Is black carbon internally or externally mixed? An experimental answer from recent laboratory and field experiments

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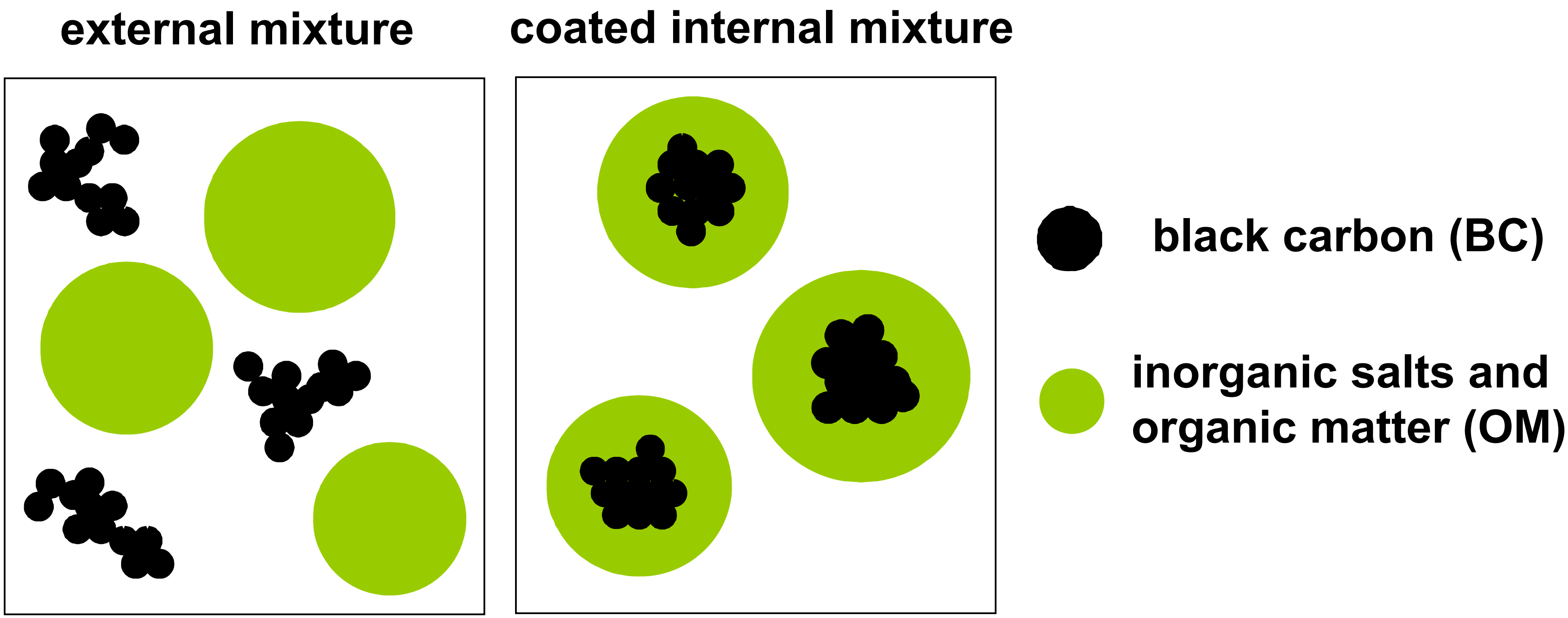
Zurich, 22/06/2009

13th ETH-Conference on Combustion Generated Nanoparticles

Mixing states of black carbon (BC):



This presentation aims at showing that:

- mixing state of BC is important for its climate effects.
- a substantial fraction of freshly emitted BC is externally mixed.
- atmospheric aging processes lead towards internally mixed BC.

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Sources of atmospheric black carbon (BC)

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industry and power generation

diesel engines

domestic heating and cooking

anthropogenic and natural forest fires

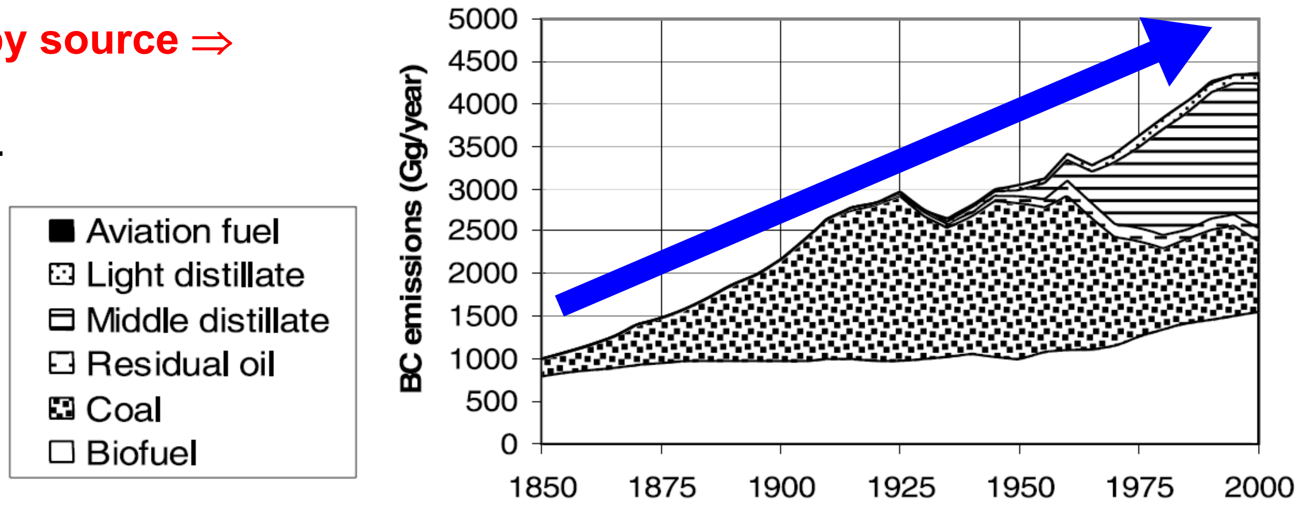
atmospheric BC is predominantly of anthropogenic origin

⇒ we can get things moving

... and we have done so in the past

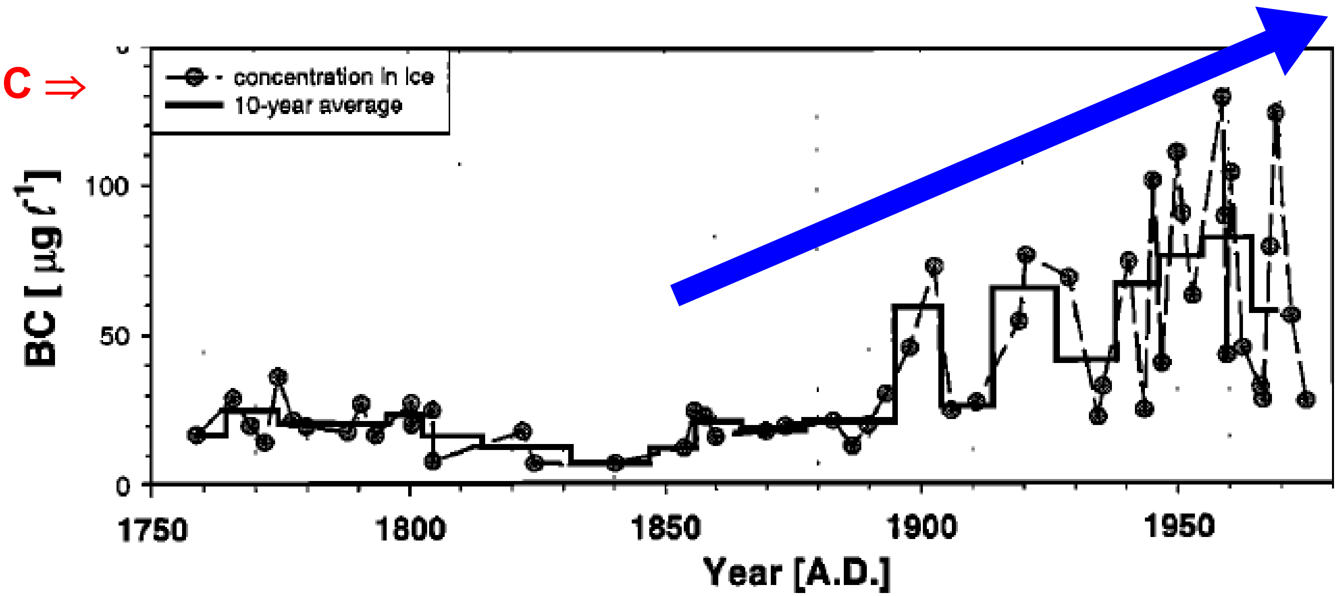
BC emission inventory by source ⇒

Bond et al.,
***Glob. Biogeochem. Cycle*, 2007.**



ice core record of BC ⇒

Lavanchy et al.,
***JGR*, 1999.**



~ fivefold increase of BC emissions from 1850 to 2000

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Importance of atmospheric BC

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- BC nanoparticles are inhalable, insoluble and cytotoxic.
  ⇒ Known to have adverse effects on human health (e.g. Laden et al., 2000).

