Transformation from hydrophobic to hygroscopic diesel soot particles by photochemical aging

T. Tritscher[1], R. Chirico[1], Z. Juranyi[1], M. Martin[2], M.F. Heringa[1], M. Gysel[1], B. Sierau[2], P.F. DeCarlo[1], J. Dommen[1], A.S.H. Prevot[1], E. Weingartner[1], U. Baltensperger[1]

[1] Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[2] Institute for Atmospheric and Climate Science, ETH Zürich, 8092 Zürich, Switzerland

Combustion emissions from natural or anthropogenic sources contribute in several areas to an important fraction of the total aerosol mass. They are a complex mixture of black carbon (BC), organics, and other compounds in the gas and particle phase. The indirect aerosol effects of BC are relevant for aerosol-cloud-interaction and lifetime and thus for the global climate. In global modeling BC is categorized in hydrophobic and hydrophilic, but the fraction of particles in each category is quite difficult to quantify. A particle is called hydrophobic, if it is non-wettable and therefore cannot act as cloud condensation nuclei (CCN) at typical supersaturation in ambient clouds. Hydrophobic particles are always non-hygroscopic. Hydrophilic particles are hygroscopic, if they can take up water at elevated RH, otherwise they are considered to be non-hygroscopic.

The hygroscopicity and the CCN activation of diesel exhaust particles were measured during experiments at the PSI smog chamber with a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) at 95% relative humidity (RH) and a Cloud Condensation Nuclei Counter (CCNC) at RH between 100.1-101.3%. The ratio of wet particle mobility diameter (D(RH)) to dry mobility diameter (D_0) is called hygroscopic growth factor (GF). The measurements were complemented by further gas and aerosol instrumentation. Diesel exhaust from different passenger cars was introduced via heated injection system into the chamber. After characterizing the primary emissions, the 4 xenon arc lamps in the chamber were turned on to start photochemical aging.

Fresh soot (BC and primary organic aerosol (POA)) is known to form nm-sized fractal like aggregates. In the course of the experiments these primary soot particles were coated with secondary organic aerosol (SOA) mass. The organic mass concentration was measured with the Aerosol Mass Spectrometer (AMS).

HTDMA and CCNC were measuring the same dry diameter to allow for a direct comparison. The top right plot in Figure 1 shows the temporal evolution of GF during a typical aging experiment. The GF is 1 in the beginning; i.e. the aerosol is non-hygroscopic. The corresponding CCN activation plots show no CCN activation even at supersaturation above the level for wettable, but non-soluble particles with D_0=200 nm (dotted line). The fresh soot particle age with time and SOA is formed and condenses on the particles. The CCN activation plot shows an activation just of a small fraction (not 100%), meaning there are still hydrophobic, non-wettable particles in the chamber, but also already some wettable (hydrophilic) particles, which are activated as CCN. This means that the aerosol is externally mixed. After several hours of aging the aerosol particles are all hydrophilic and activate as CCN.

Figure 2 conceptually illustrates the observed findings. The first row shows the fresh soot emissions. They are hydrophobic as they do not activate as cloud droplets even at high supersaturations like non-hygroscopic but wettable, insoluble particles do. In the first column the soot aggregate is shown under dry conditions (GF=1 by definition), the SOA coating appears after lights were turned on and its thickness increases with photochemical aging time. Slightly aged particles were found to be CCN-active and thus they are hydrophilic. However, the GF of the H-TDMA was <1, indicating a shrinking of these particles. This restructuring

was confirmed with a pre-humidifier, which makes the particles compact and less fractal in front of the H-TDMA. The magnitude of the restructuring effects is dependent on the photochemical aging time and on the particle size. Continued aging of diesel exhaust leads to CCN-active particles with a GF >1, indicating the hygroscopicity of these particles.

The hygroscopicity of the diesel aerosols from the passenger cars was generally very low, but the difference to the non-hygroscopic and even hydrophobic particles in the beginning was clearly observed. Our measurements show that photochemical aging with SOA formation can change a hydrophobic (non-wettable) soot particle into a hygroscopic particle.

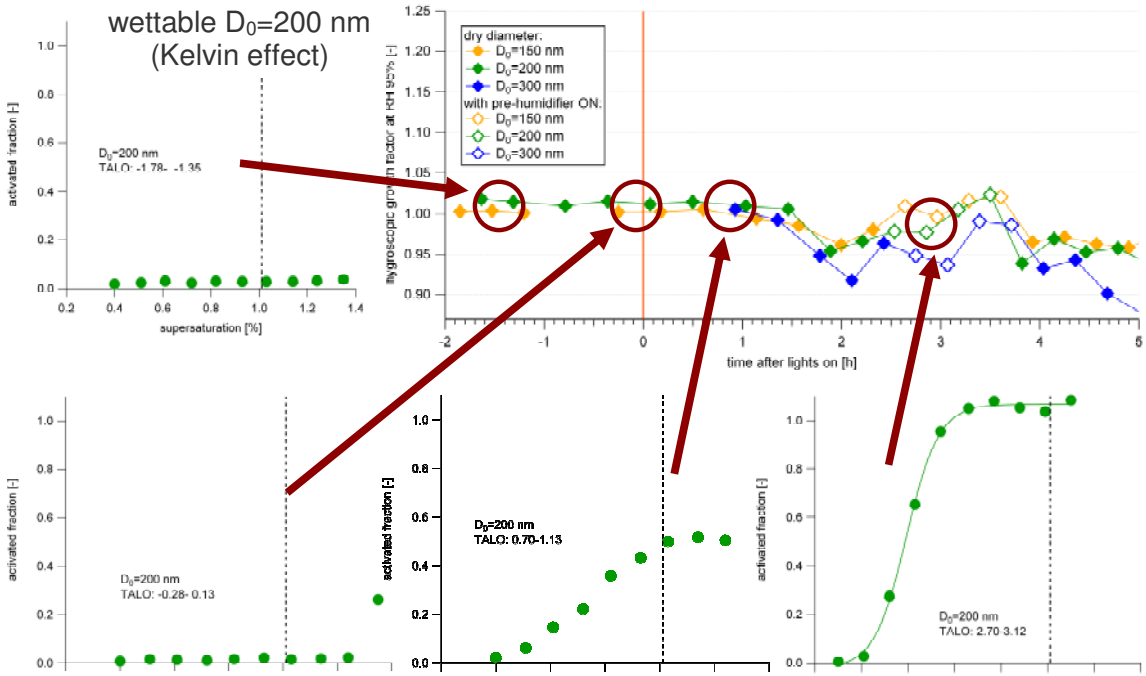


Figure 1: Hygroscopic growth factor at 95% versus time after lights on (top right plot) with 4 CCN activation plots for D_0=200 nm with changing supersaturation. The activation behavior of the aerosols in the smog chamber change clearly with aging time from hydrophobic to hygroscopic. The diameter D_0=200 nm was also measured in the HTDMA and thus can be directly compared.

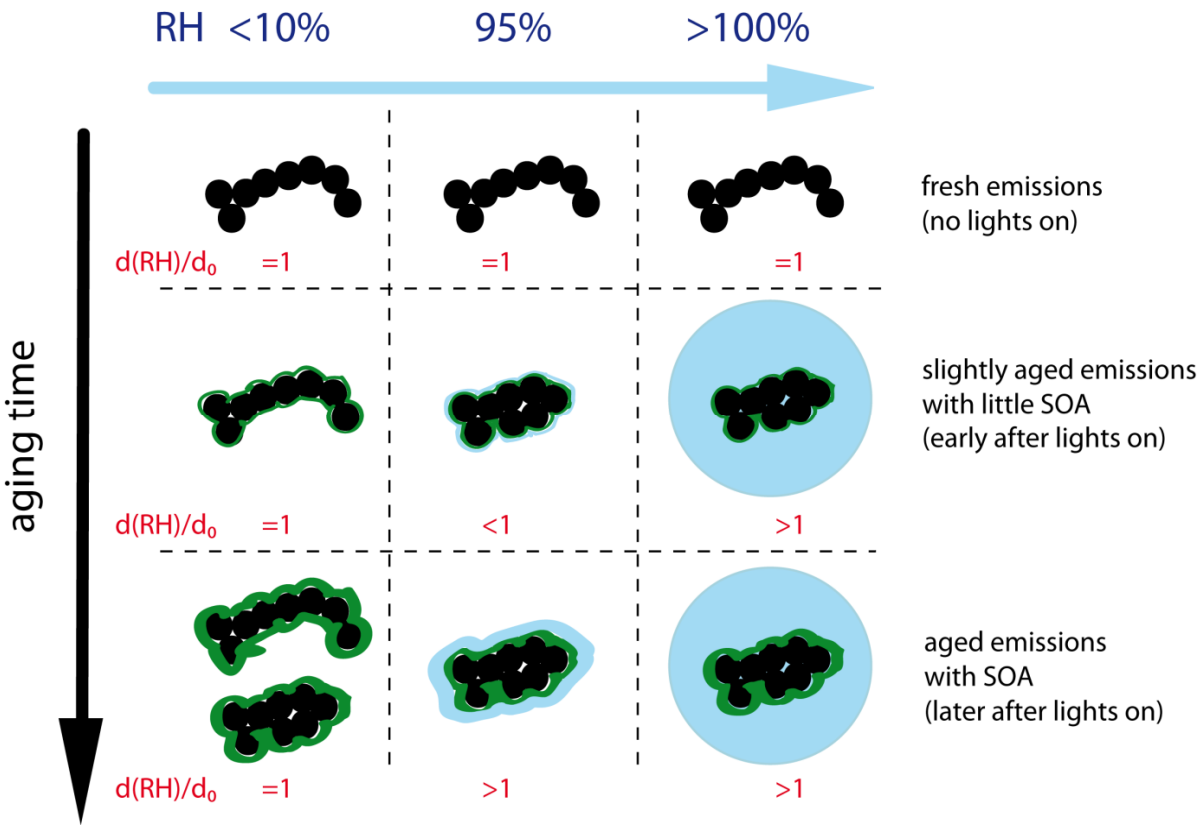


Figure 2: Schematic of the water interaction and water uptake by soot particles during the aging process (black aggregate = BC + POA). The SOA coating (green) is increasing with aging time, thus coated particles are able to interact with water (blue).

