Change of Physical and Chemical Properties of Soot Particles by Aging Processes 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 an OC). Besides the soot mode at a diameter of about 100 nm a second mode is clearly seen in traffic-influenced areas, with a mode around 20 to 30 nm (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 processes result in a significant change of the chemistry of these soot particles.

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. Hygroscopicity measurements with a tandem differential mobility analyzer (Weingartner *et al.,* 2002) are a highly suitable means for the determination of the growth factor (i.e., the diameter d for a specified high relative humidity RH divided by the dry diameter, d_0).

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.*, 1997, Baltensperger *et al.*, 2002). Under these conditions, the growth factor can be attributed to the amount of water soluble inorganic species adsorbed on the soot particles (Weingartner *et al.*, 1997). At moderately high sulfur content of the fuel this mainly corresponds to sulfate (Gysel *et al.*, 2002).

After aging, i.e., at a remote site such as the Jungfraujoch in the Swiss Alps (3580 m asl), the soot particles are most probably internally mixed with a high fraction of water soluble material (typically 80 to 90%), which results in a monomodal distribution of the growth factor, with growth factors of 1.55, 1.62, and 1.67 for d_o = 50, 100, and 250 nm, respectively, at RH=90% (Weingartner *et al.*, 2002). Typically 50% of the organic carbon of this aged aerosol is water soluble (Krivacsy *et al.*, 2001).

A number of processes may contribute to this increased growth factor, including coagulation with water soluble particles, gas to particle conversion (heterogeneous nucleation), adsorption and reaction of gaseous molecules, (photo)-chemical degradation of the aerosol particle surface, and 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 with diesel soot (Gutzwiller *et al.,* 2002 and references therein). Processes of this type may be responsible for an increased hygoscopicity on aging diesel soot particles in a dark bag (Weingartner *et al.,* 1995). (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 (E. Villenave, pers. communication), 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. However, for this process the particles require a certain size to be activated during cloud formation (Henning *et al.,* 2002).

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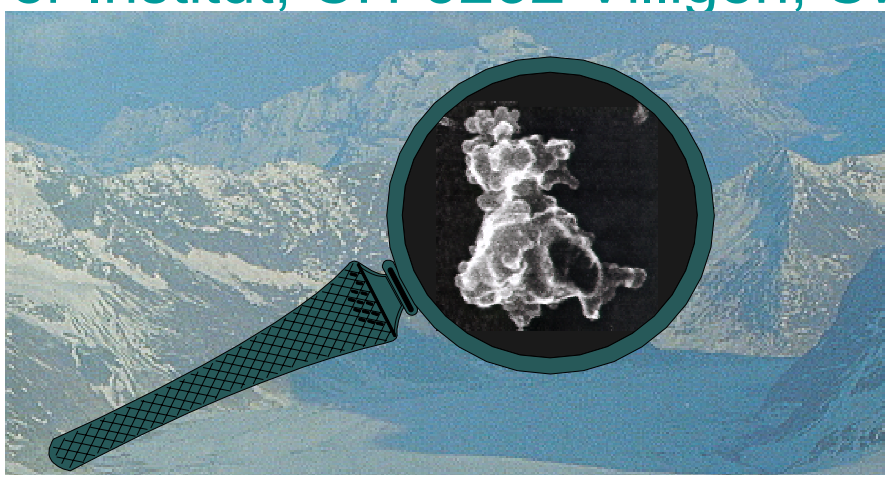
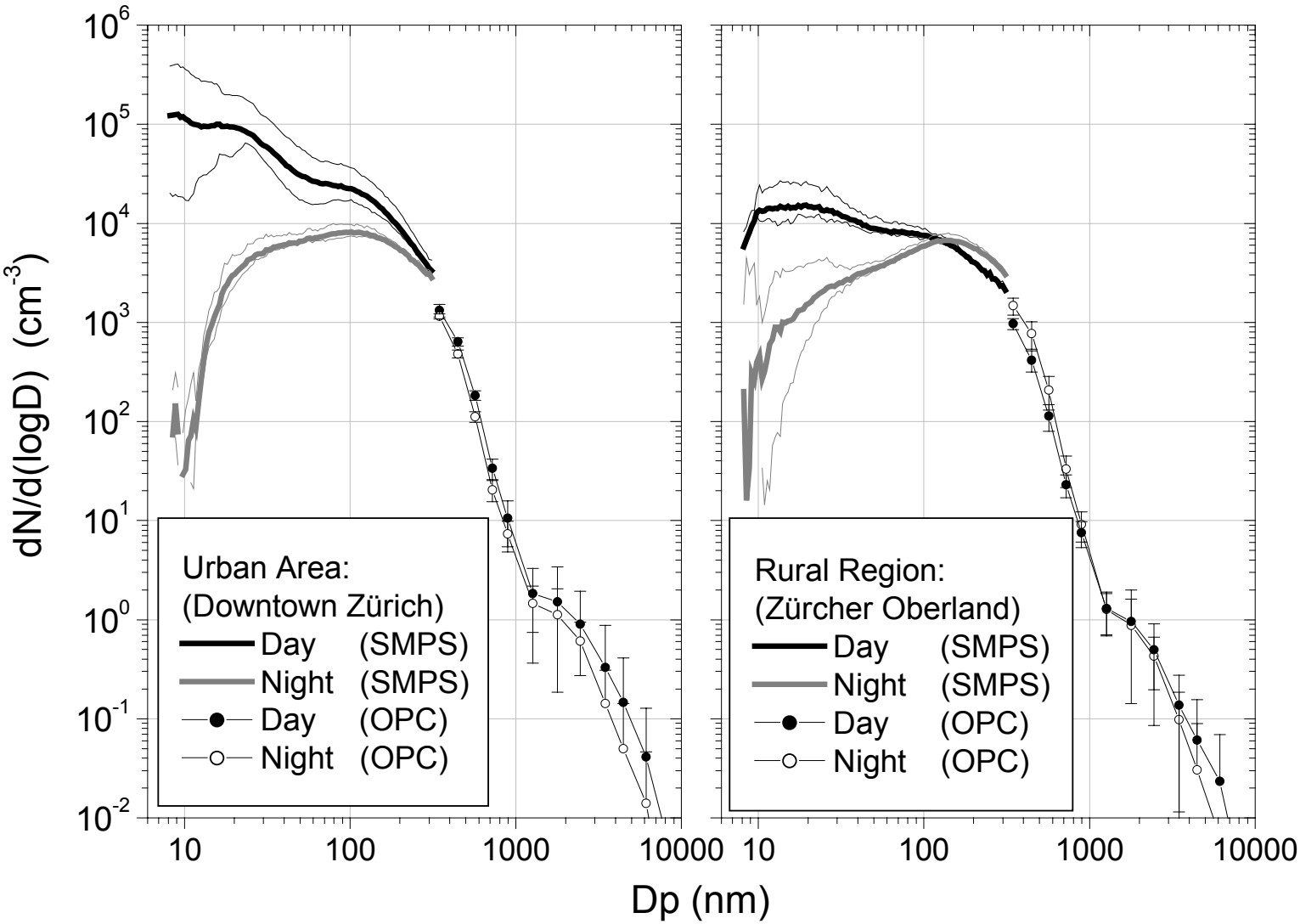


