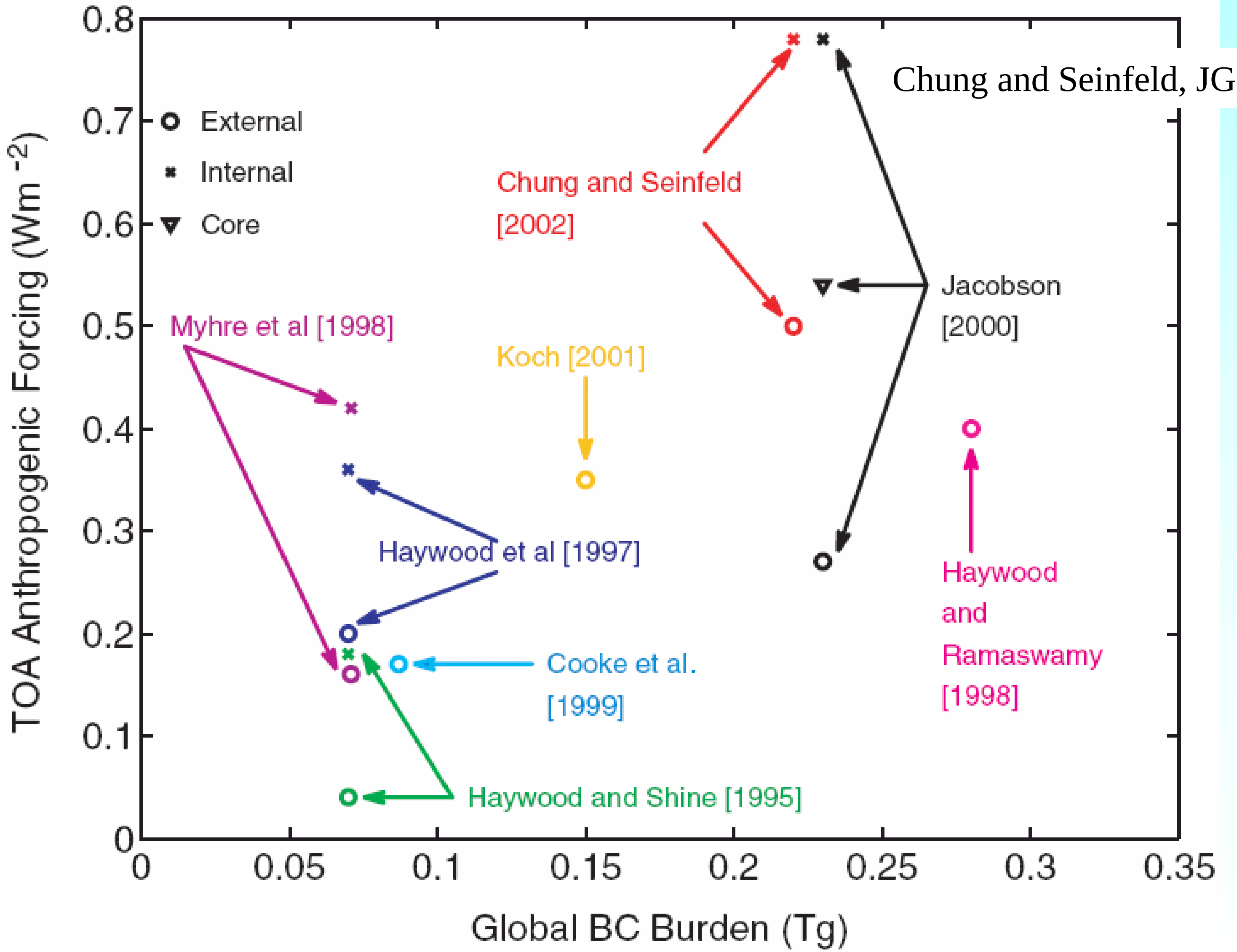
+ water soluble coating
mix of organic and inorganic substances

dry particle

+ rel. humidity

Ambient aerosol
(solution droplet)

Model results: radiative forcing of black carbon



Reasons for the uncertainties in the estimation of the radiative forcing of BC: different assumption about the mixing state and lack of a precise BC emission inventory

Conclusions

- Aging processes affect the hygroscopic behavior, the optical properties and the lifetime of the soot particles

- The mixing state of carbonaceous aerosol is important in determining its radiative effect.