Transformation from hydrophobic to hygroscopic diesel soot particles by photochemical aging

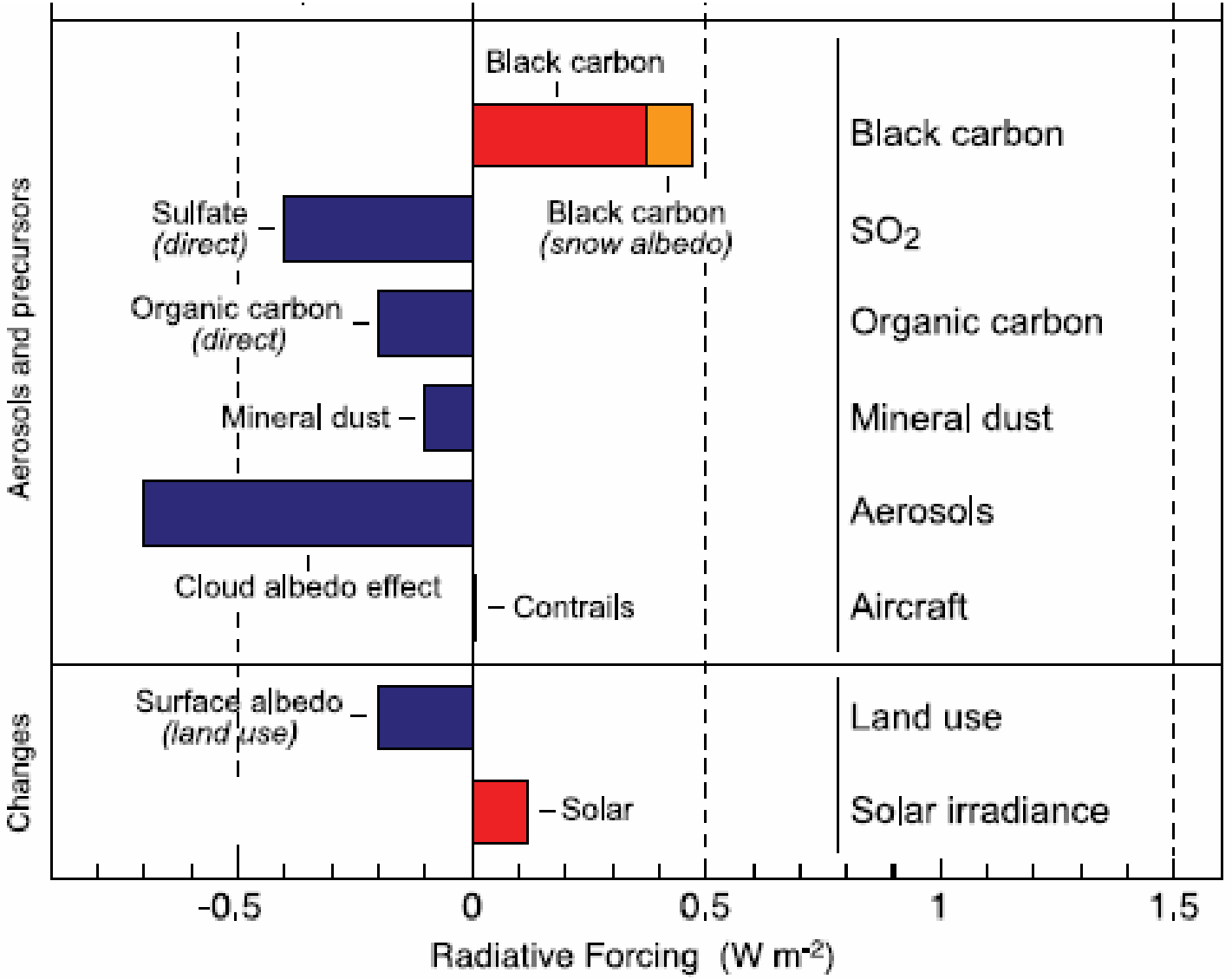
14th ETH Conference on Combustion Generated Nanoparticles

Torsten Tritscher

Roberto Chirico, Zsófia Jurányi, Maria Martin, Maarten Heringa, Martin Gysel, Berko Sierau, Peter DeCarlo, Josef Dommen, André Prévôt, Ernest Weingartner, Urs Baltensperger

Laboratory of Atmospheric Chemistry (LAC), Paul Scherrer Institut, Switzerland
Institute of Atmospheric and Climate Sciences (IAC), ETH Zurich, Switzerland

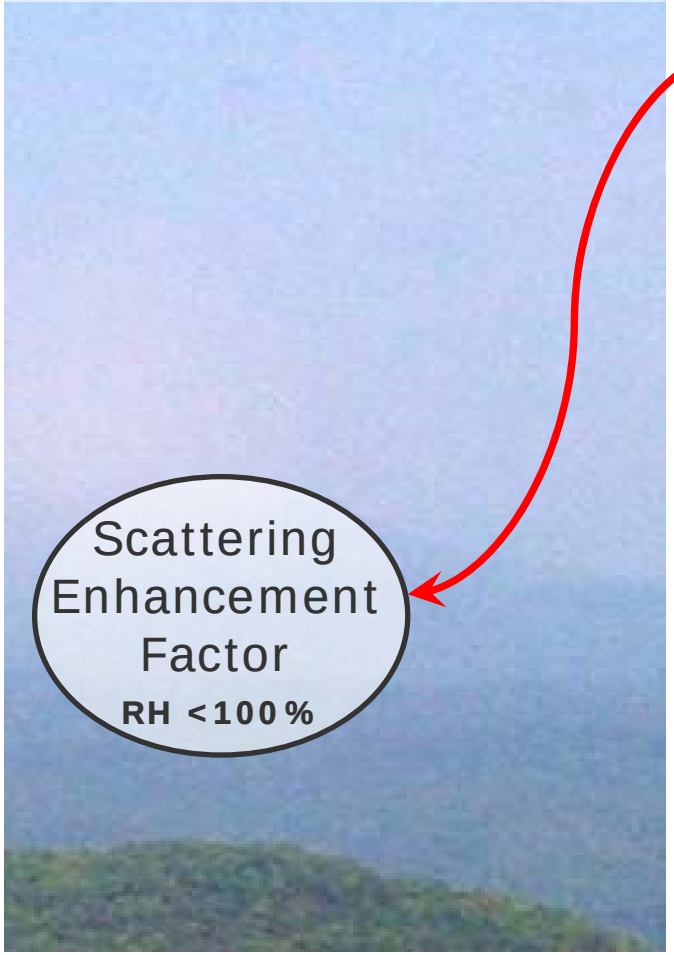
The global mean radiative forcing of greenhouse gases and aerosols for 2000, relative to 1750



IPCC (2007)

Why is the aerosol hygroscopicity important ?

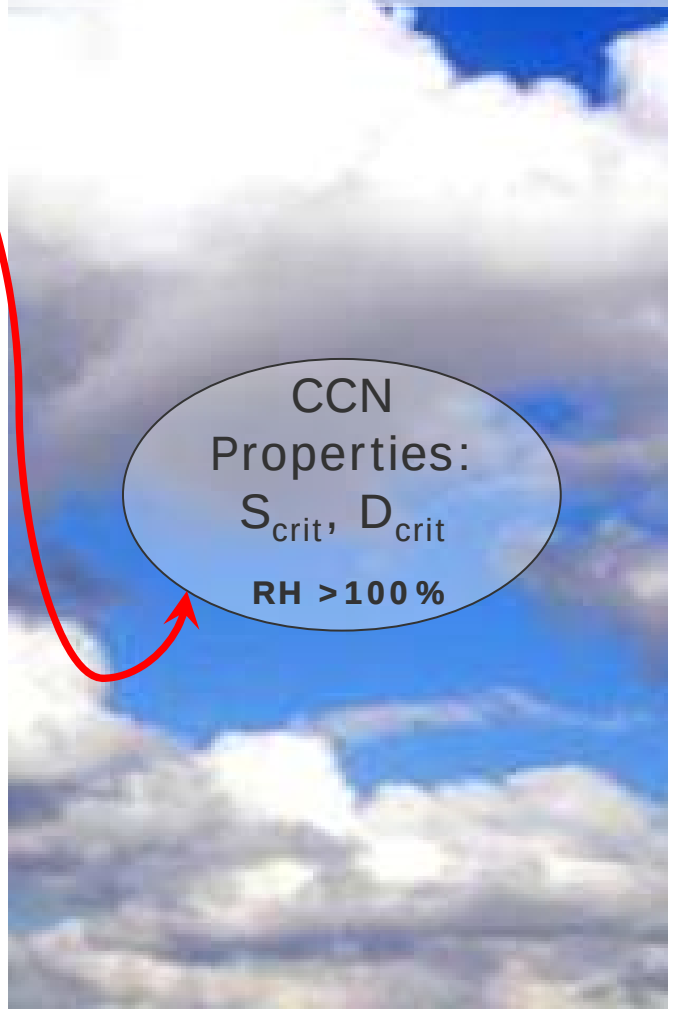
Direct effect
(light scattering and absorption)