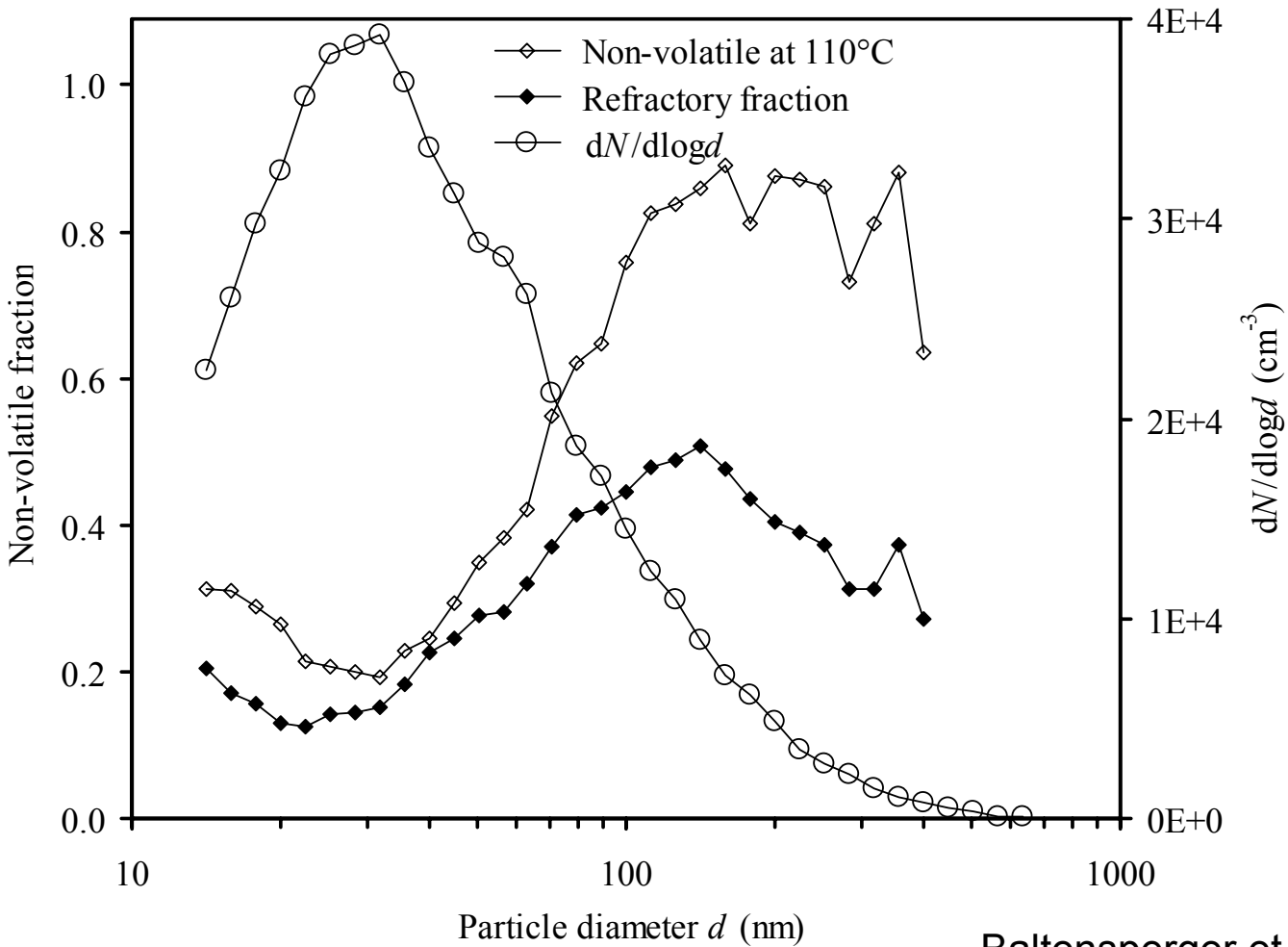
6th ETH Conference on Nanoparticle Measurement,