- While freshly emitted soot particles are initially hydrophobic and externally mixed, they are transferred into an internal mixture by coagulation, condensation or photochemical processes.

Thank you for your attention !

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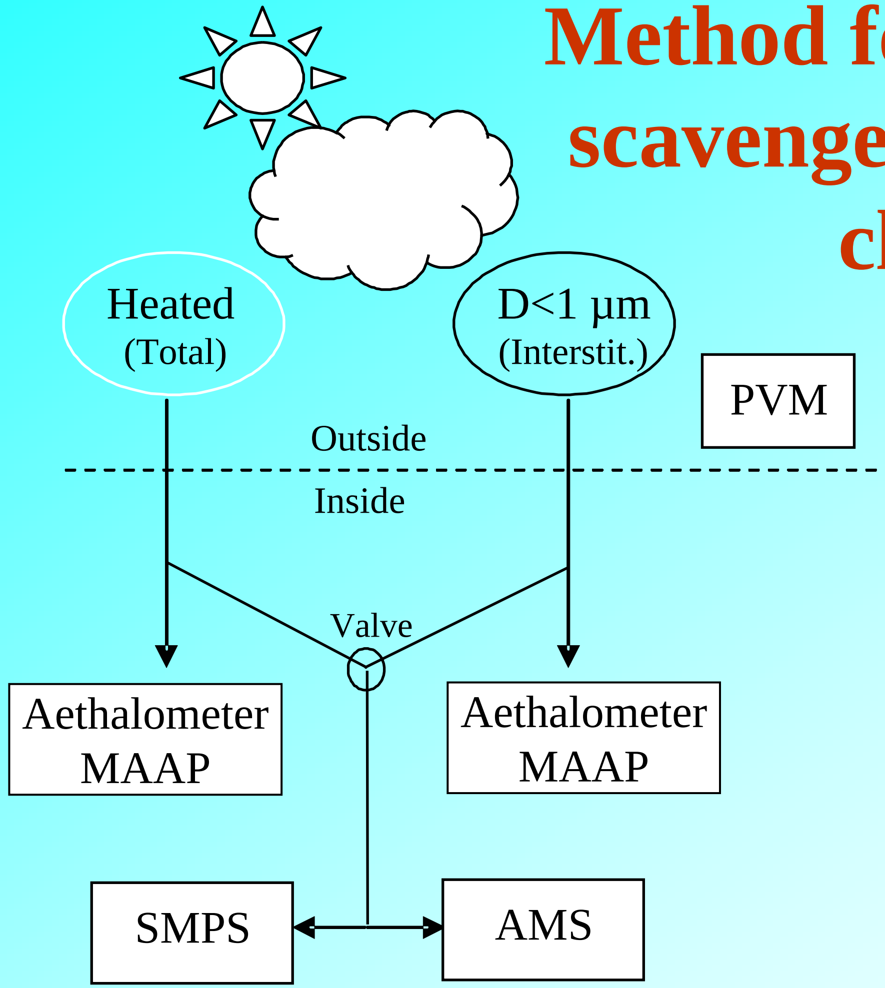
Method for measuring scavenged fraction in clouds



Heated (Total)

D<1 µm (Interstit.)