Scattering Enhancement Factor
RH <100%

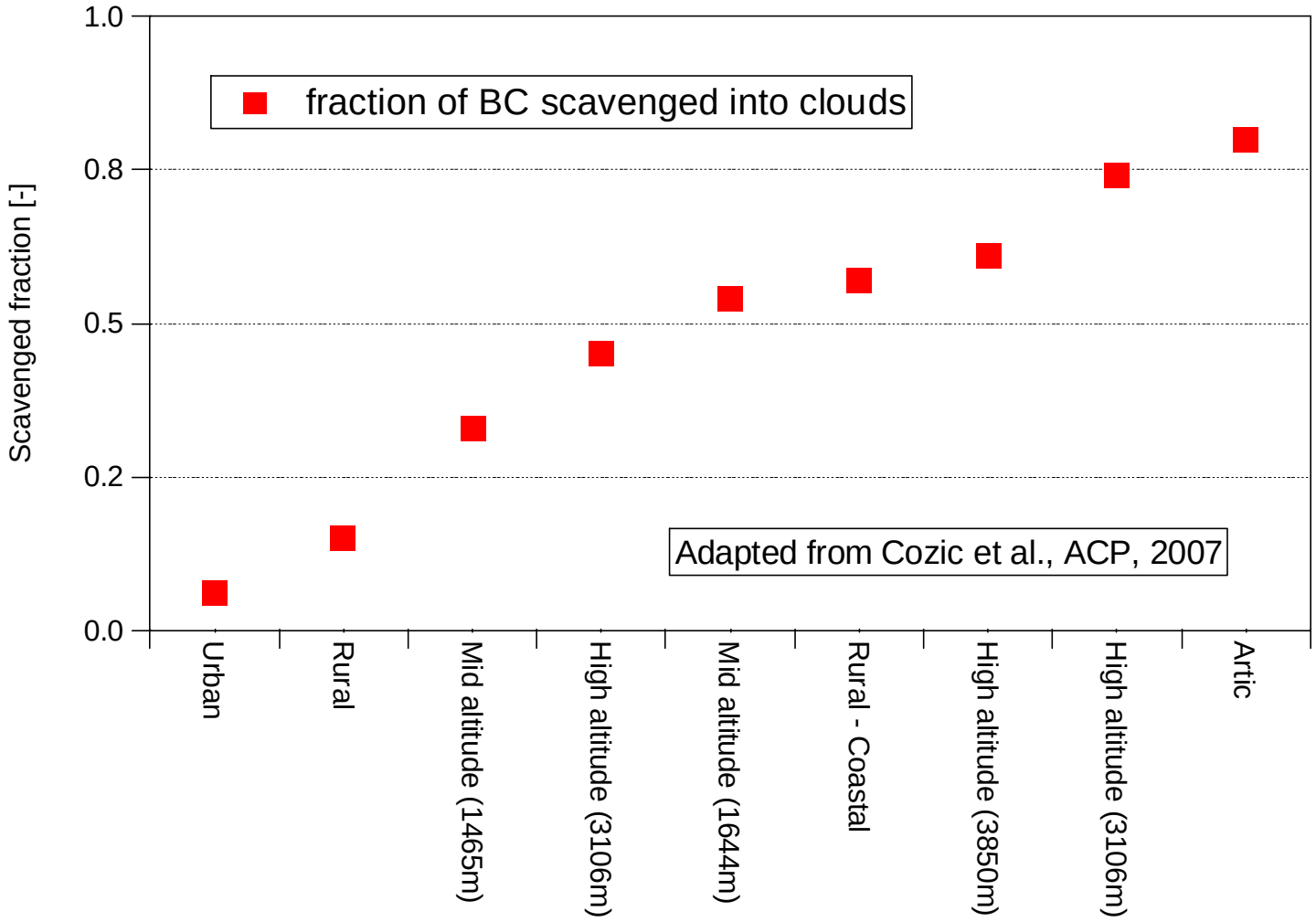
Hygroscopic growth factor
RH <100%

Indirect effect
(change of cloud properties)



CCN Properties:
S_{crit}, D_{crit}
RH >100%

Scavenging of BC into clouds



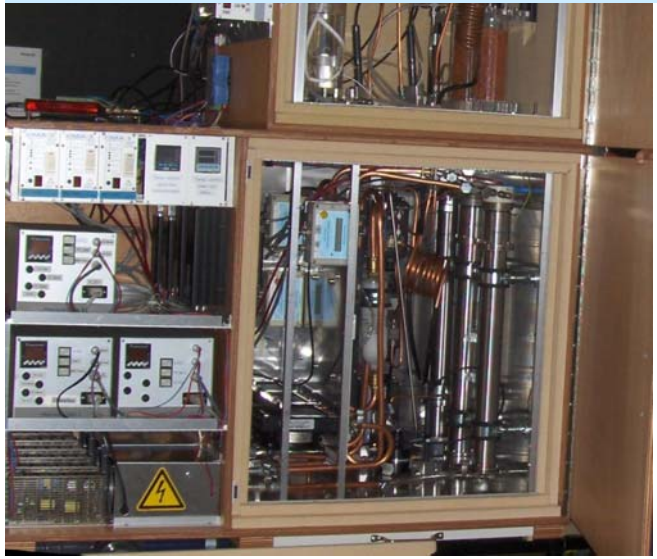
→ BC (black carbon) scavenging increases with air mass age

PSI - Smog chamber

- aging of primary aerosol emissions:
  - wood smoke from 3 burners
  - diesel exhaust from 3 cars

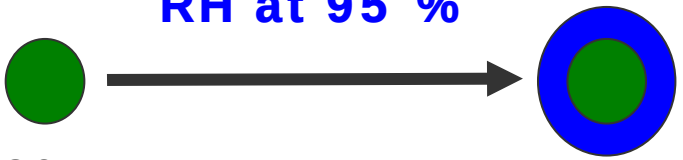
→ formation of Secondary Organic Aerosol (SOA)

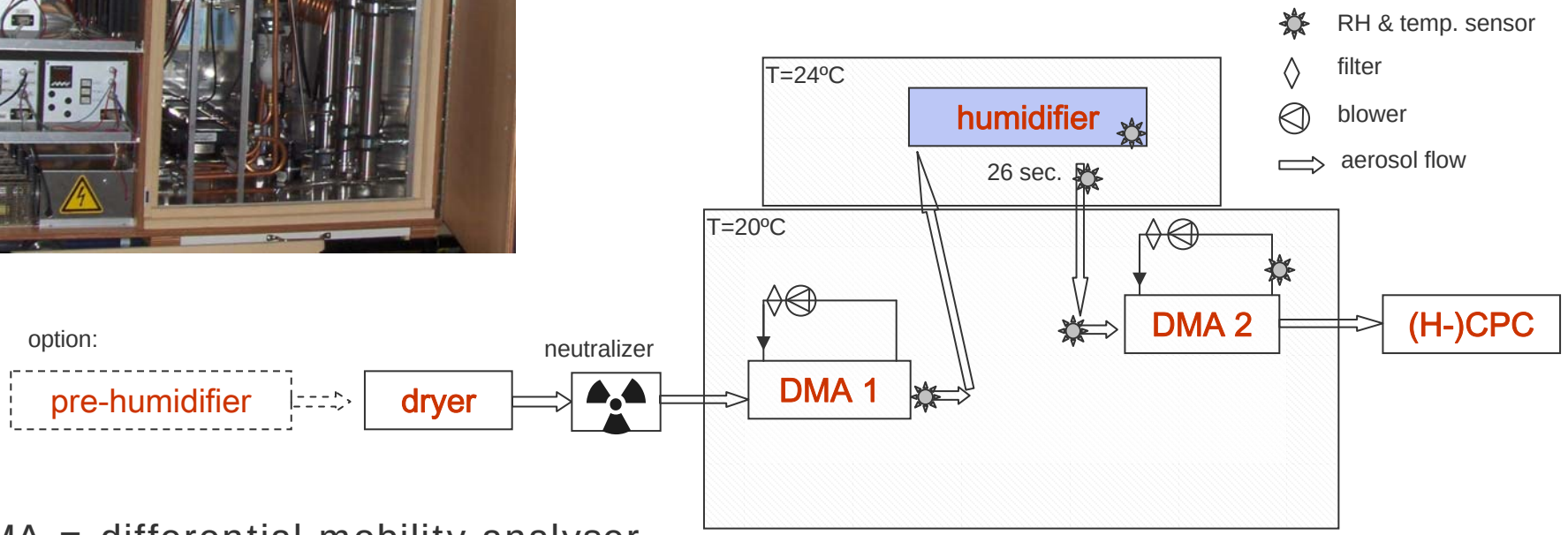
$$\text{hygroscopic growth factor (GF)} = \frac{\text{wet particle diameter } (D_{wet})}{\text{dry particle diameter } (D_0)}$$



- hygroscopicity
- mixing state
- chemical composition

subsaturation
RH at 95 %

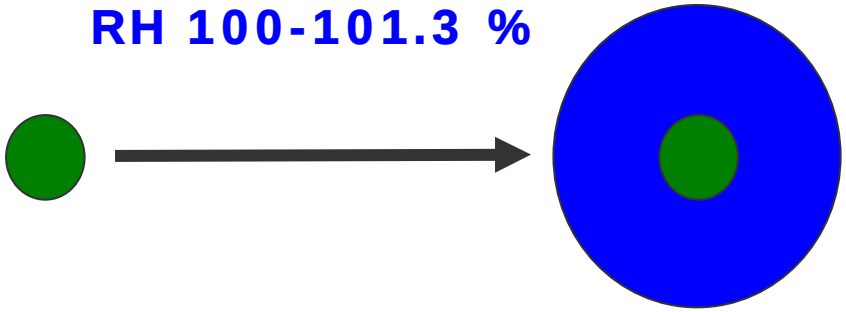




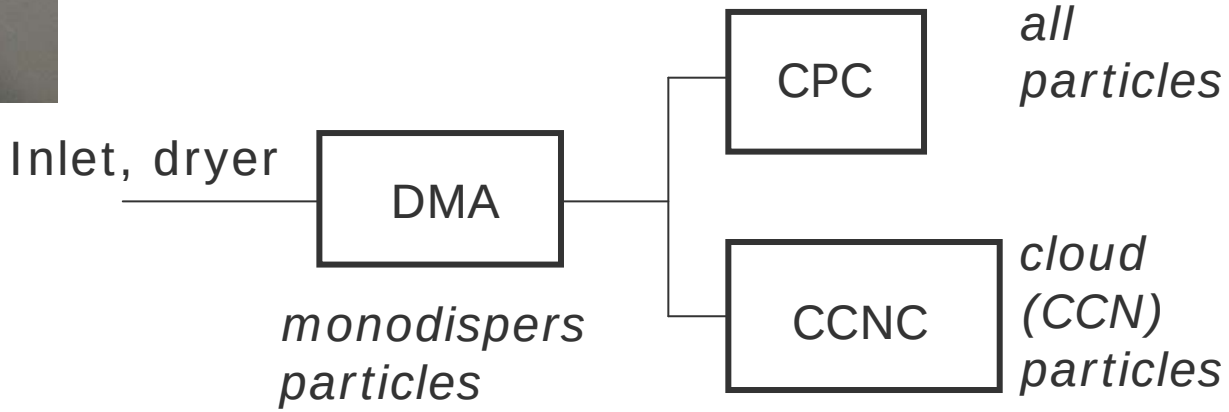
DMA = differential mobility analyser
CPC = condensation particle counter