Zurich, 19 to 21 August, 2002

Aerosol size distributions in the Zurich area

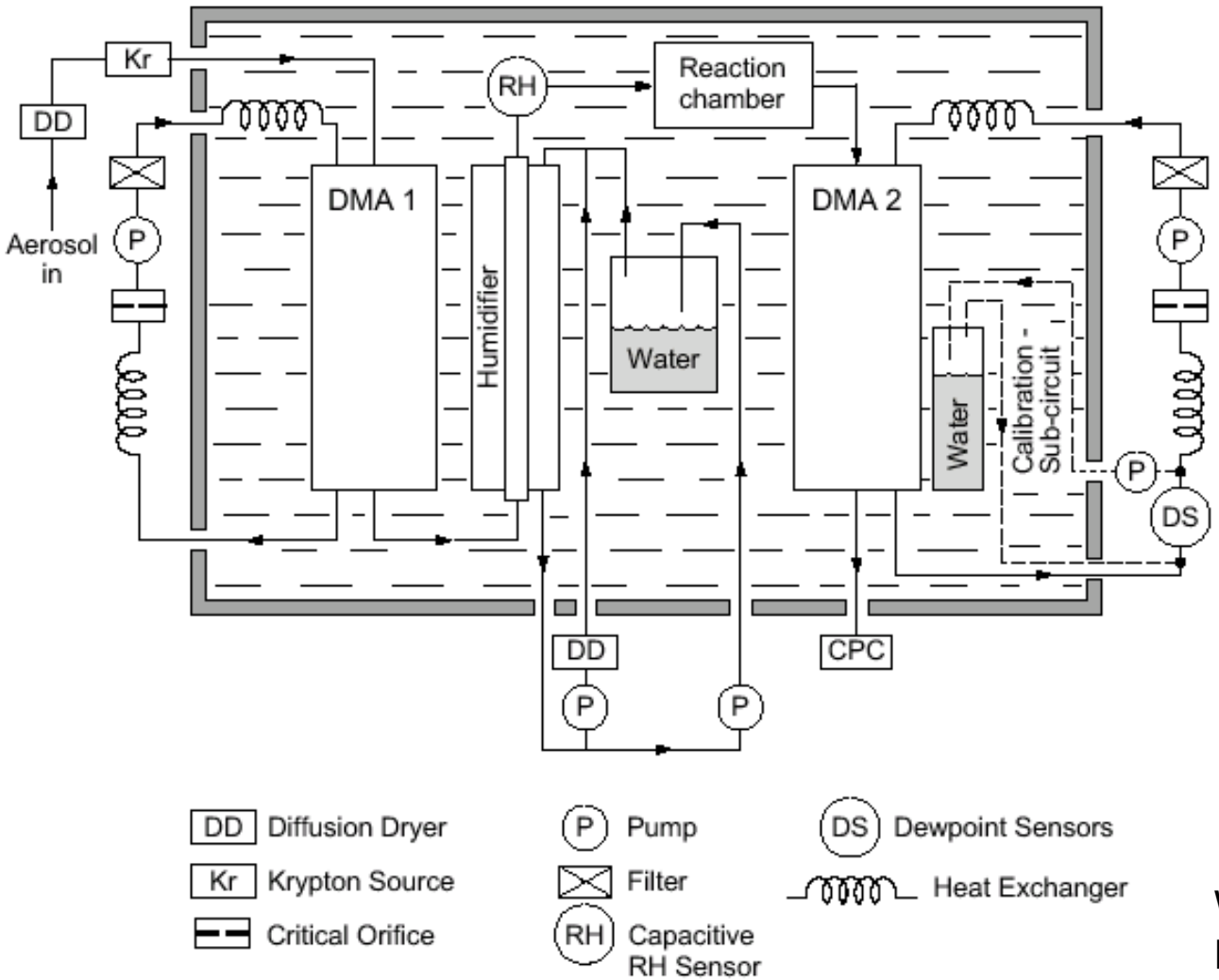


Size distribution and non-volatile fraction of traffic aerosol in Milan



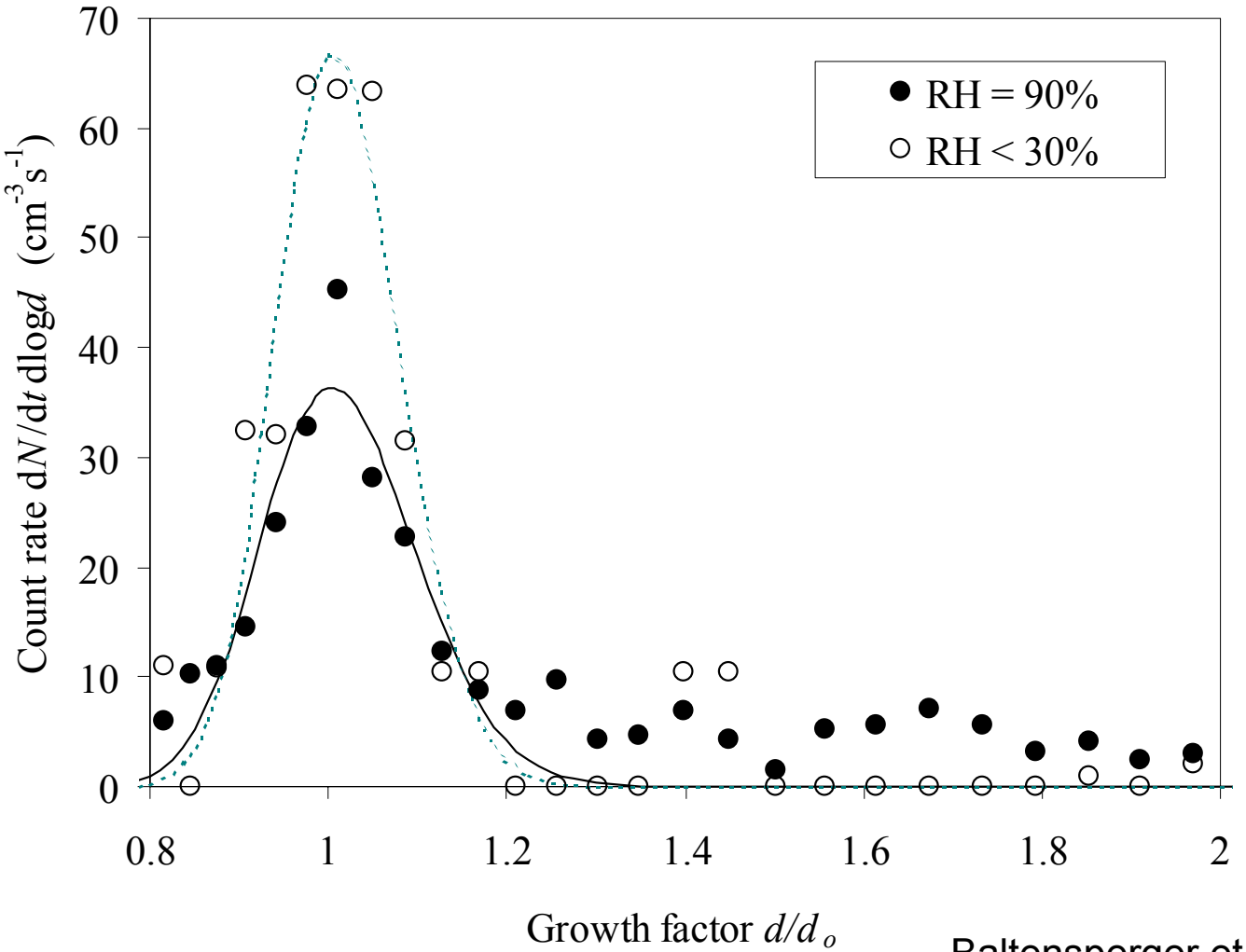
Baltensperger et al., JGR (2002)