- BC nanoparticles strongly absorb solar radiation.
  ⇒ Direct effect on the earth's radiative balance.

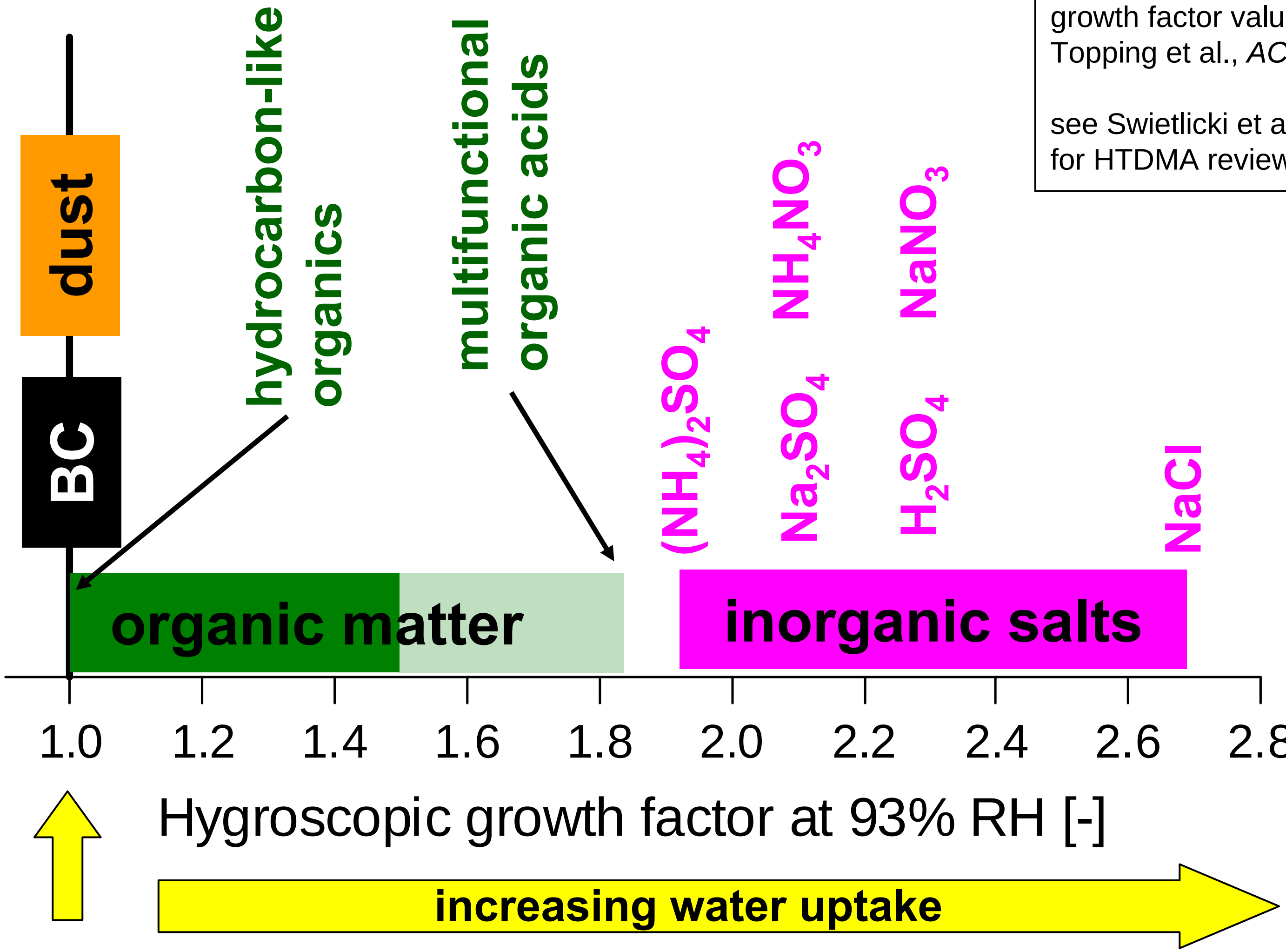
- BC nanoparticles have the potential to act as cloud condensation nuclei (CCN) and ice nuclei (IN) in atmospheric clouds.
  ⇒ Indirect effect on the earth's radiative balance through modification of cloud properties.

mixing state of BC matters

Hygroscopic growth and composition of aerosol particles: HTDMA (Hygroscopicity Tandem Differential Mobility Analyzer)

growth factor values from ADDEM, Topping et al., *ACP*, 2005a,b

see Swietlicki et al., *Tellus*, 2008 for HTDMA review

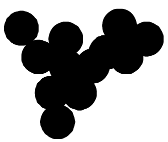


HTDMA data provide additional information on:

- **mixing state**
- **possible chemical composition**

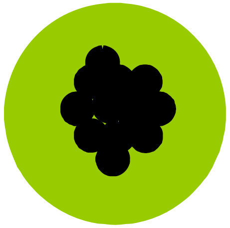
Atmospheric aging processes of BC

external mixture



- **coagulation**
- **acquisition of condensable gases**
- **cloud processing**
- **…**

internal mixture



mixing state of atmospheric BC evolves towards internal mixture (to be shown)