CCNC: Cloud condensation nucleus counter

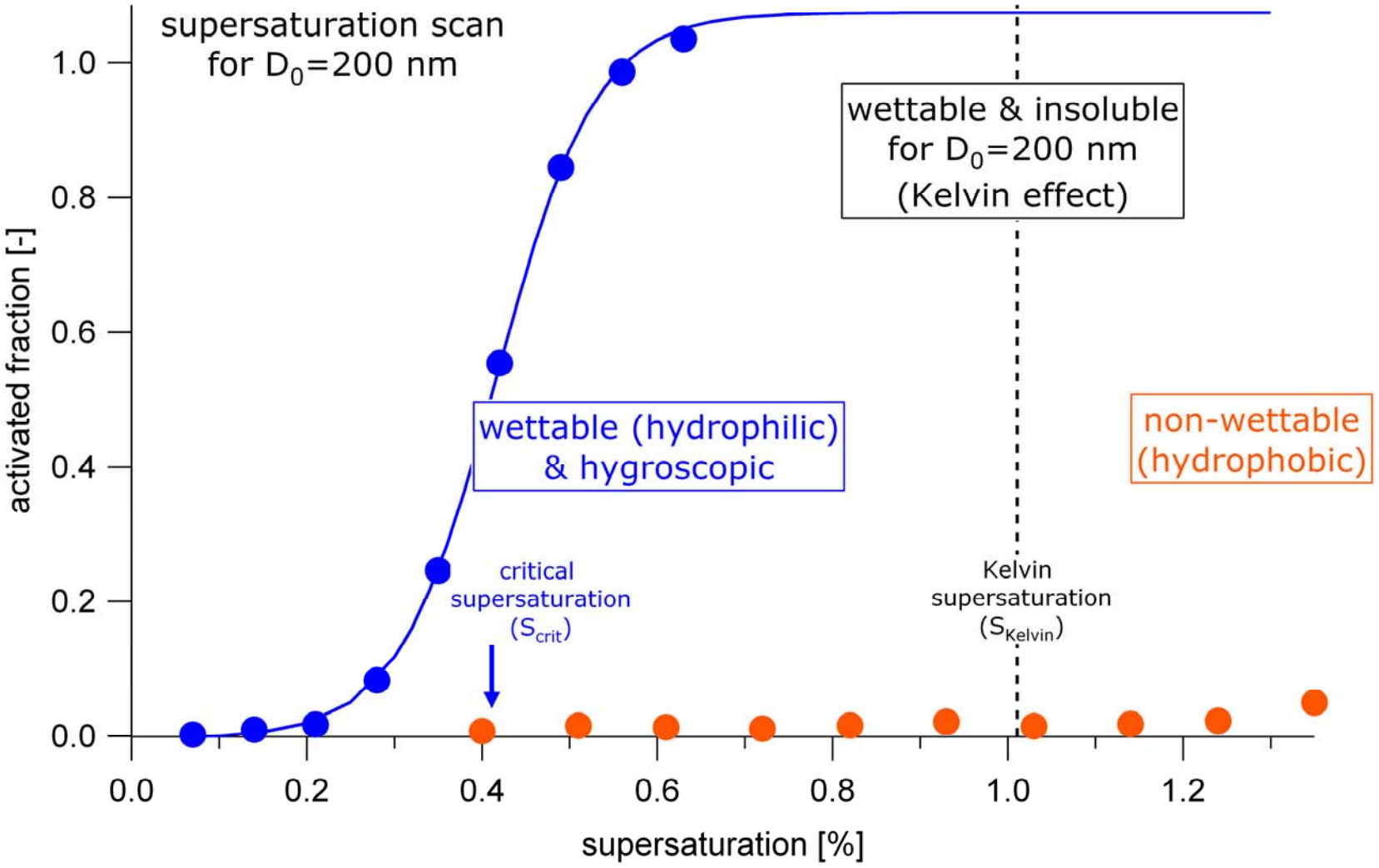
supersaturation
RH 100-101.3 %



Setup at the smog chamber:

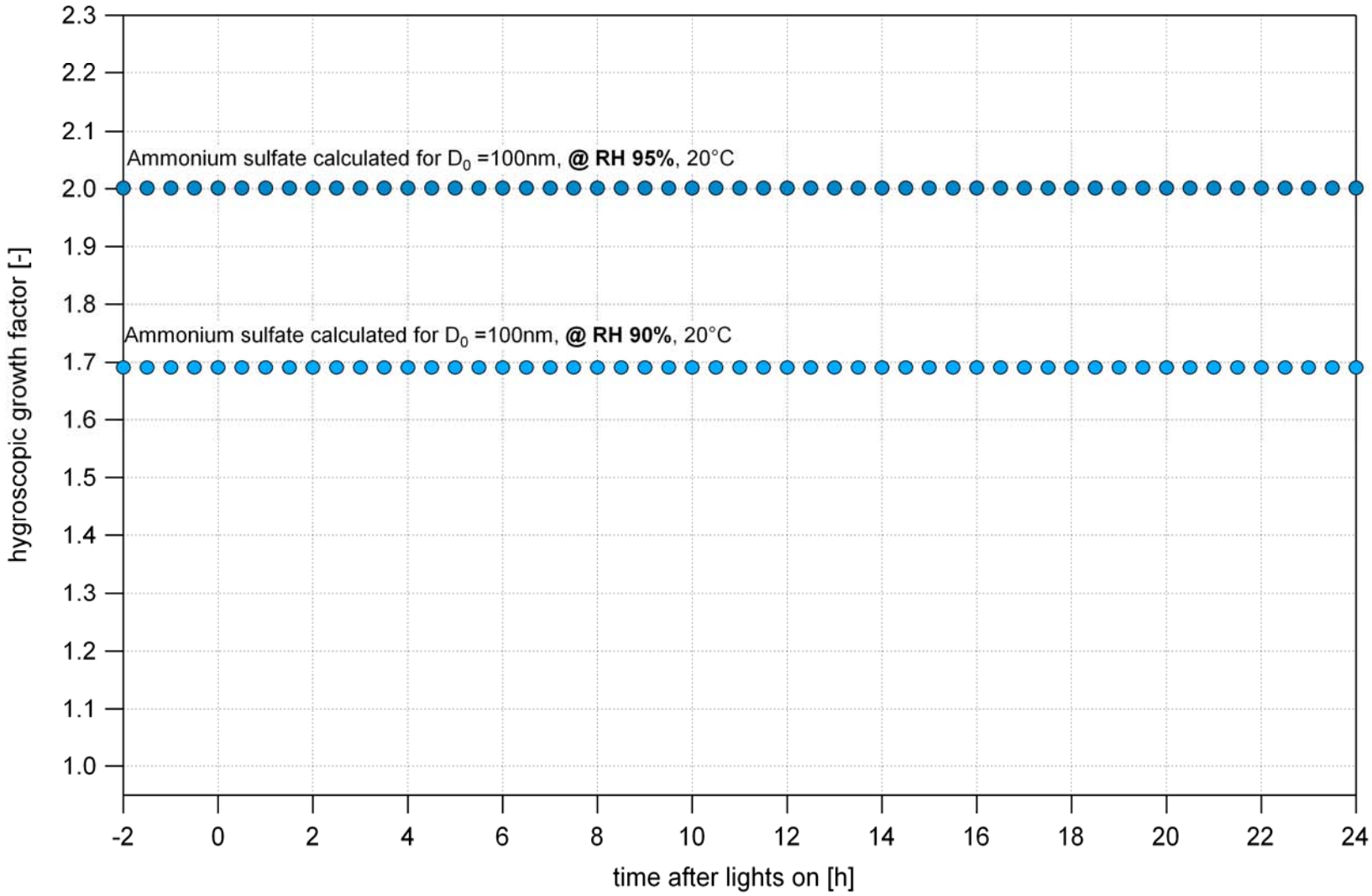


Hydrophobic / hydrophilic; cloud condensation nuclei (CCN) activation curve



Hygroscopic growth of aerosol particles

inorganic salts



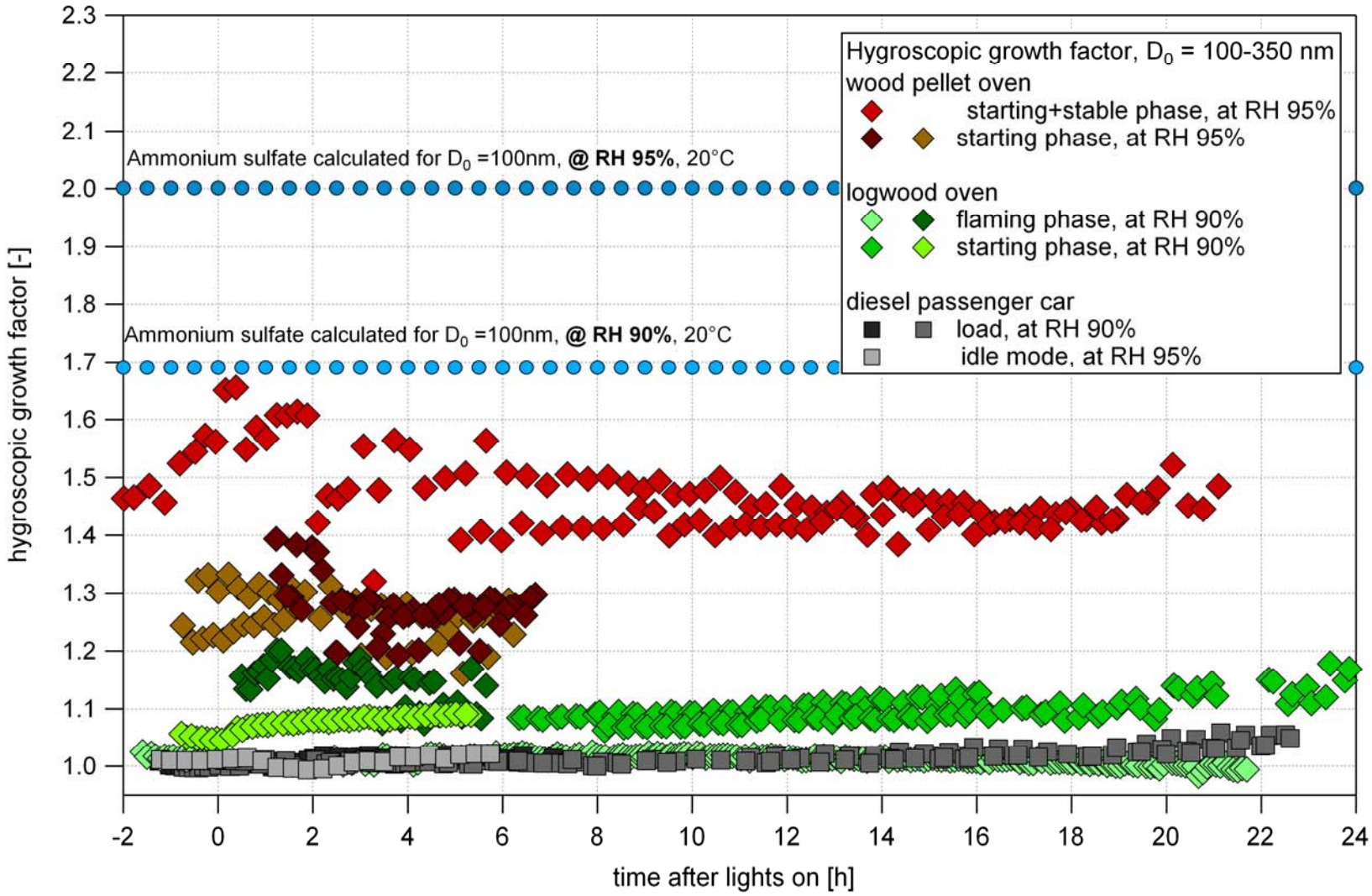
Hygroscopic growth of aerosol particles : diesel and wood emissions (2008)