Setup of the Hygroscopicity Tandem DMA



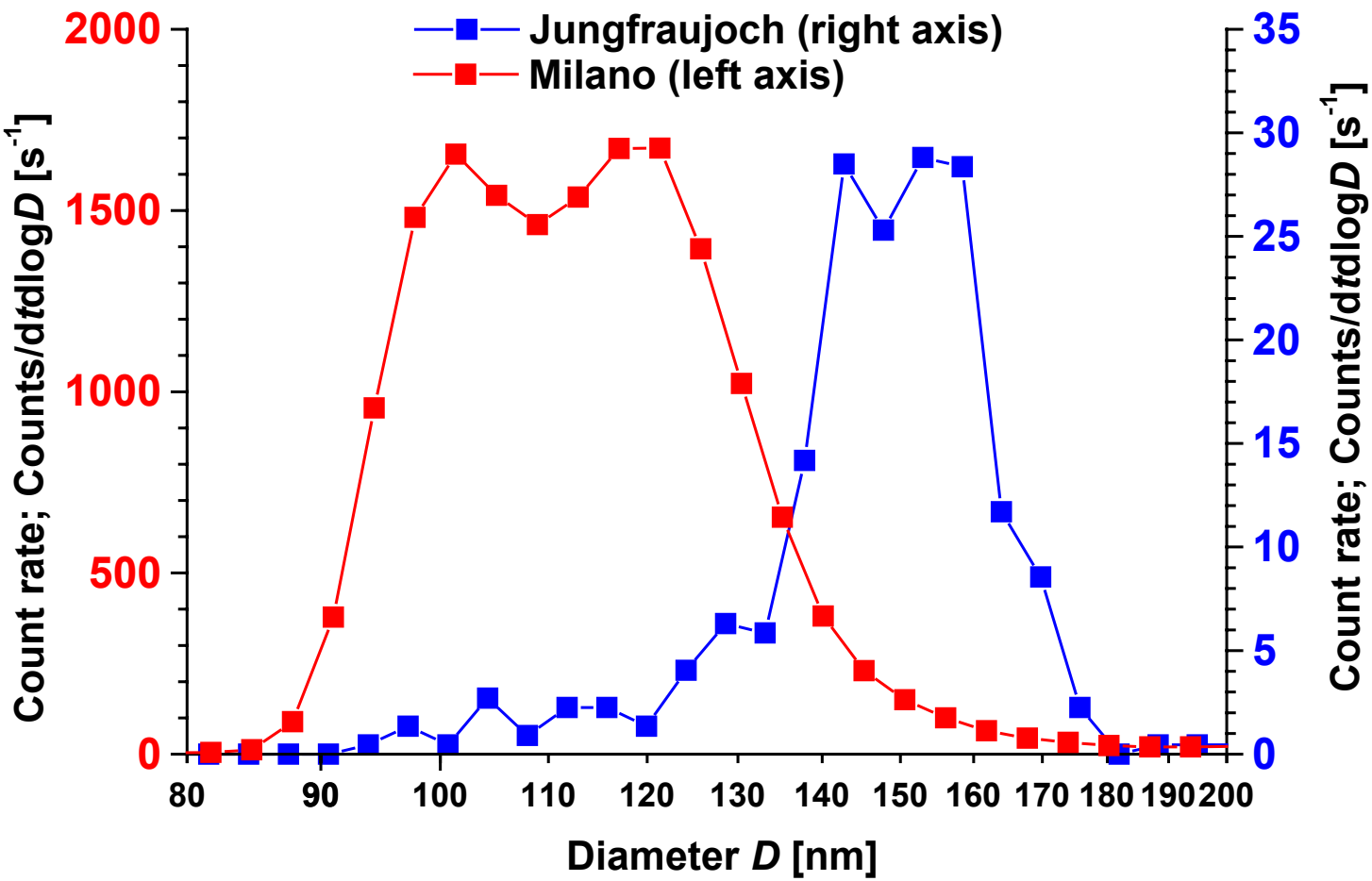
Weingartner et al., ES&T (2002)

Hygroscopic growth factor of 20-nm particles in Milan



Baltensperger et al., JGR (2002)

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



Possible reasons for increasing hygroscopicity with aging time

- Coagulation with water soluble particles
- Gas to particle conversion (heterogeneous nucleation)
- Adsorption and reaction of gaseous molecules
- (Photo)-chemical degradation of aerosol particle surface
- Cloud processing

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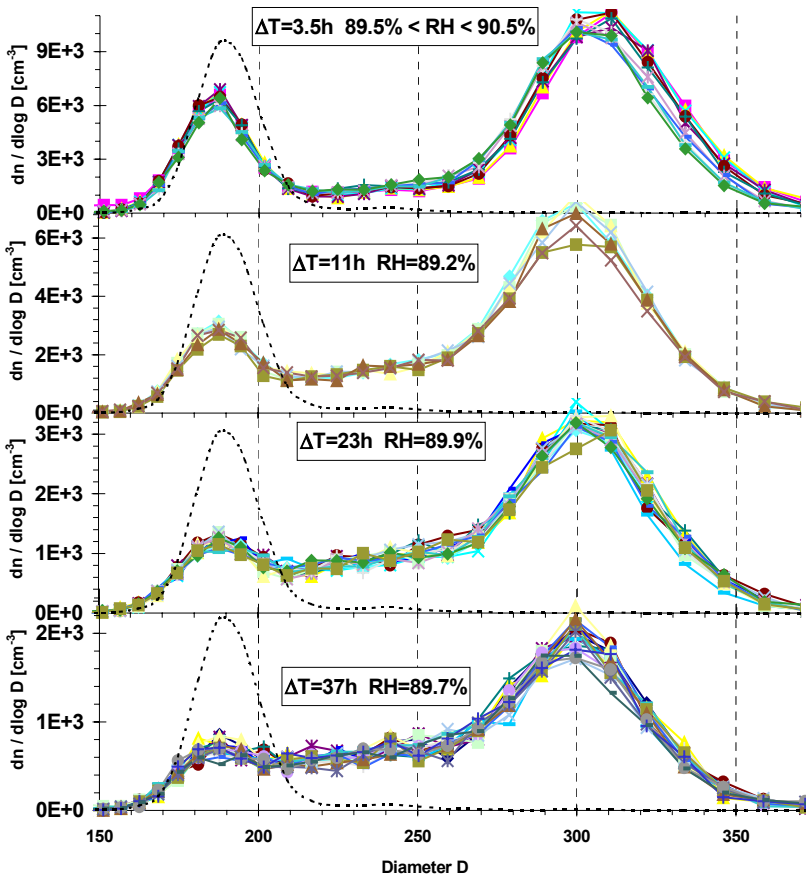
HTDMA size spectra of a mixture of Diesel and $(NH_4)_2SO_4$ aerosols