PVM

Outside

Inside

Valve

Aethalometer MAAP

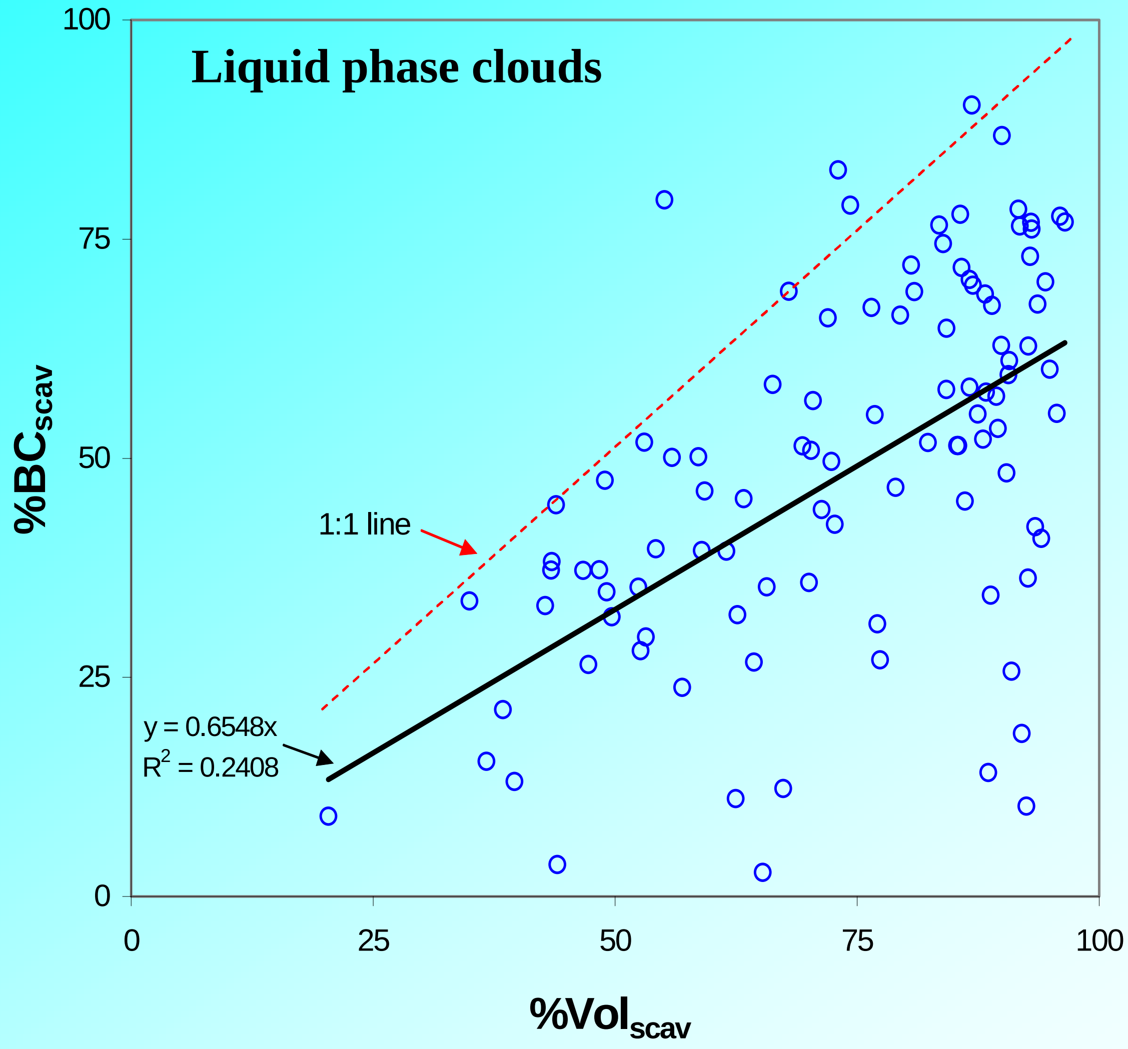
Aethalometer MAAP

SMPS

AMS

$$\text{Scavenging Ratio} = \frac{N_{cloud}}{N_{total}} = \frac{N_{TOT} - N_{INT}}{N_{TOT}}$$