inorganic salts

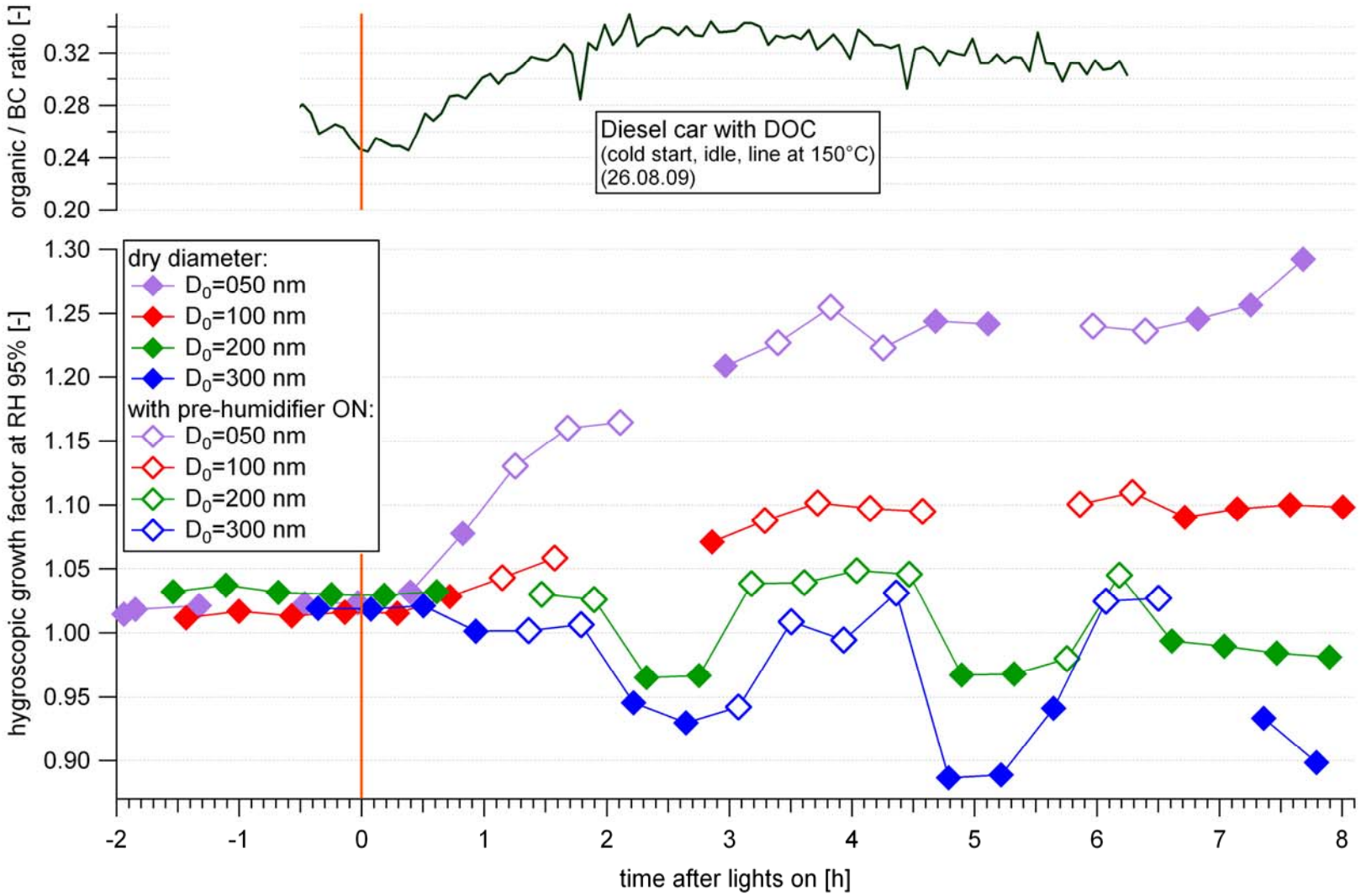
organic matter

Dust

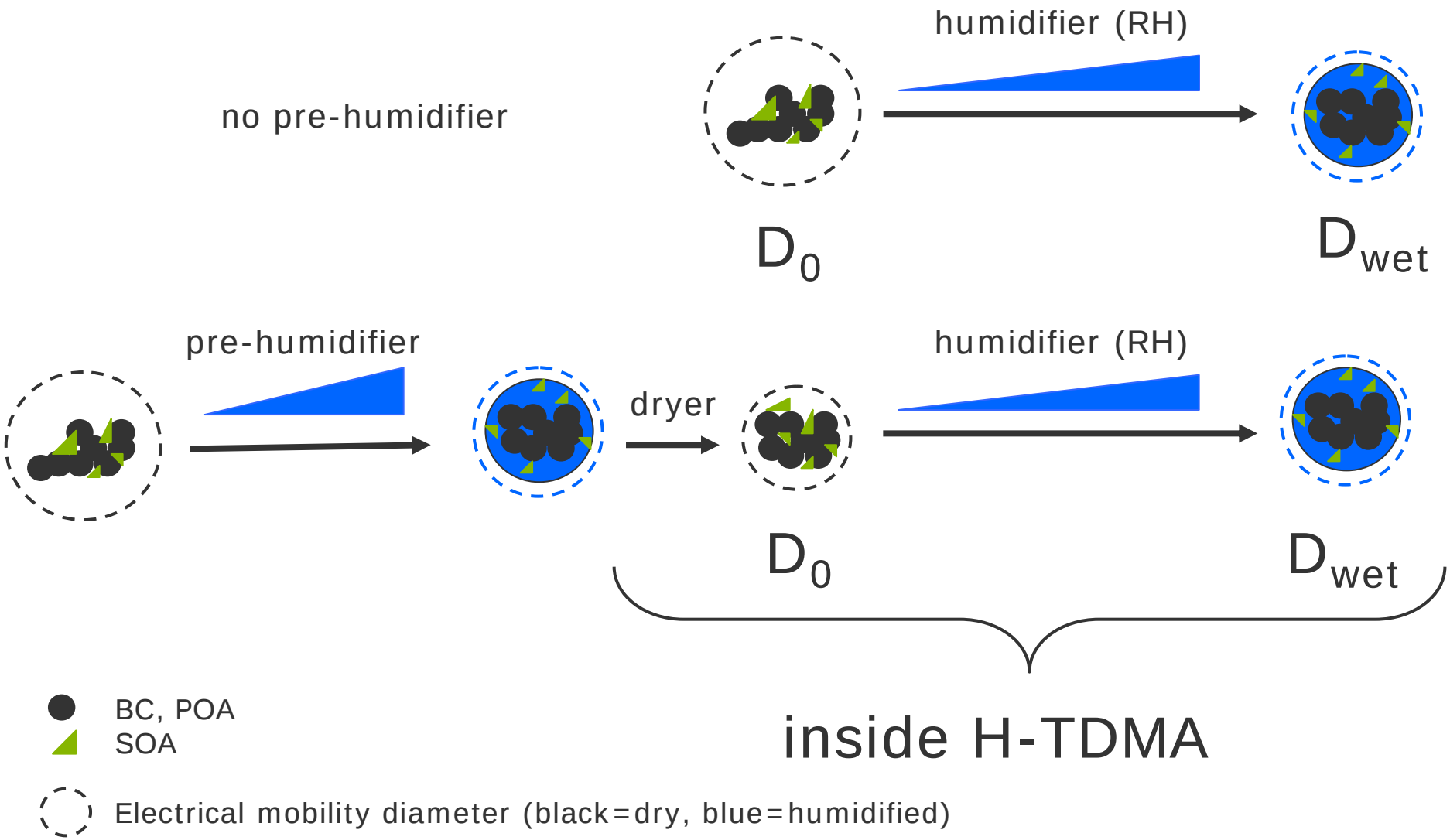
BC



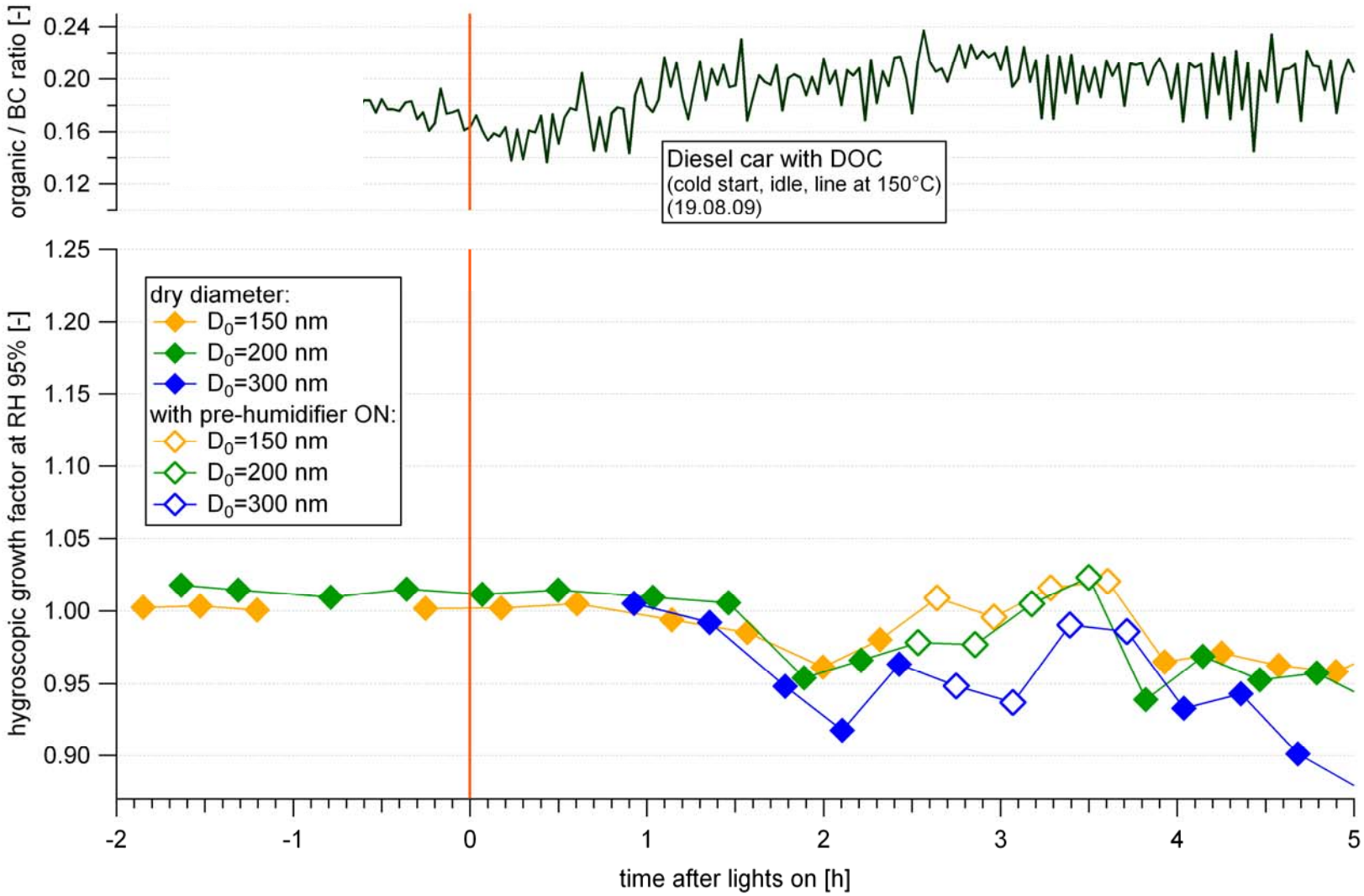
Hygroscopic growth during aging experiment



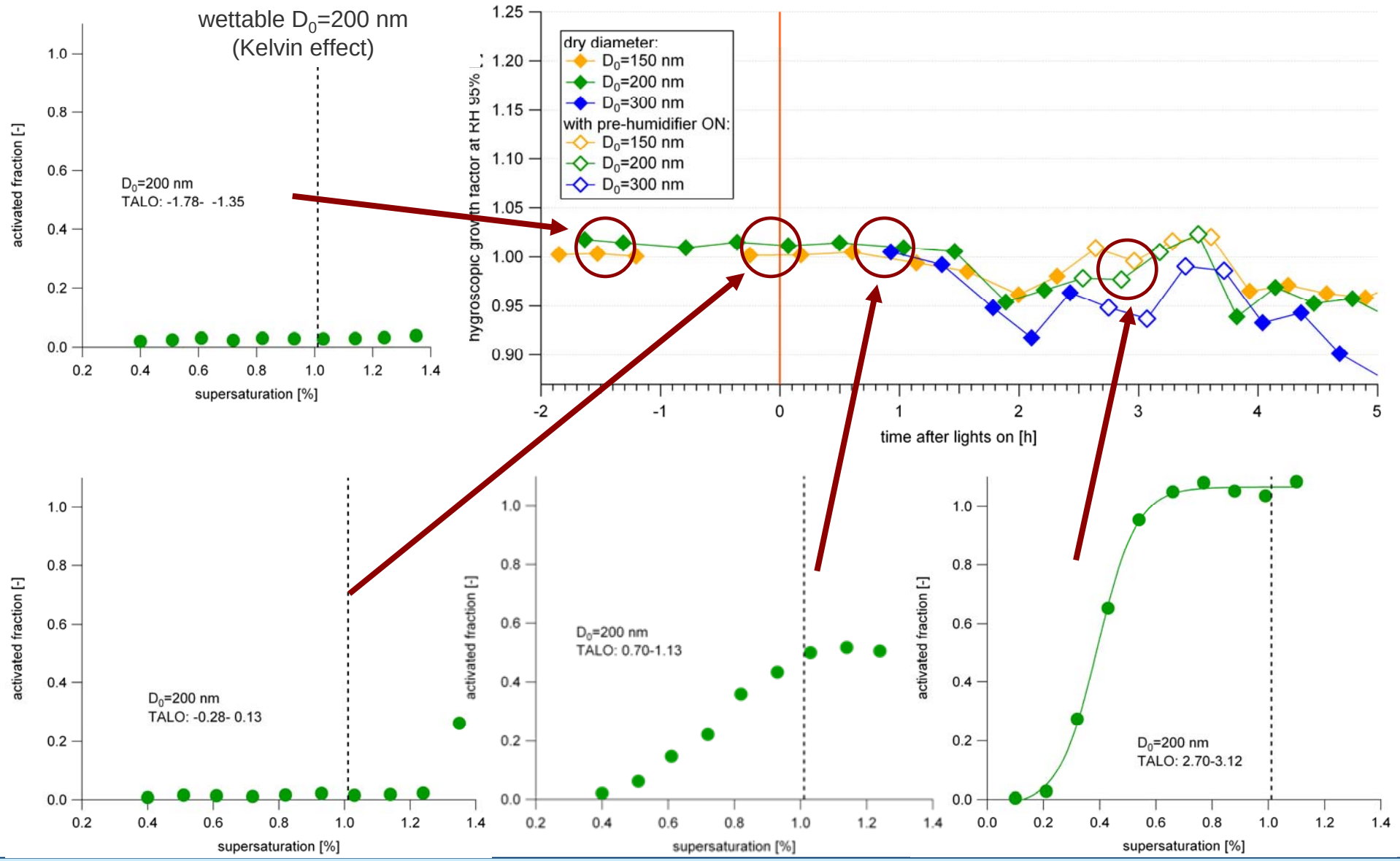
Restructuring hypothesis with pre-humidifier in front of the H-TDMA



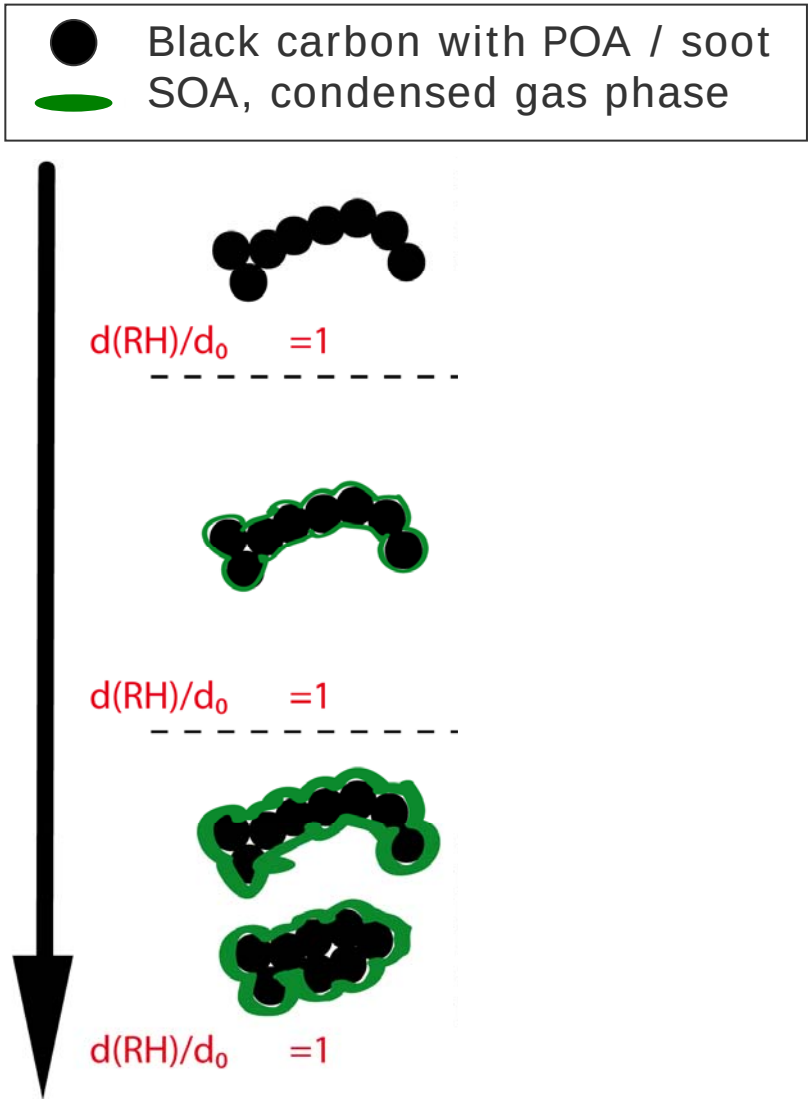
Hygroscopicity and CCN-activity: diesel car (Opel Astra)