After drying, 190-nm particles are selected and exposed to high RH



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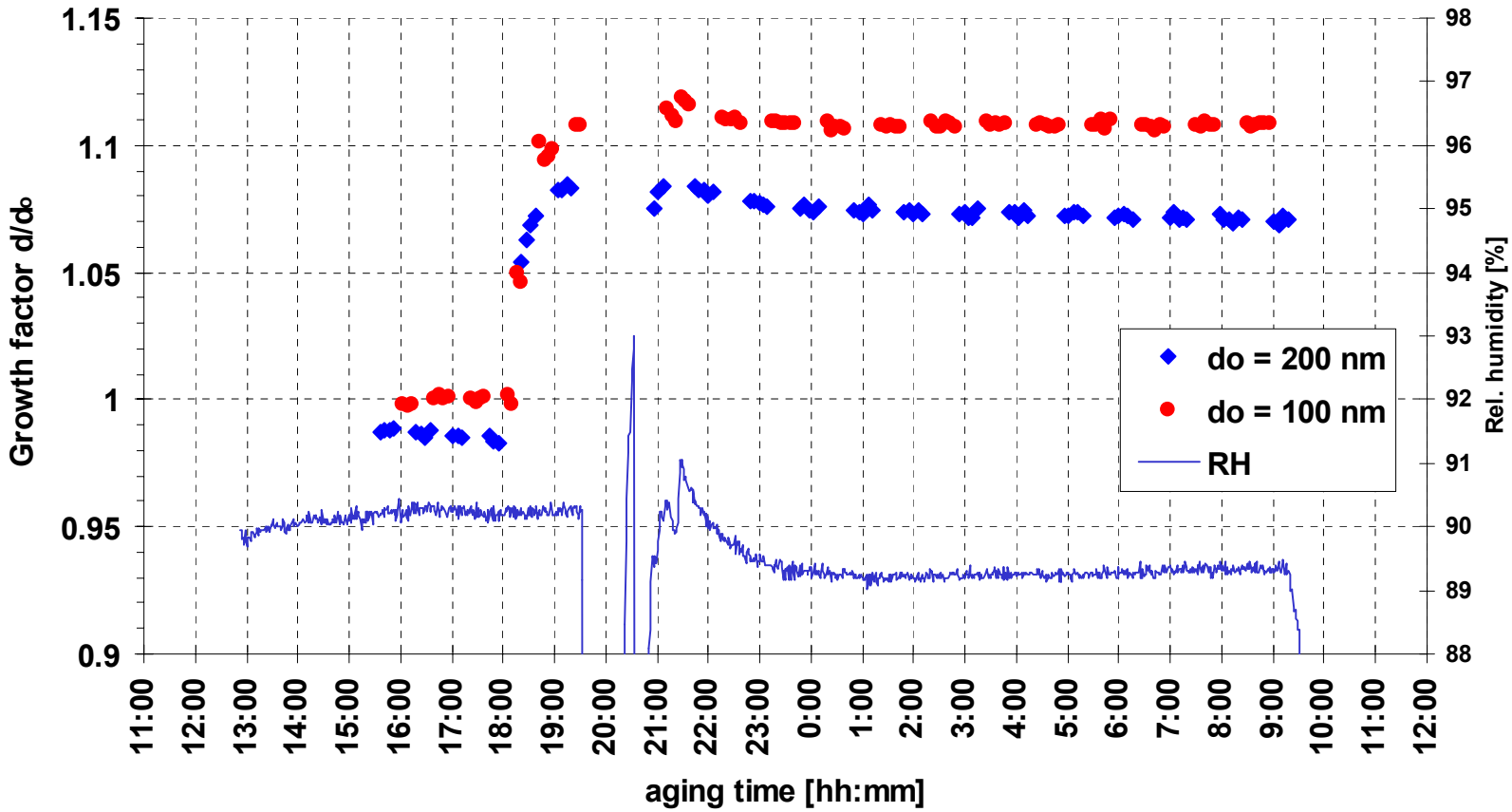
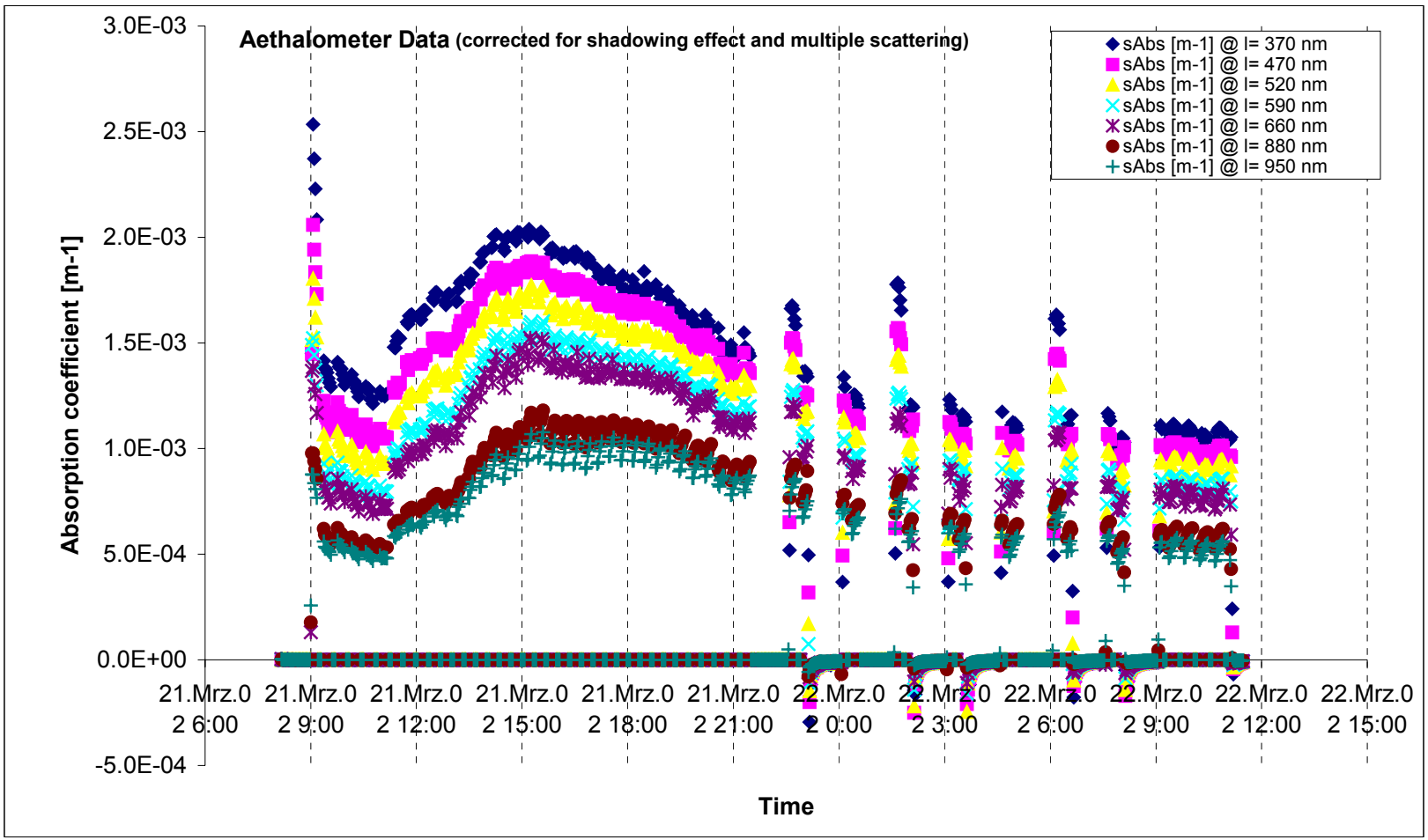
Change of the hygroscopic growth factor of Diesel soot by condensation of oxidation products of α-pinene