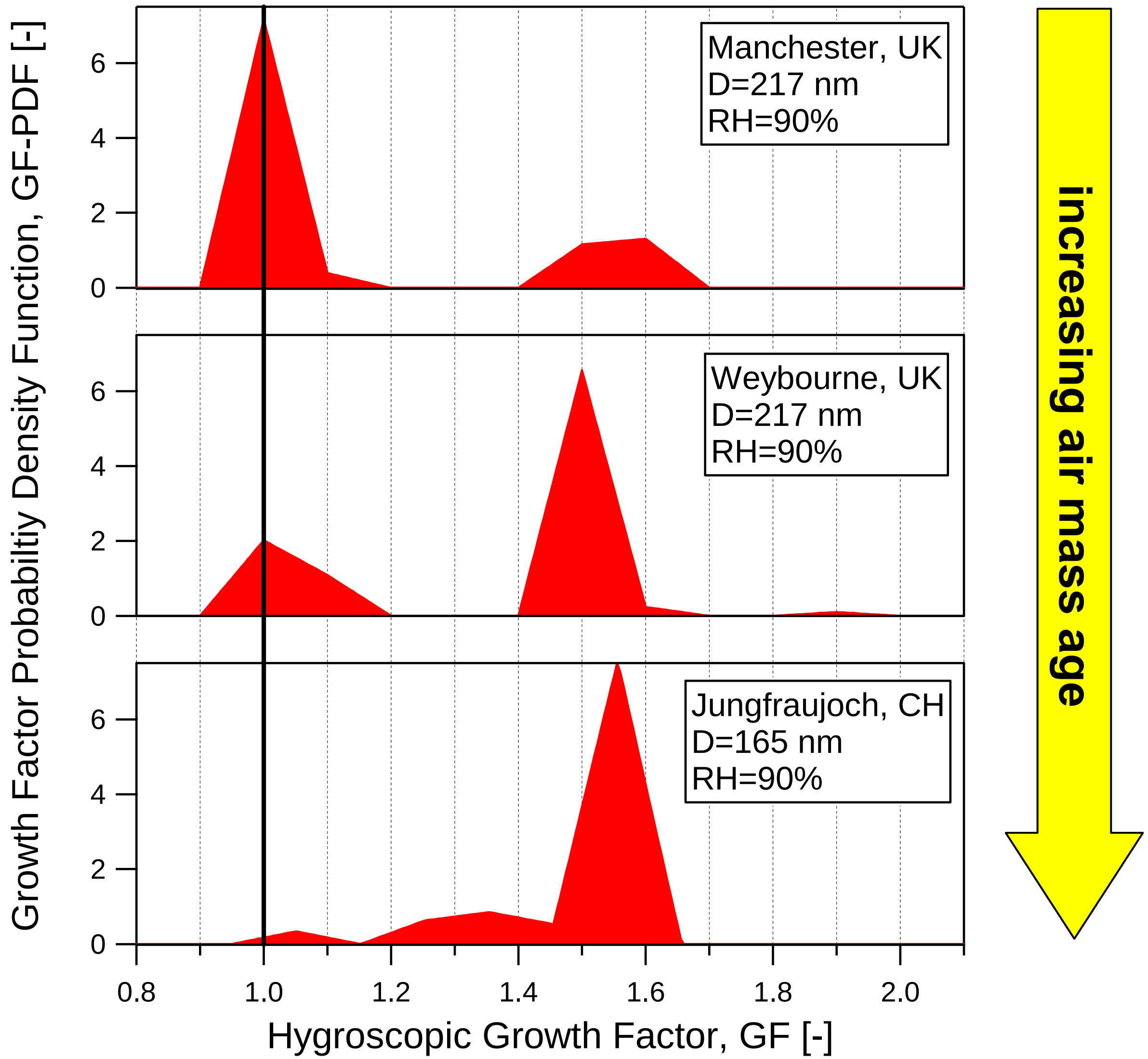
Hygroscopic growth of ambient aerosol

"Typical examples"

urban (fresh emissions)**:**

rural (aged polluted outflow)**:**

free troposphere (highly aged)**:**

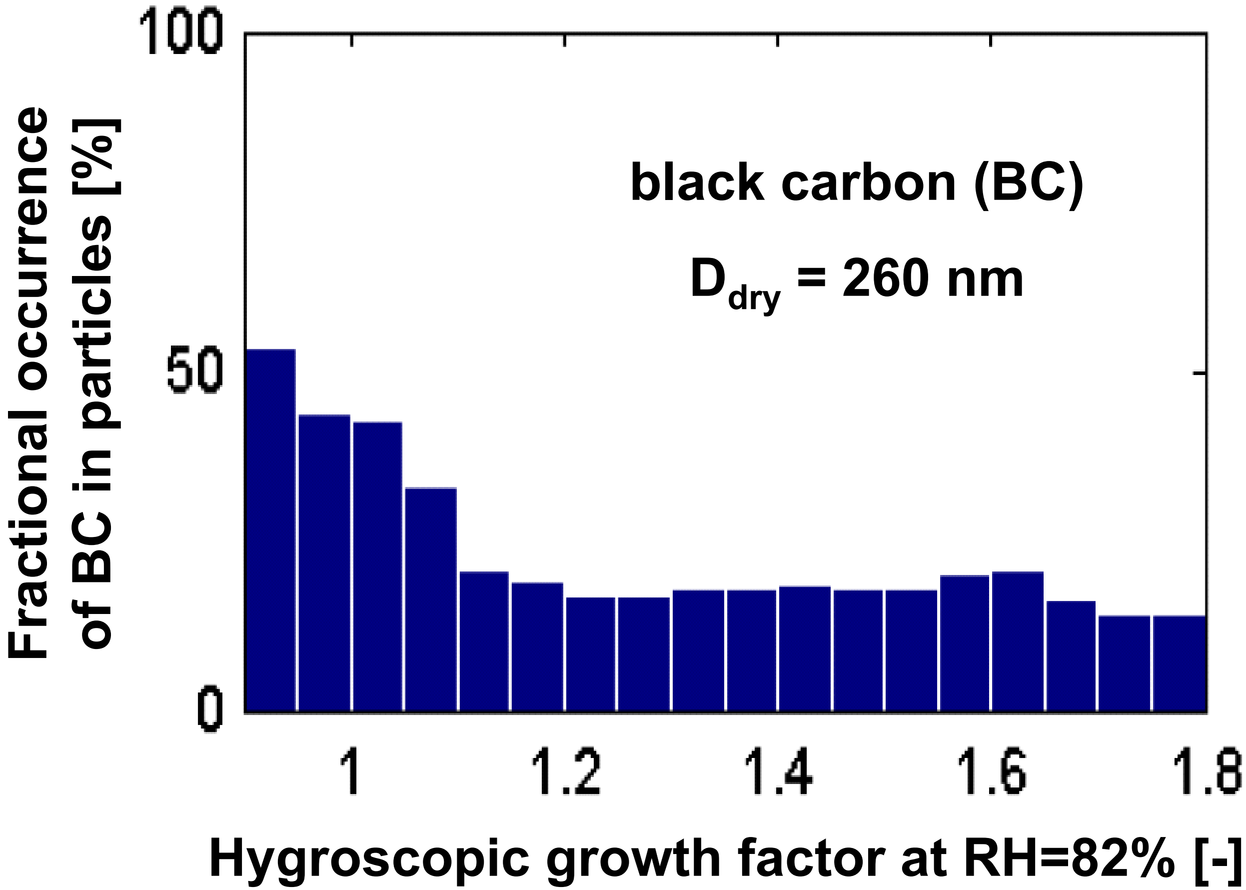


⇒ number fraction of externally mixed BC decreases typically with air mass age

Mixing state of BC in Zurich aerosol (urban)

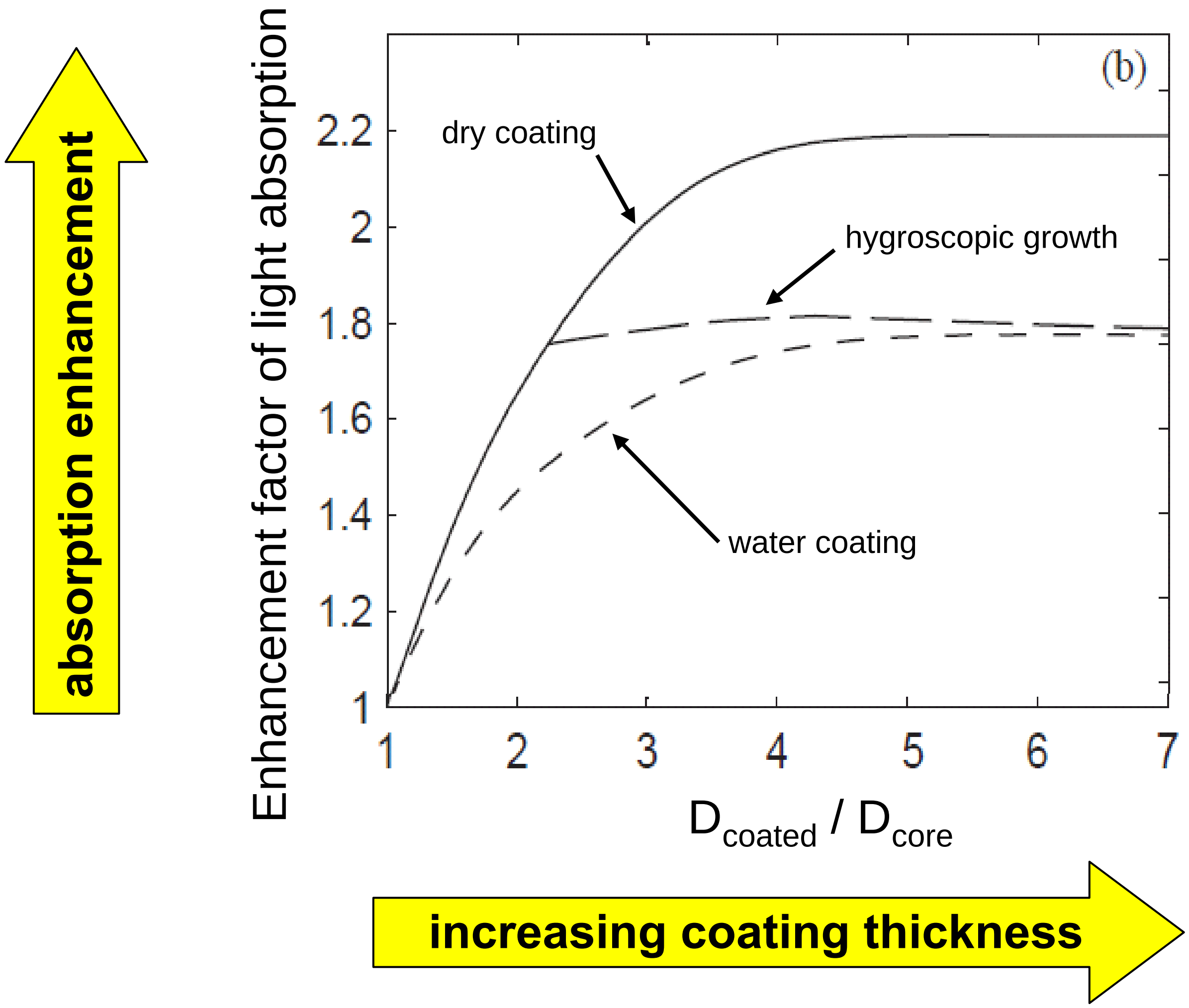
Collaboration with ETH Zurich; Herich et al., *JGR*, 2008

experimental setup: ambient sample → HTDMA → ATOFMS



⇒ BC in Zurich aerosol is partially externally mixed and partially internally mixed

Direct climate effect:
light absorption enhancement by coating on BC core



Nessler et al., *J. Aerosol Sci.*, 2005.