Hygroscopicity and CCN-activity: diesel car (Opel Astra)



Water interaction of soot during the aging

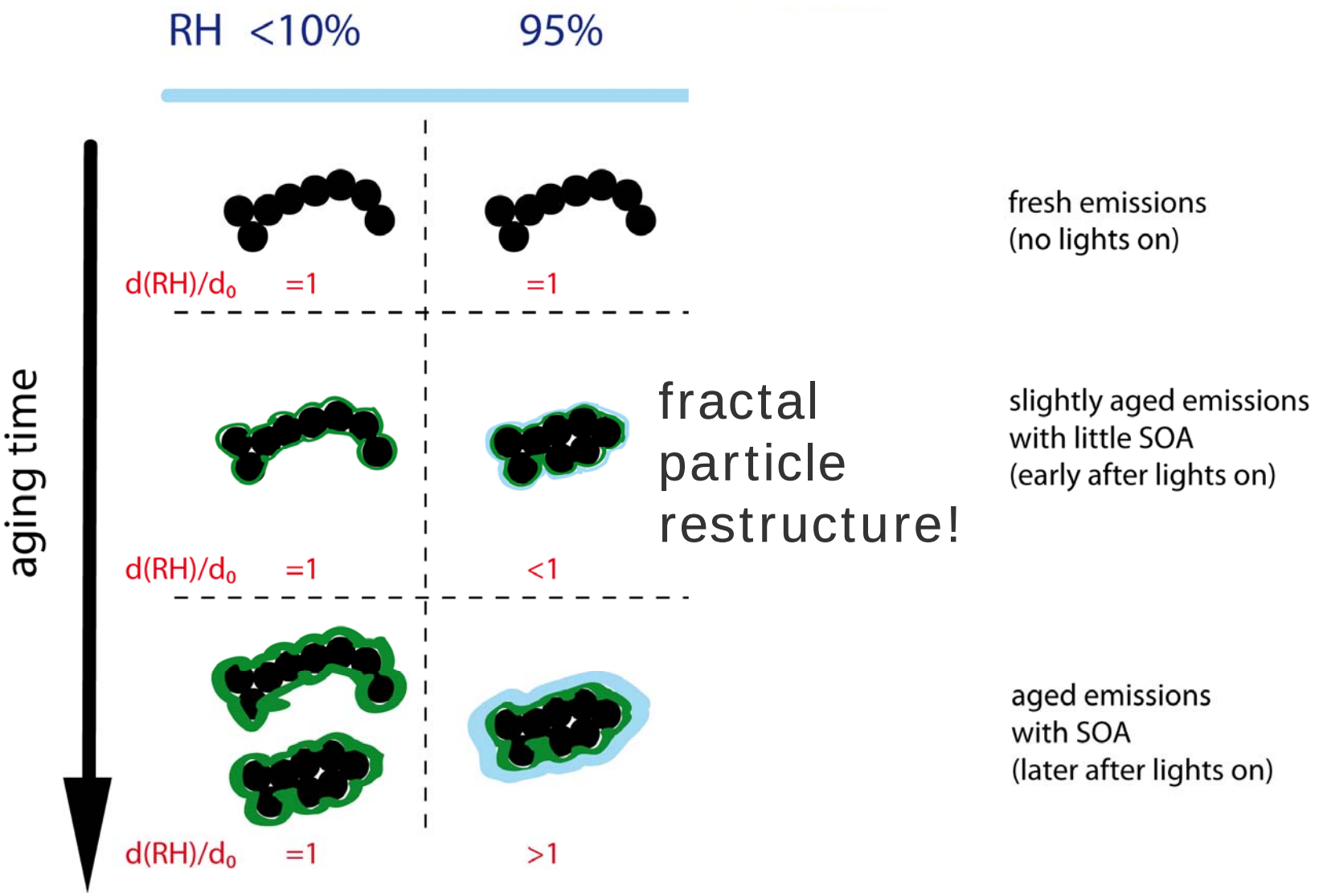


fresh emissions
(no lights on)

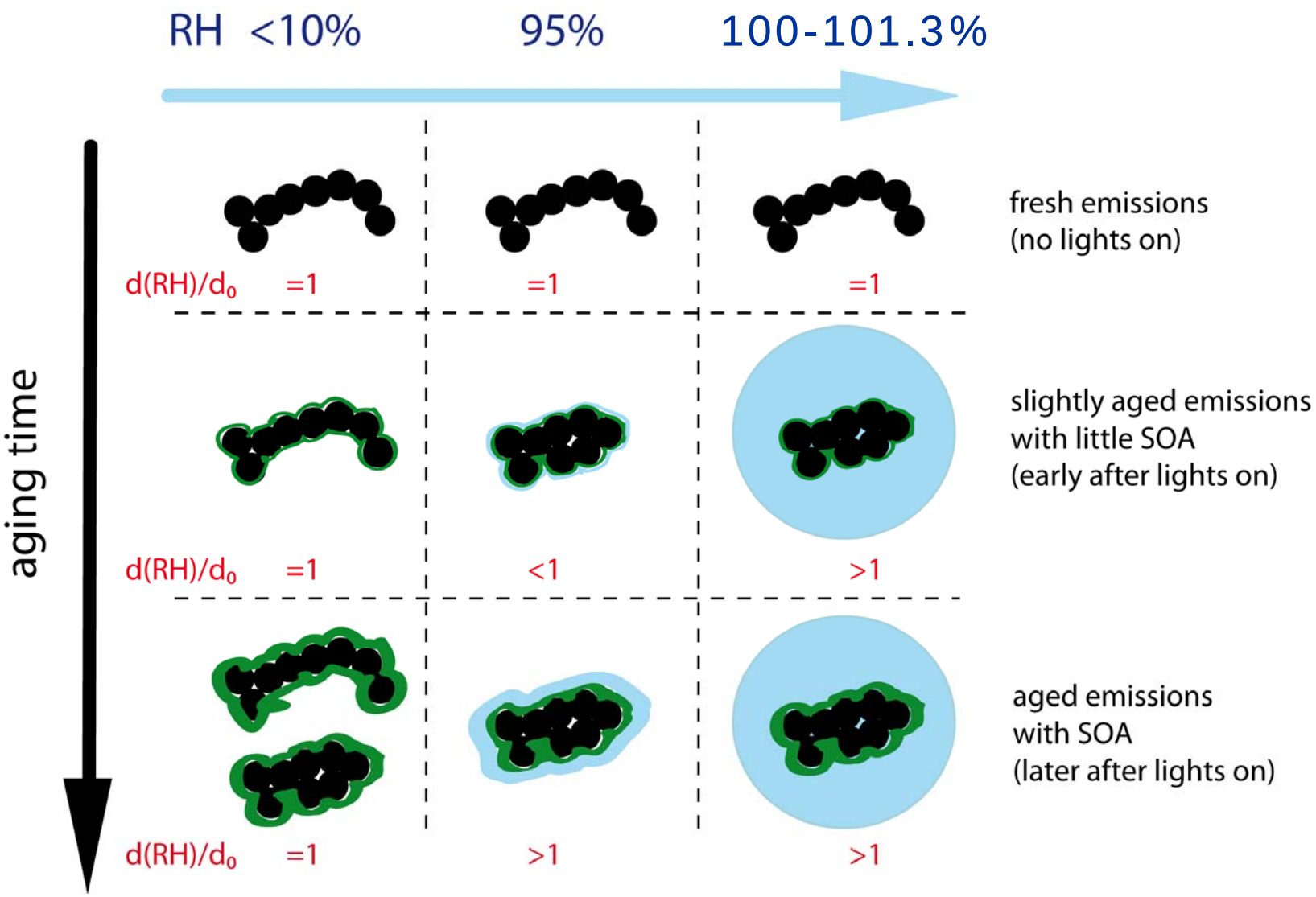
slightly aged emissions
with little SOA
(early after lights on)

aged emissions
with SOA
(later after lights on)