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



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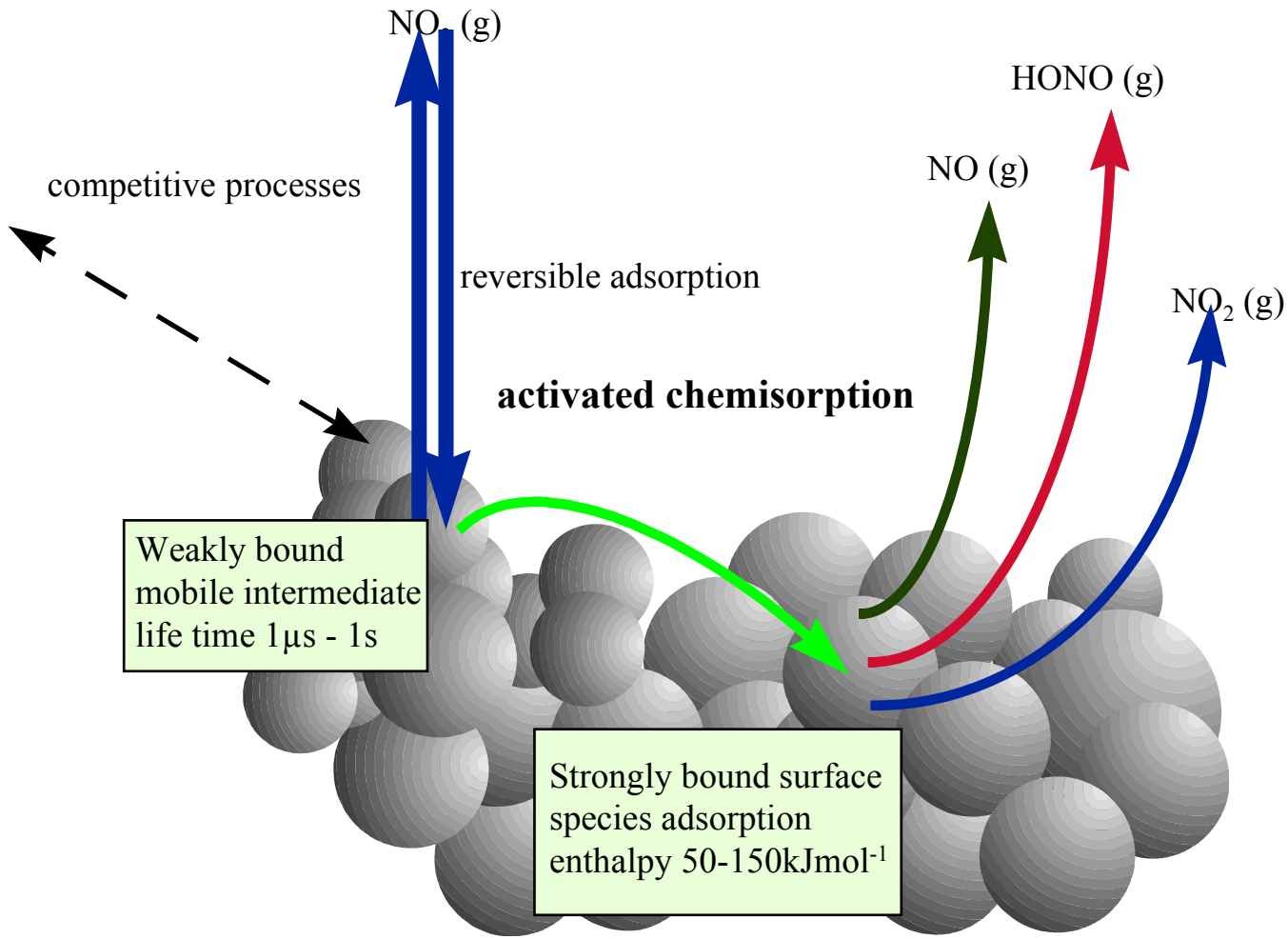
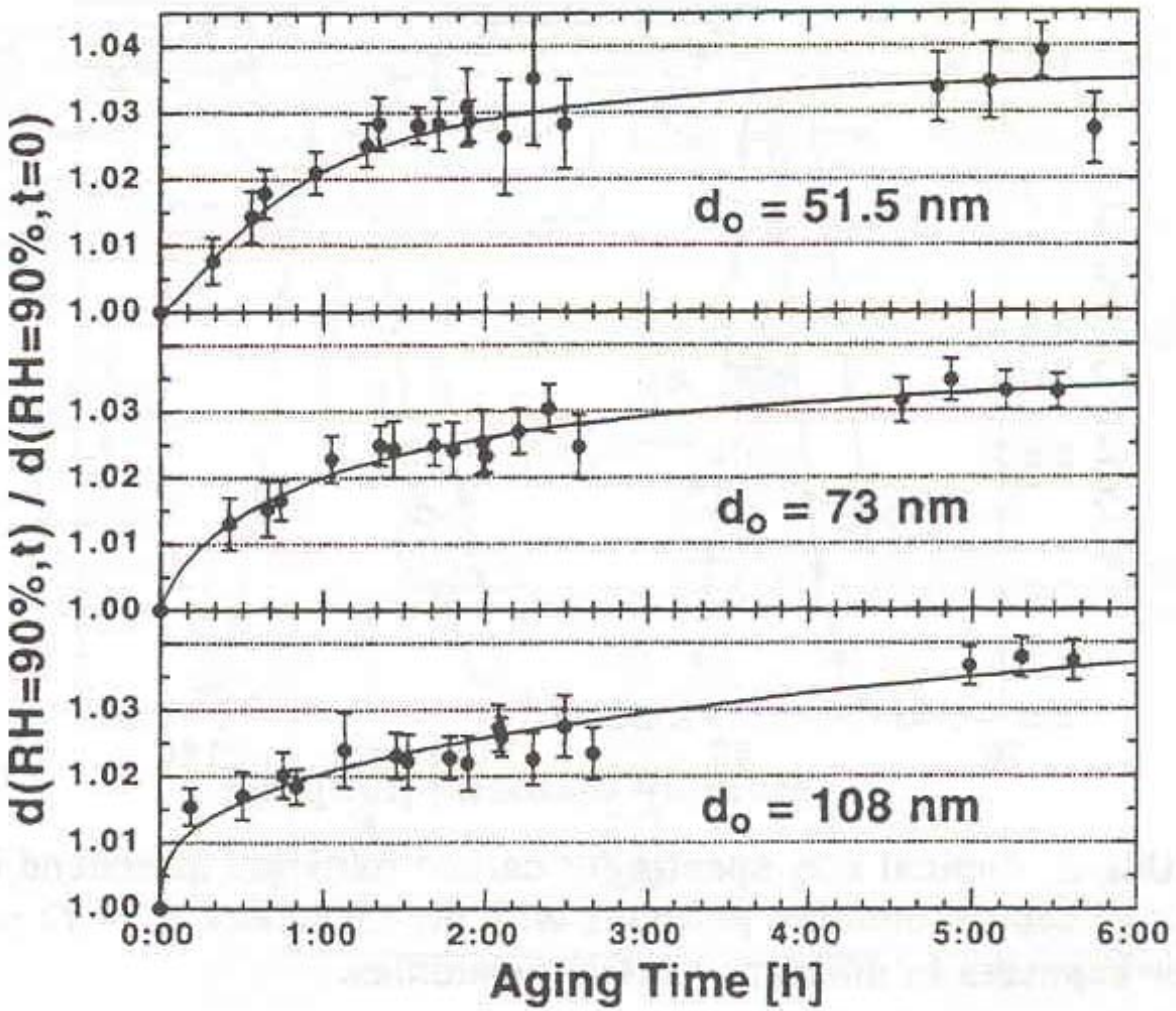
Adsorption and reaction of aerosol particle surface: Reaction of NO_2 with diesel soot



Relative increase of the growth factor of soot particles on aging in a dark bag



Weingartner et al., ES&T (1997)