- **Coating enhances light absorption by the BC core.**
- **Enhancement factor does not exceed a factor of ~2-3.**

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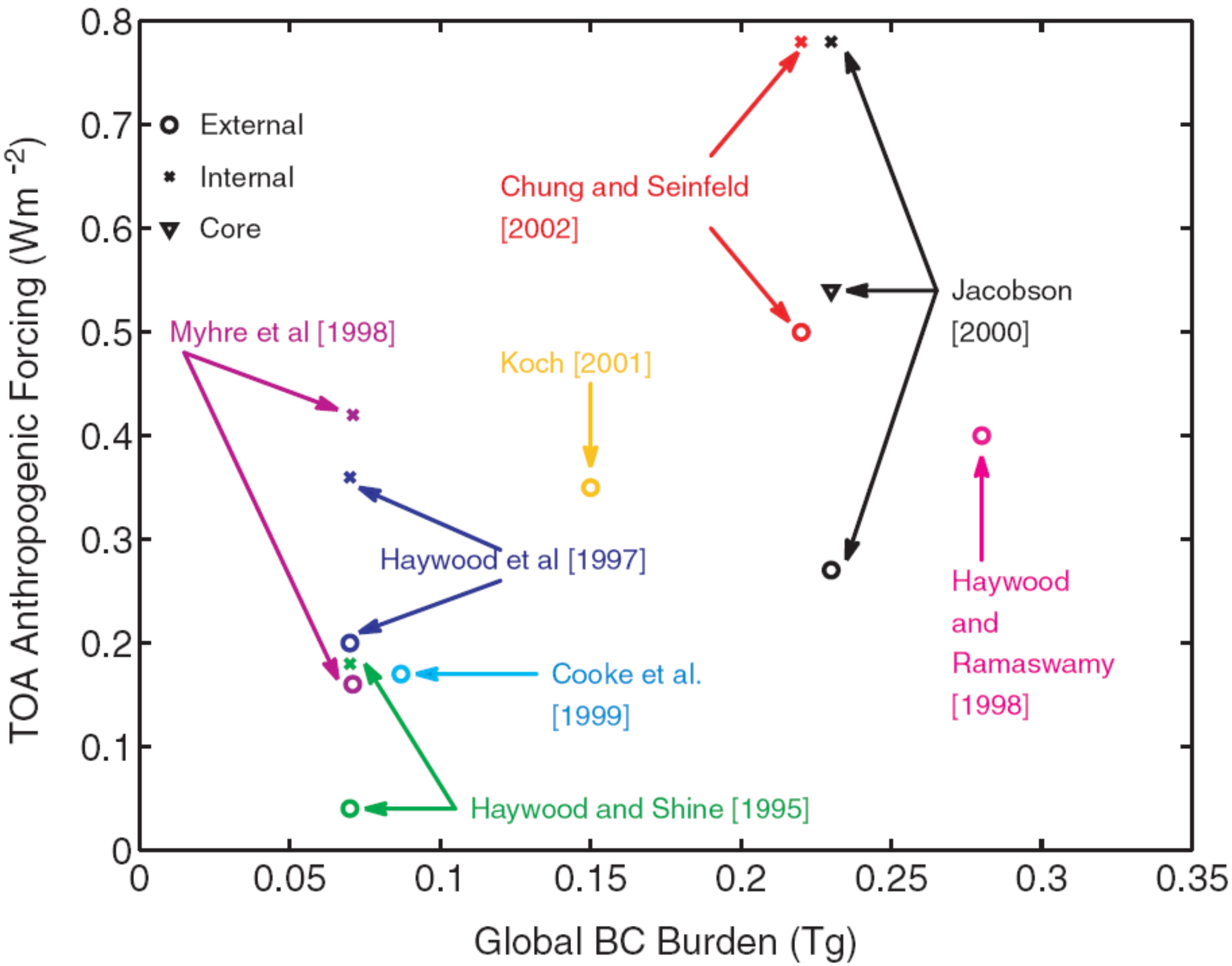
Direct climate effect: TOA anthropogenic forcing from BC



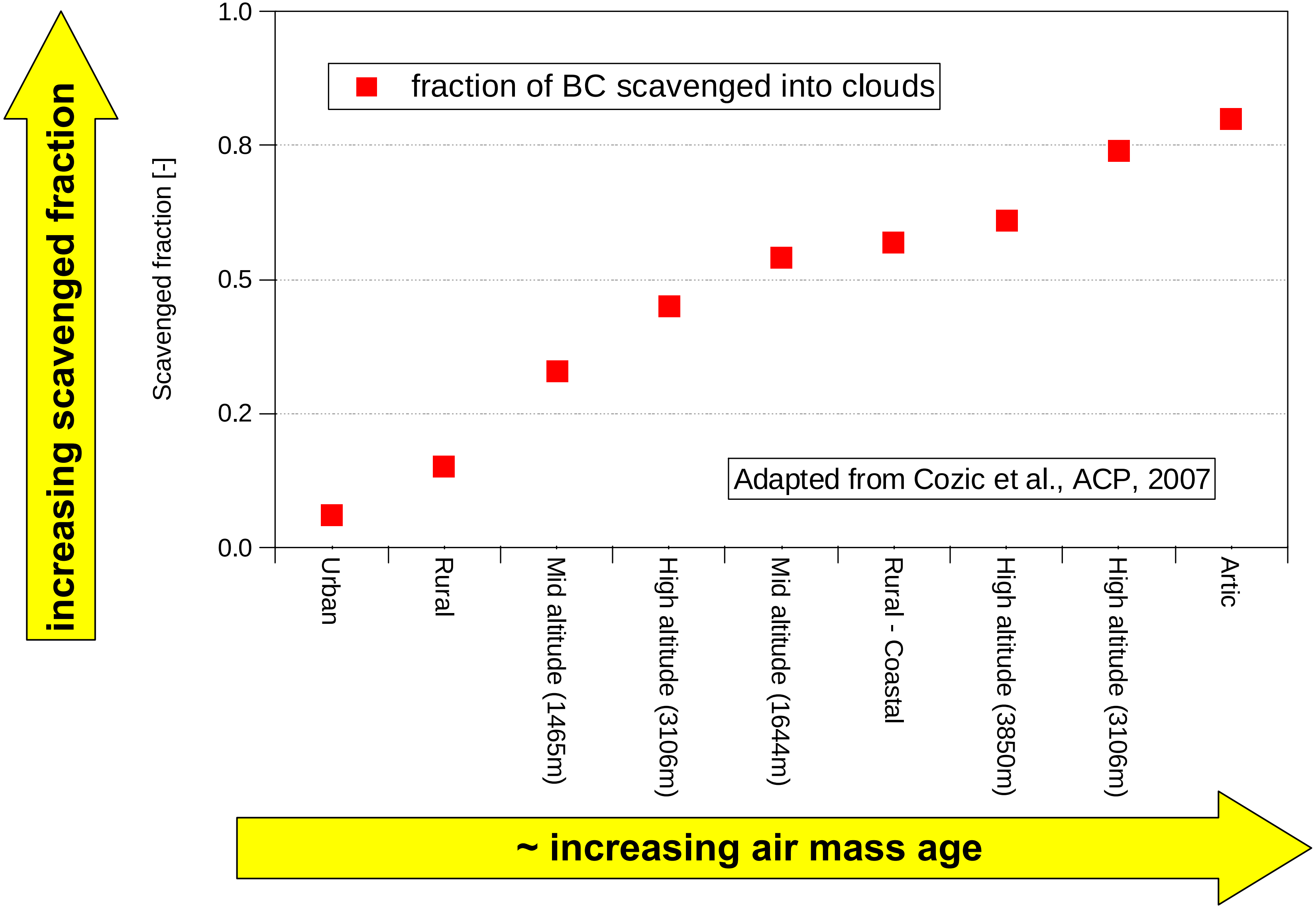
Mixing state of BC:

- internal
- external

Chung and Seinfeld, *J. Geophys. Res.*, 2002.