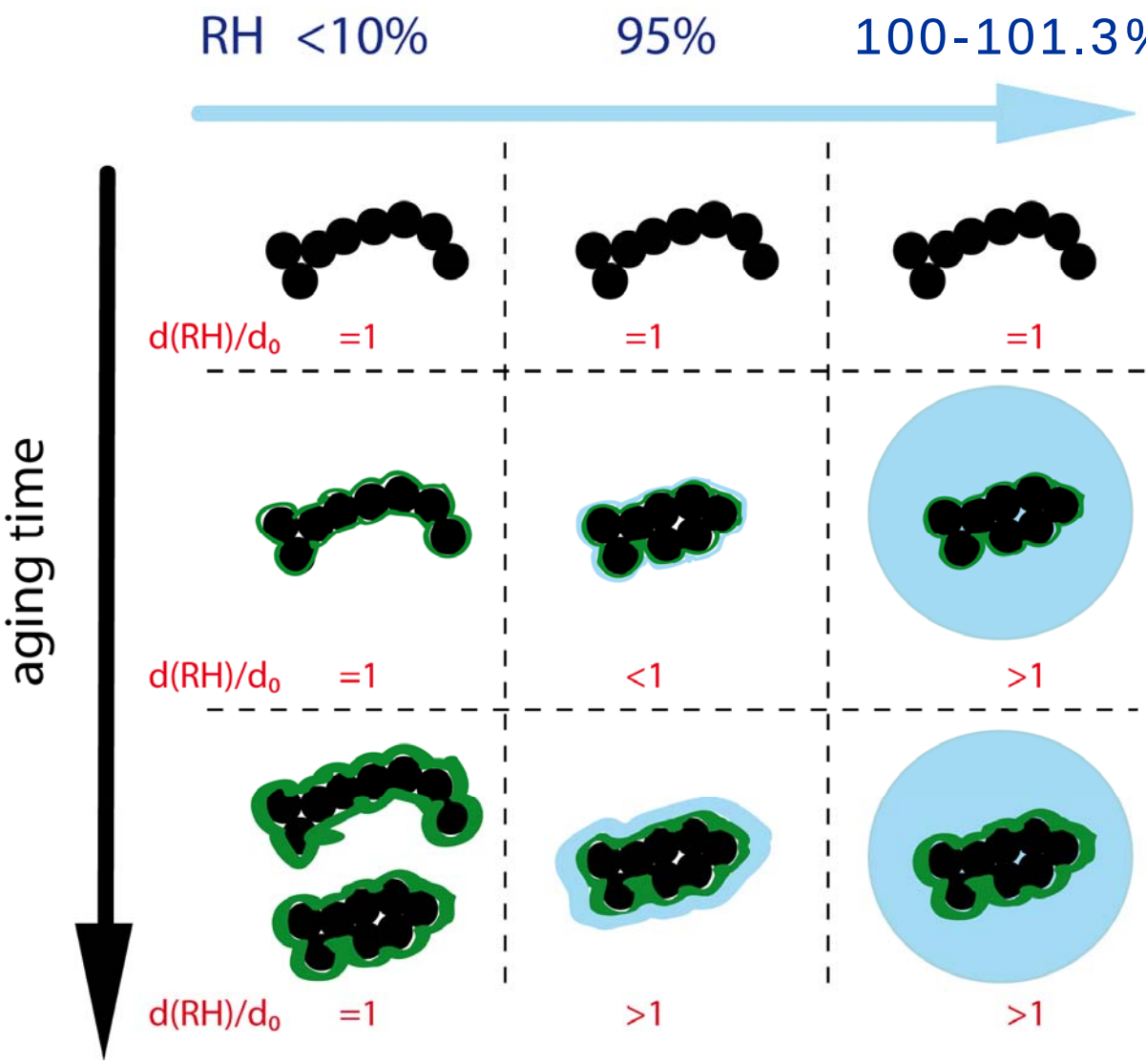
Water interaction of soot during the aging



Water interaction of soot during the aging



Water interaction of soot during the aging



Soot is…

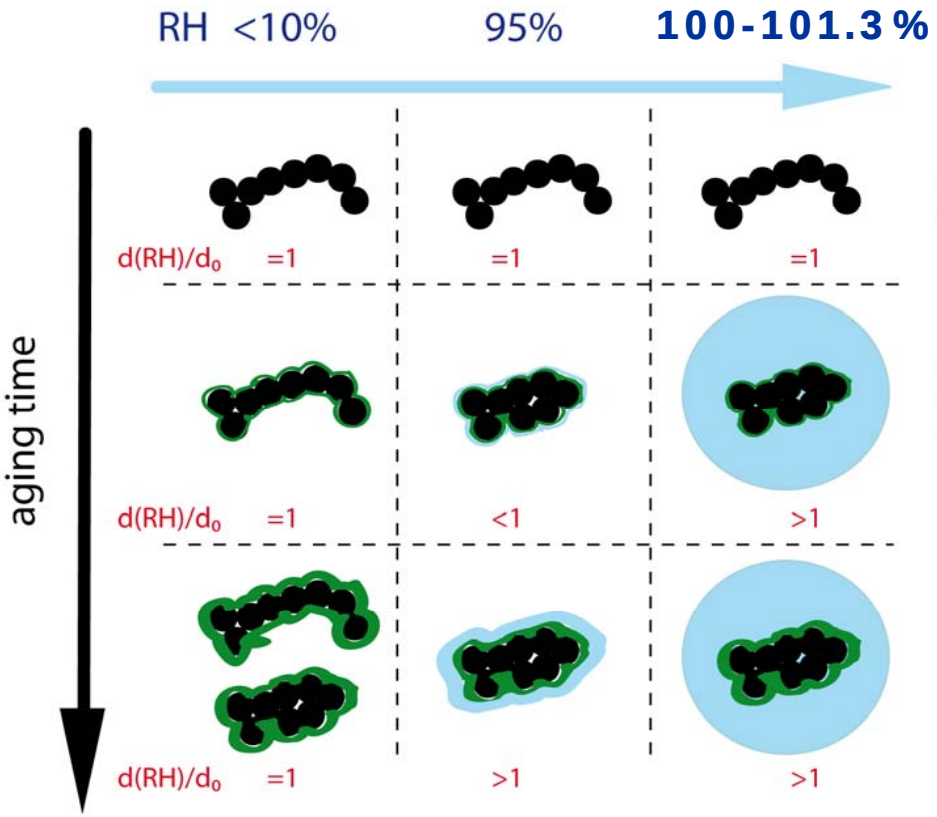
hydrophobic

hydrophilic & non-hygroscopic

hydrophilic & hygroscopic

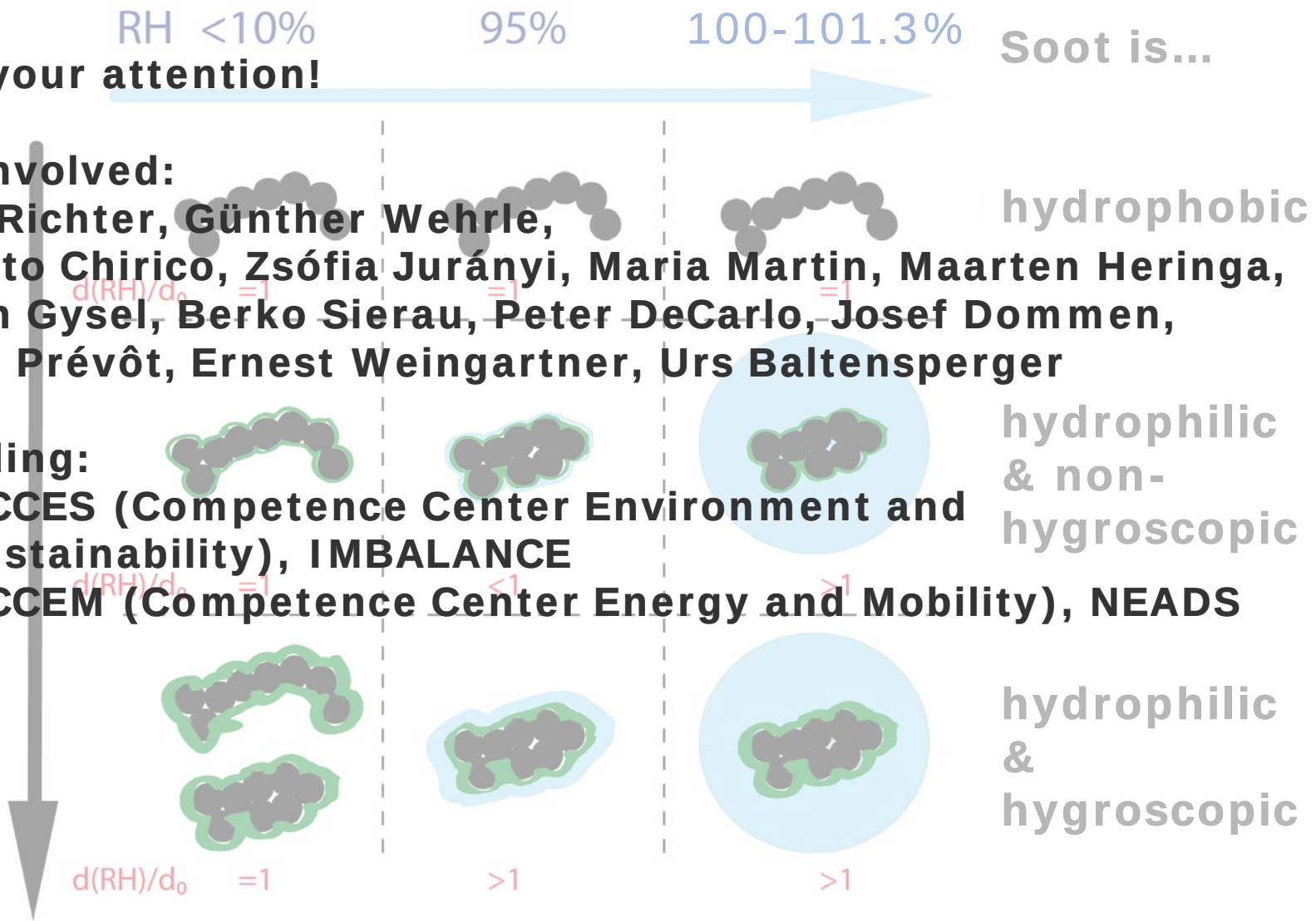
Conclusion

- Diesel soot particles:
  - External mixture hydrophobic and hydrophilic soot particles
  - show low hygroscopic growth behavior (wood emissions and pure organics higher)
  - restructuring effects dependent on photochemical aging and particle size



- Atmospheric implication:
  - different BC/soot types consideration in models
  - mixing state changes with aging

Thanks ...



- for your attention!

- all involved:

René Richter, Günther Wehrle, Roberto Chirico, Zsófia Jurányi, Maria Martin, Maarten Heringa, Martin Gysel, Berko Sierau, Peter DeCarlo, Josef Dommen, André Prévôt, Ernest Weingartner, Urs Baltensperger

- funding:
  - CCES (Competence Center Environment and Sustainability), IMBALANCE
  - CCEM (Competence Center Energy and Mobility), NEADS