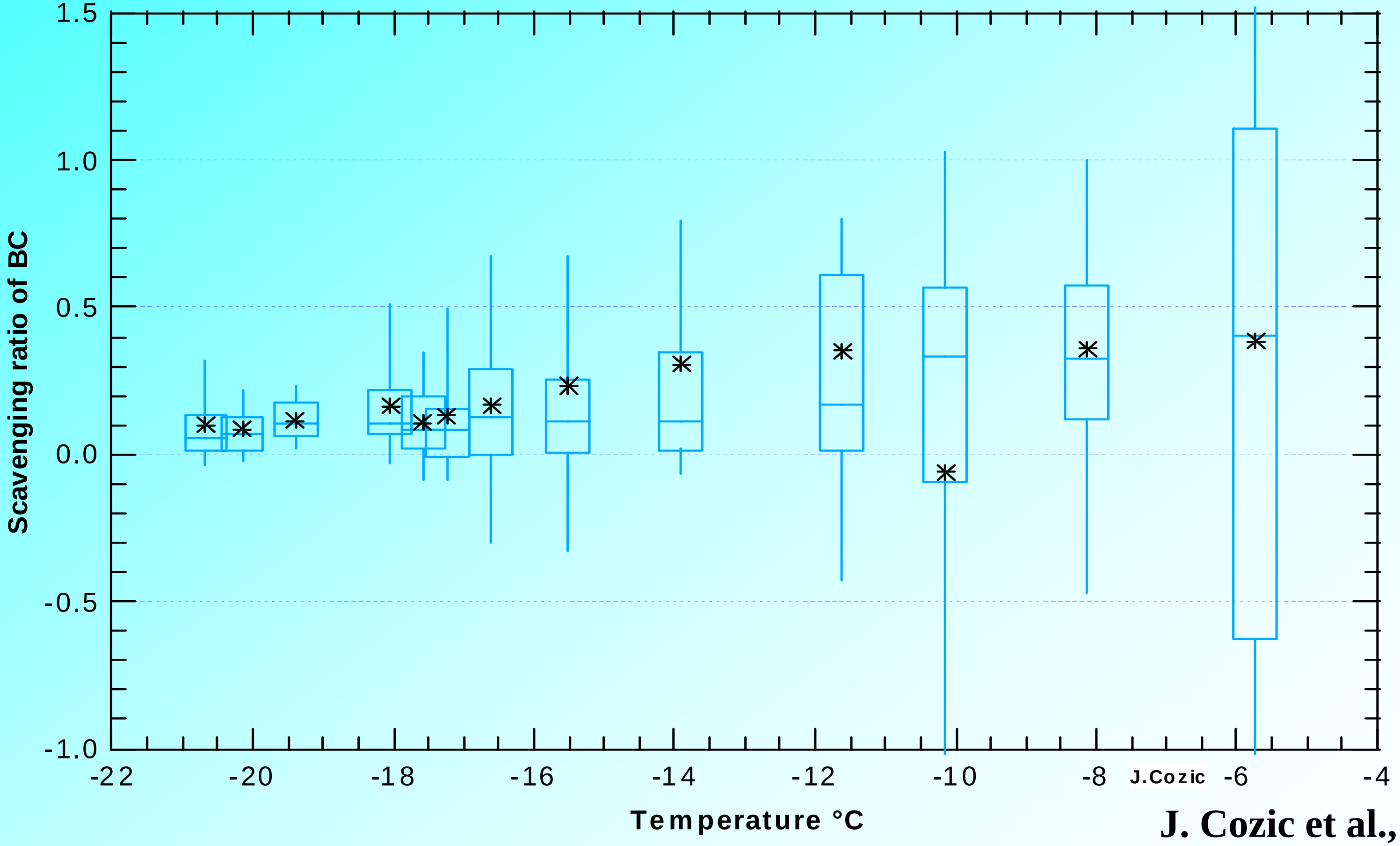
Correlation of Scavenged BC and (SMPS-)Volume in Summer (CLACE 2)



In Summer, on average, 48% of the total BC concentration is present in the cloud phase (i.e. is activated to cloud droplets)

Winter data (CLACE3) is different!

Winter data: The fraction of activated BC decreases with temperature.



J. Cozic et al., 2005

-> BC activation in mixed phase clouds is different!

Bergeron/Findeisen-Process