⇒ factor of ~2 difference in the estimated radiative forcing by BC depending on the assumed mixing state

Indirect climate effect: scavenging of BC into cloud droplets



⇒ BC scavenging increases with air mass age

BC characterization: SP2 (Single Particle Soot Photometer by DMT)

Key features of the SP2:

- Uses laser-induced incandescence (LII) to detect refractory BC.
- Detection of single particles.
- Quantitative measurement of BC uninfluenced by other material in the particle.
- Qualitative and semi-quantitative information on the mixing state of BC.

Technical paper: Stephens et al., *J. Appl. Opt.,* 2003

Indirect climate effect: mixing state of BC and CCN activation (SP2 data)

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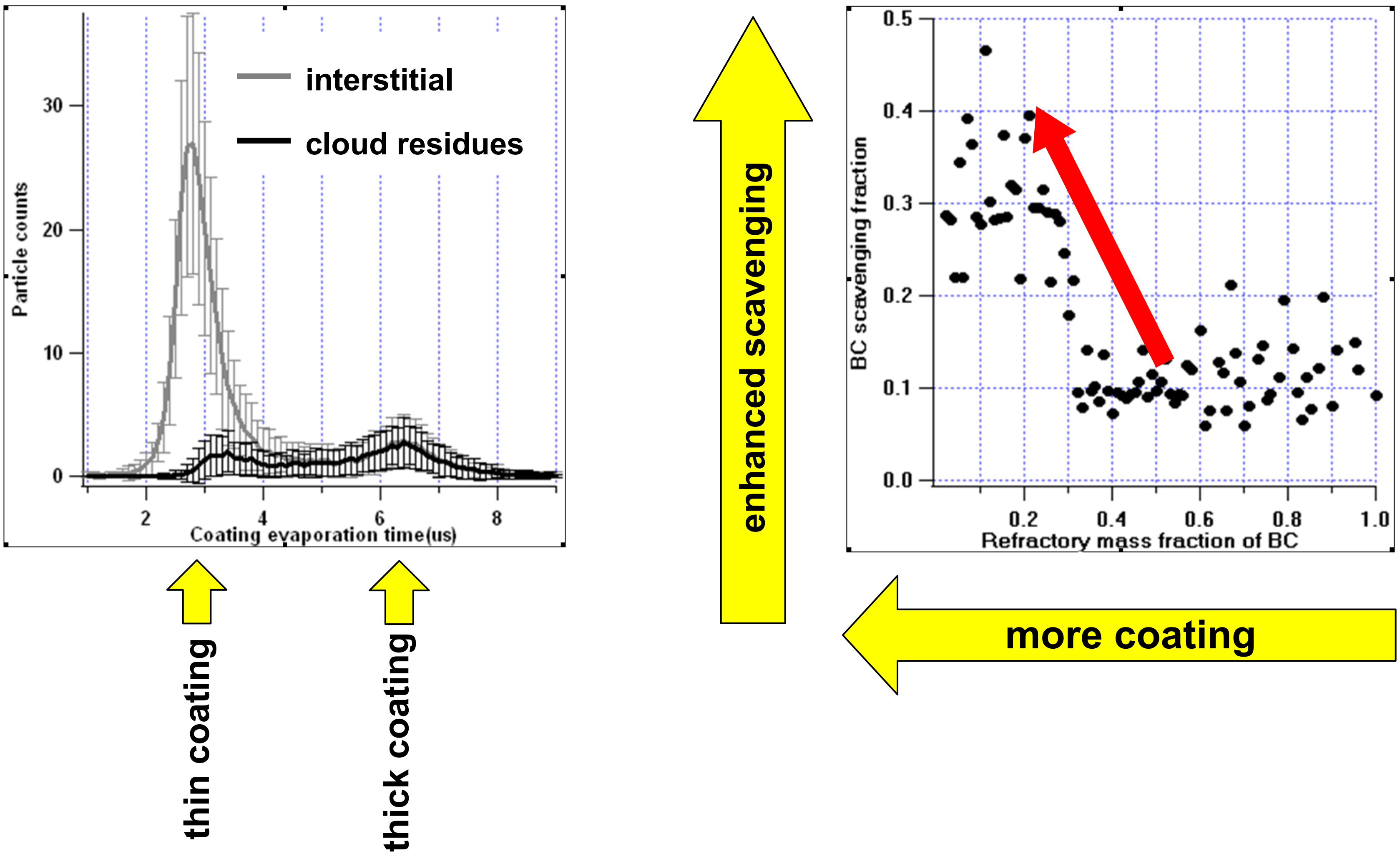
Cloud residues and interstitial particles of an orographic cloud in urban outflow (Holme Moss, UK).

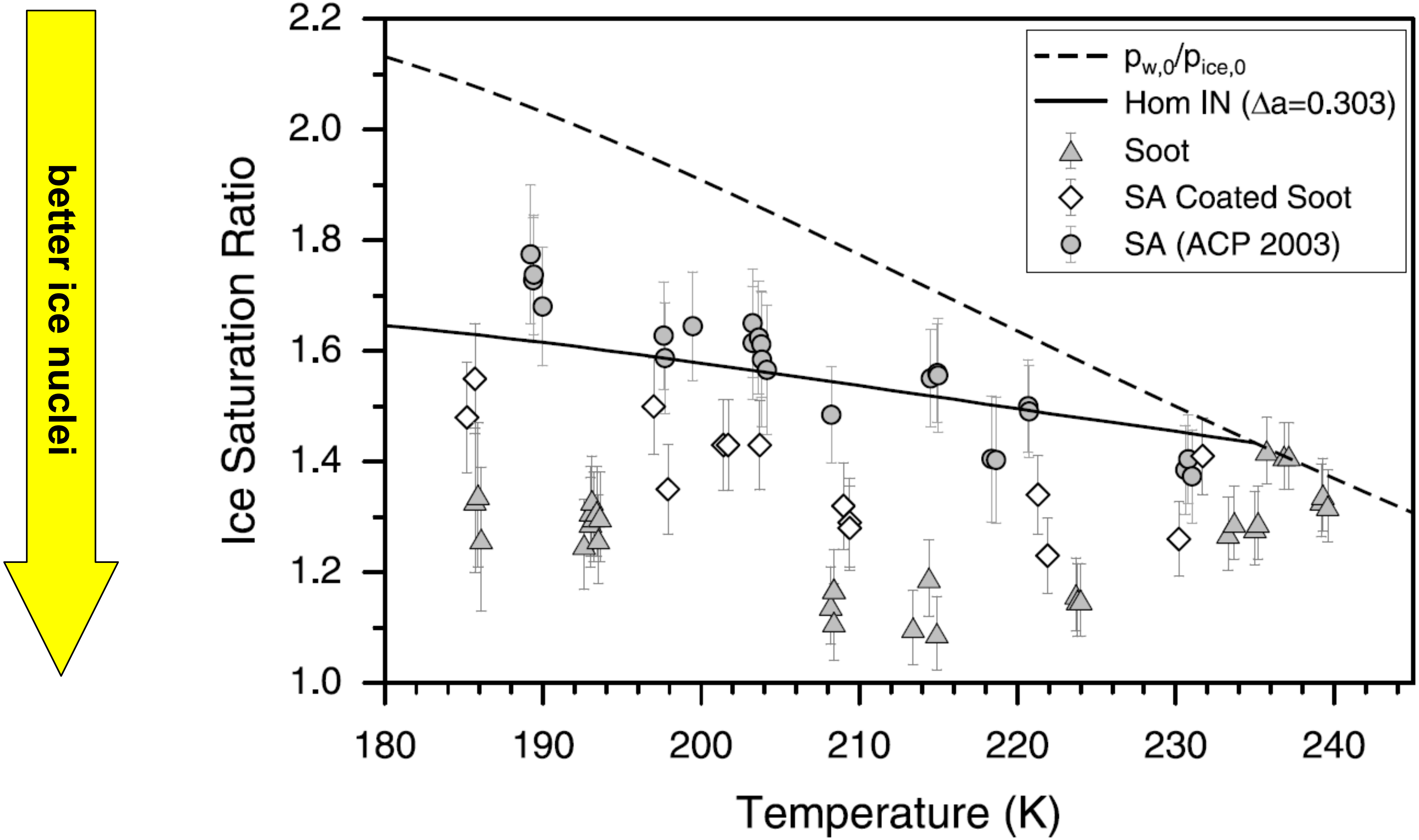
Courtesy of D. Liu, M. Flynn, H. Coe (Univ. of Manchester) and B. Andrews, J. Ogren (NOAA)