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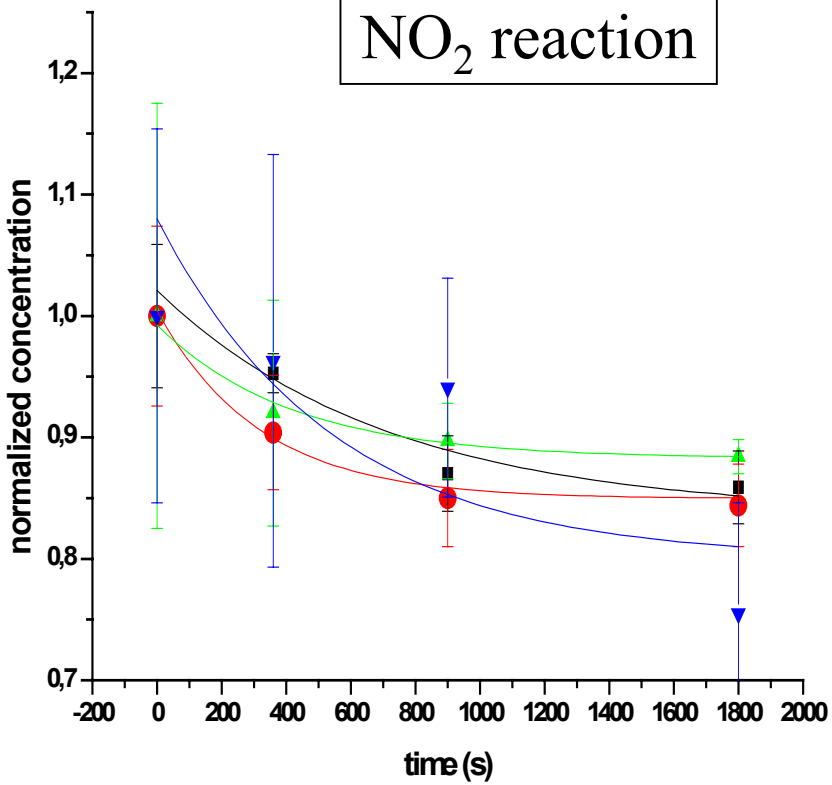
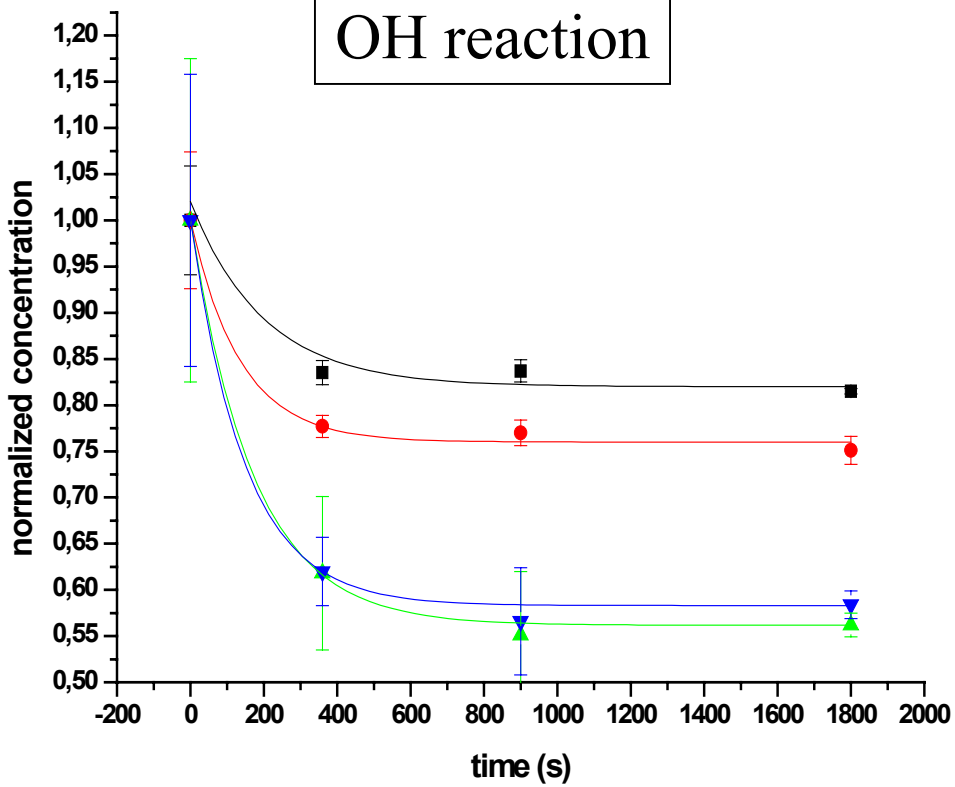
KINETICS OF REACTIONS OF PAHs IN DIESEL EXHAUST PARTICLES (SRM 1650a)

NO_2 reaction



OH reaction



Phenanthrene *Pyrene* *B(e)P* *B(a)P*

Eric Villenave, Univ. Bordeaux

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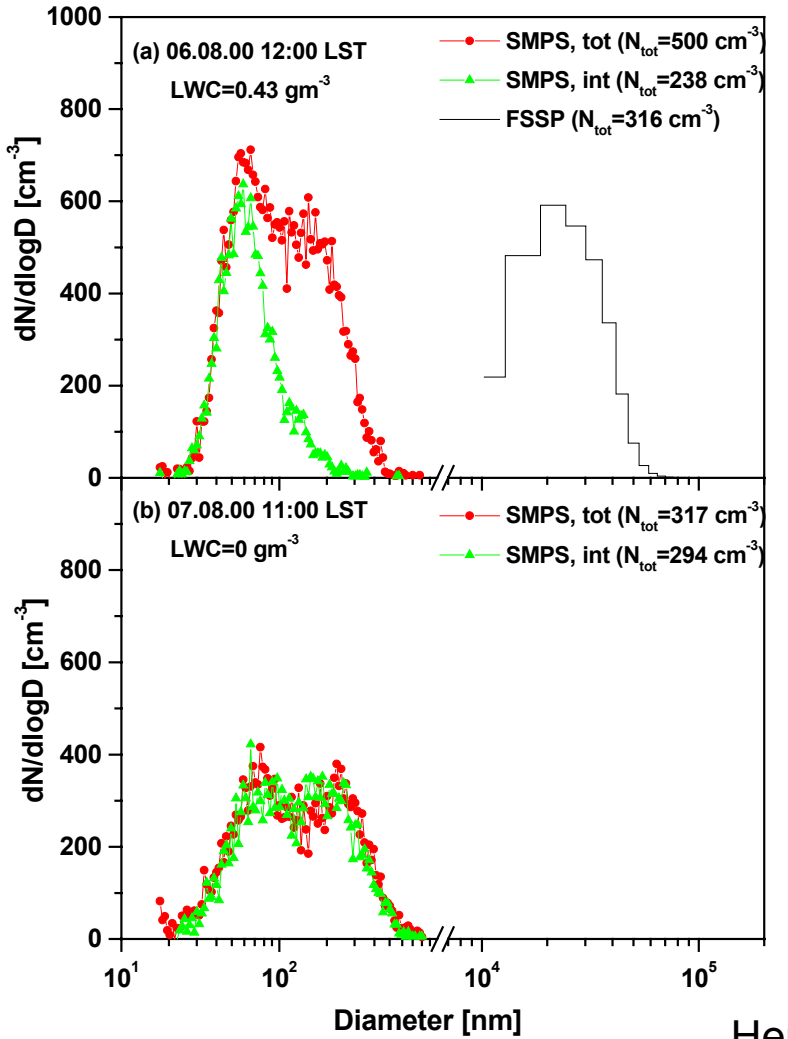
Cloud processes



Henning et al., Tellus (2002)

Conclusions

- Aging processes transform soot from an external to an internal mixture
- Major changes of soot characteristics by condensation and cloud processes
- Changes reflected in changes of hygroscopicity, optical properties, etc.
- Surface reactions may also change gas phase chemistry

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