⇒ coating increases cloud condensation nuclei (CCN) activity of BC

Ice nuclei activity of BC with/without sulphuric acid coating

Laboratory experiments at the AIDA chamber by Möhler et al., *JGR.*, 2005



⇒ sulphuric acid (SA) coating reduces ice nuclei activity of BC

Lab experiments: example combustion particles

EURO 3 diesel car:
at 60 km/h

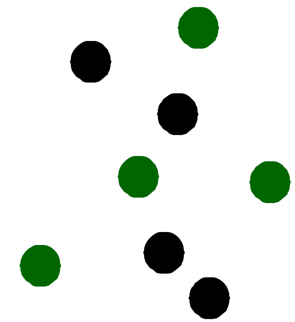
wood pellet oven:
starting phase

wood pellet oven:
stable burning phase

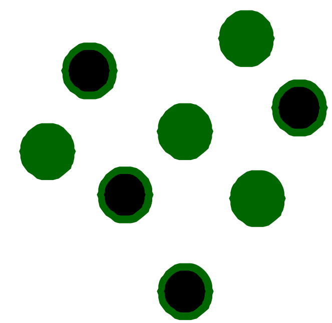
Exhaust is diluted and sampled into PSI's 27 m^3 smog chamber prior to further characterization.

Possible mixing states

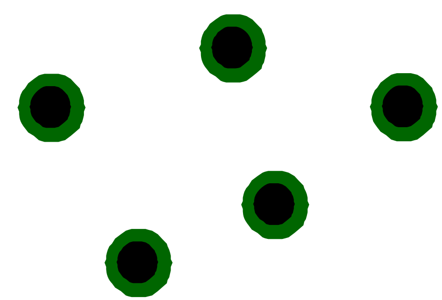
external mixture of BC and scattering compounds



2 different particle types:
- **BC internally mixed with scattering compounds**
- **pure scattering particles**



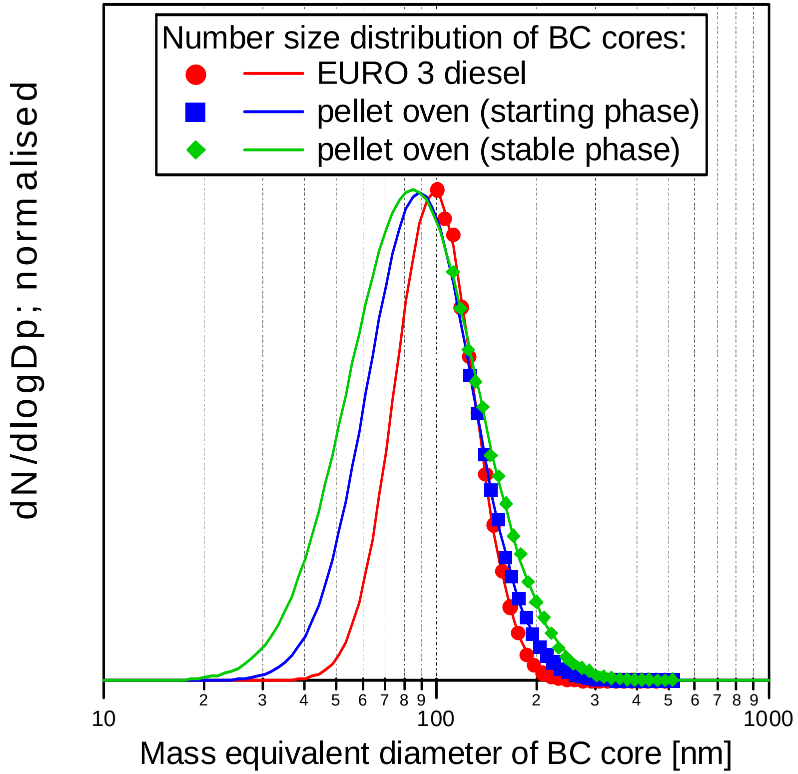
internal mixture of BC and scattering compounds



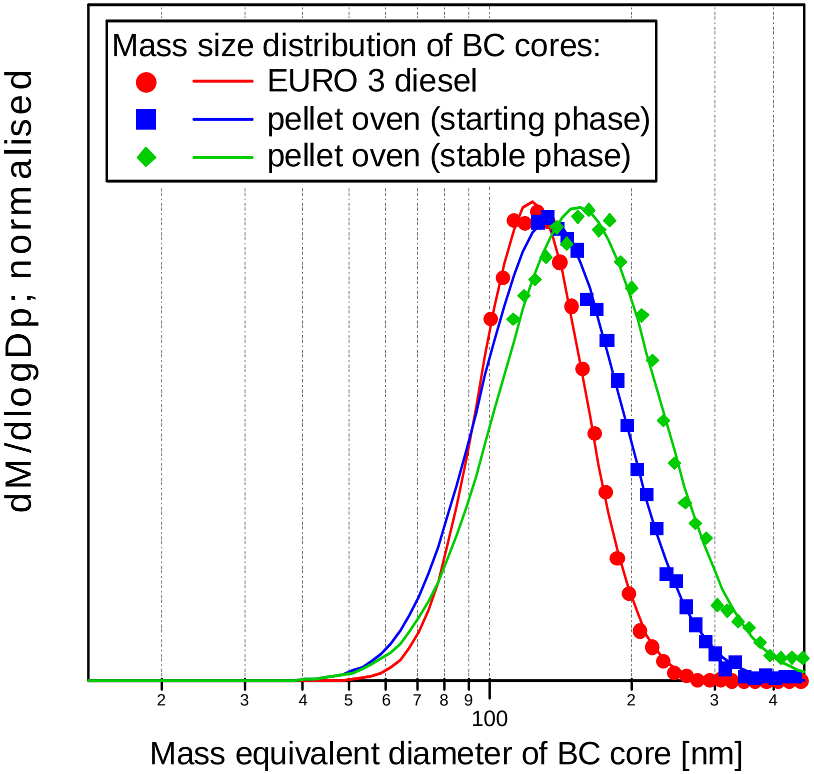
Number and mass size distributions of BC cores (SP2)

● EURO 3 diesel ● pellet oven (starting) ● pellet oven (stable)

number



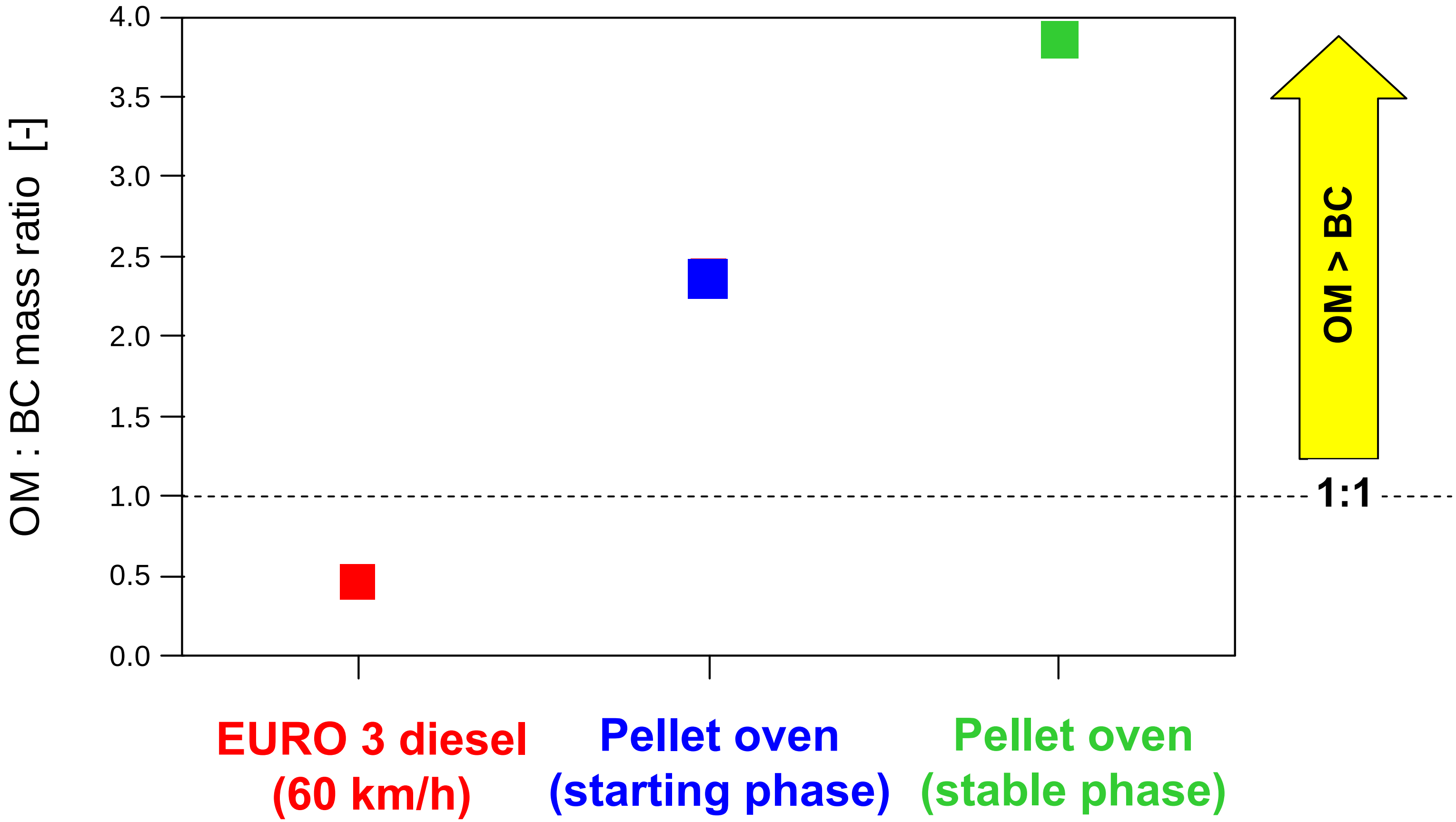
mass



⇒ **shape of BC core size distribution is similar for all three examples (absolute emission factors are of course different)**

OM : BC ratio

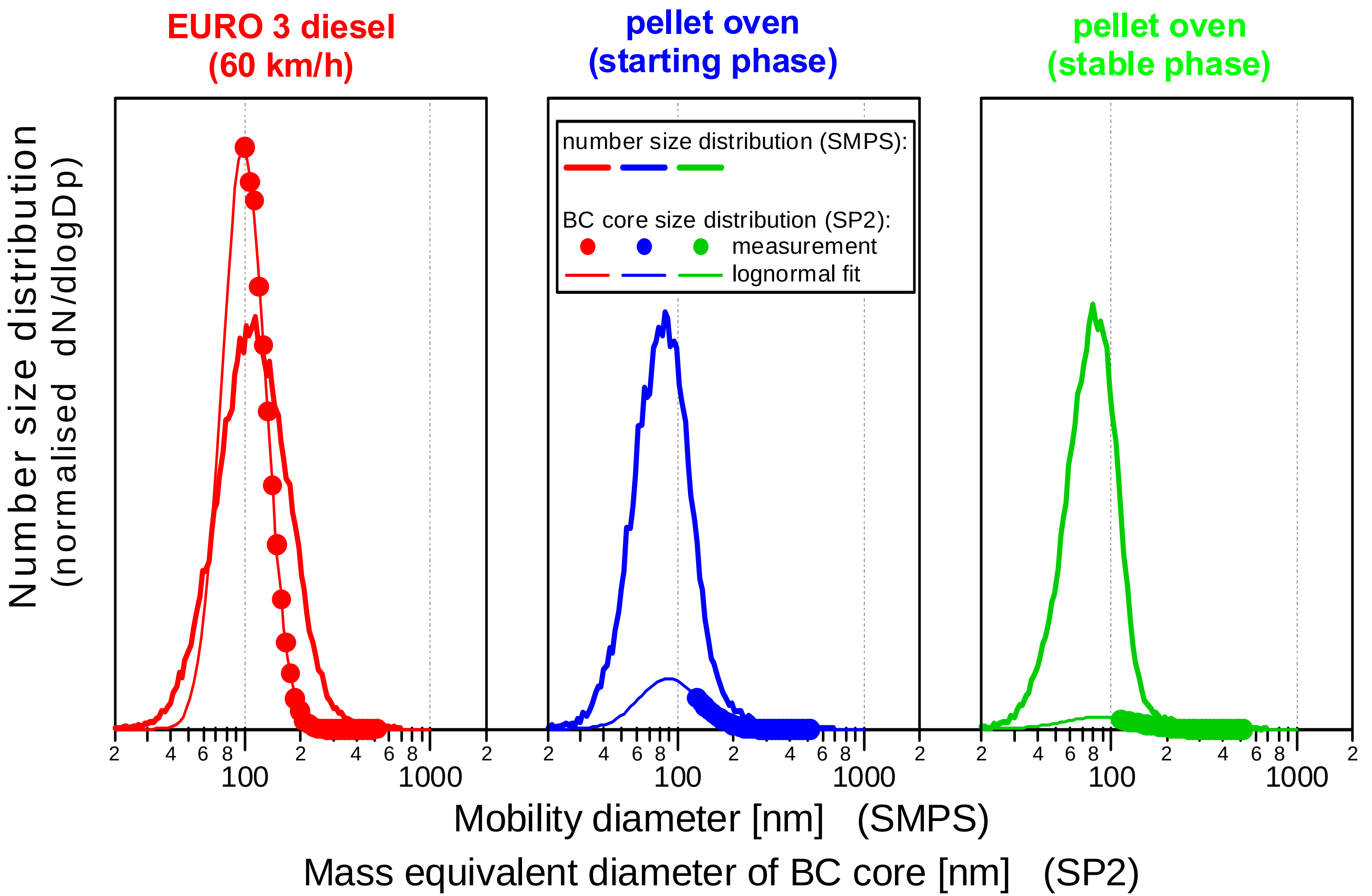
Organic matter (OM) measured on-line using an Aerodyne HR-ToF Aerosol Mass Spectrometer



⇒ EURO 3 diesel: BC dominates over OM.

⇒ Pellet oven: BC is only a minor mass fraction.

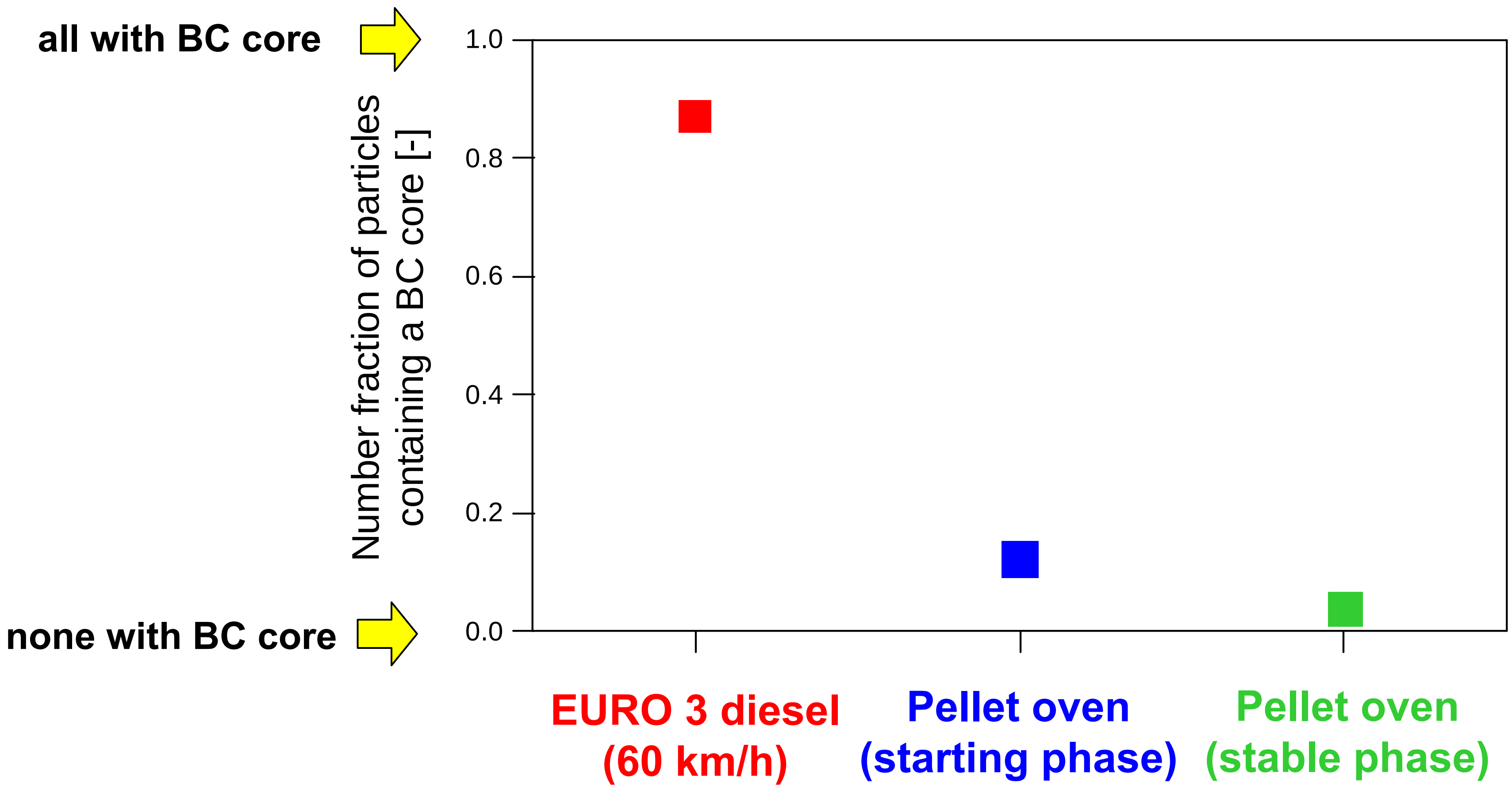
BC core size distr. compared to number size distr.



⇒ **EURO 3 diesel:** **number of particles ≈ number of BC cores**

⇒ **Pellet oven (both):** **number of particles >> number of BC cores**

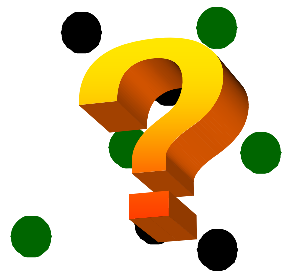
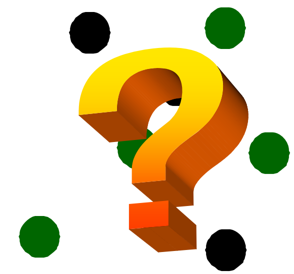
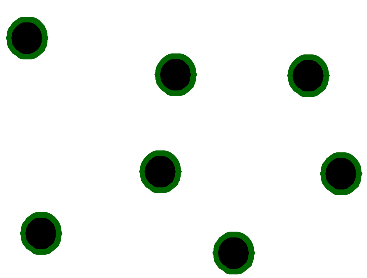
Number fraction of particles with BC core



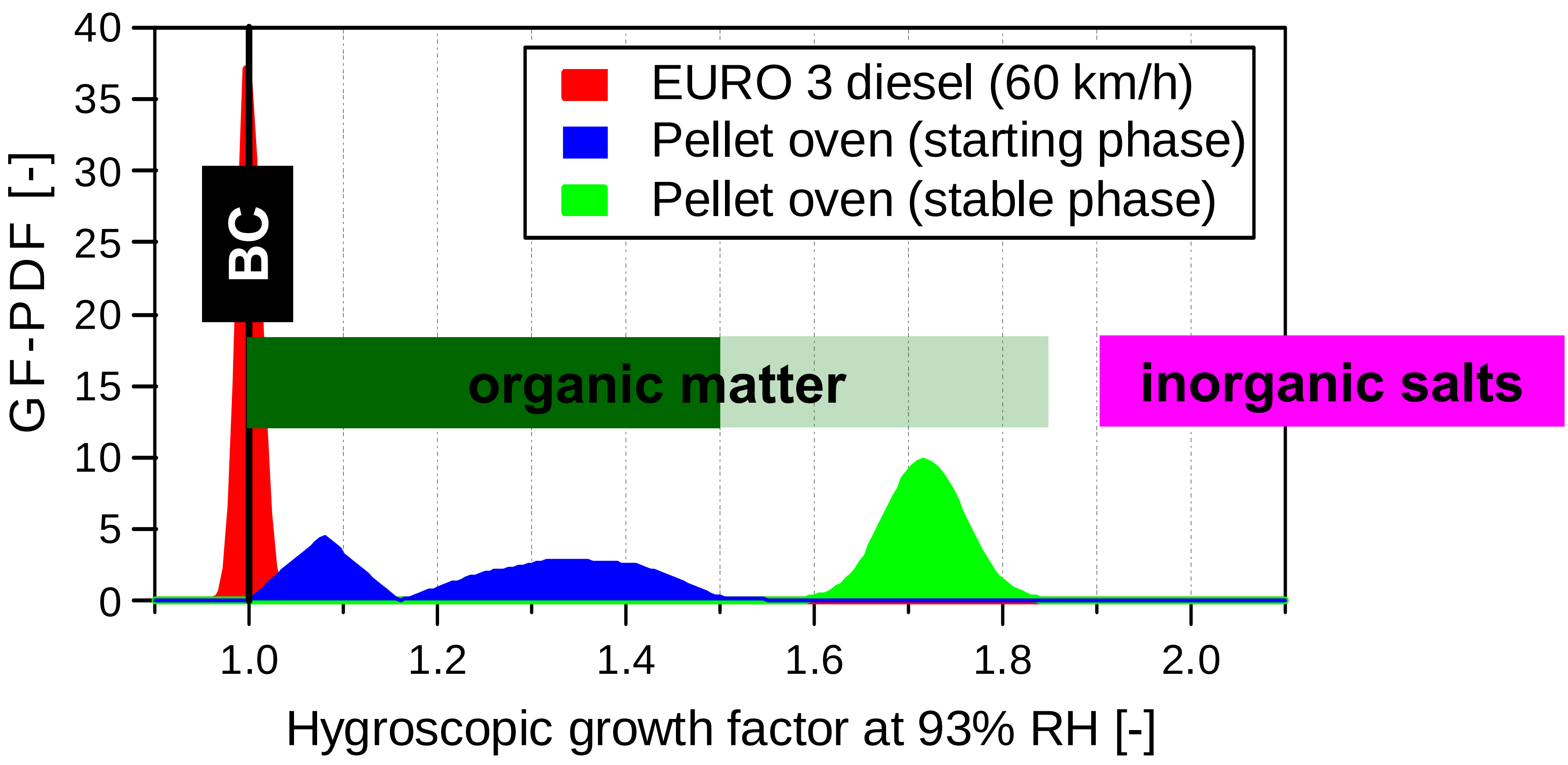
⇒ **EURO 3 diesel: ~every particle contains a BC core**

⇒ **Pellet oven: dominant fraction of particles without BC core**

Mixing state determination

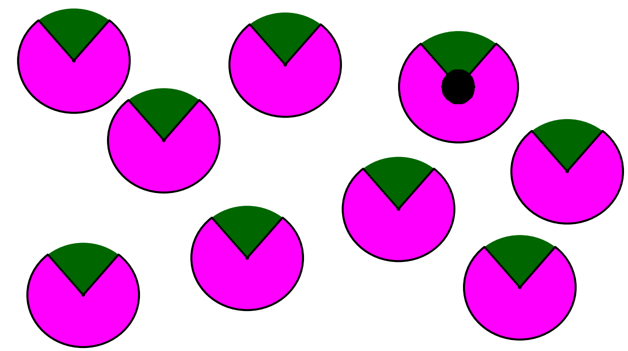
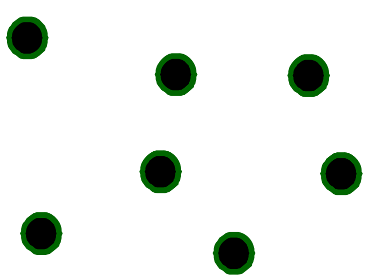
EURO 3 diesel (60 km/h)	pellet oven (starting phase)	pellet oven (stable phase)
X		
X		
	X	X

Different growth factors indicate different composition

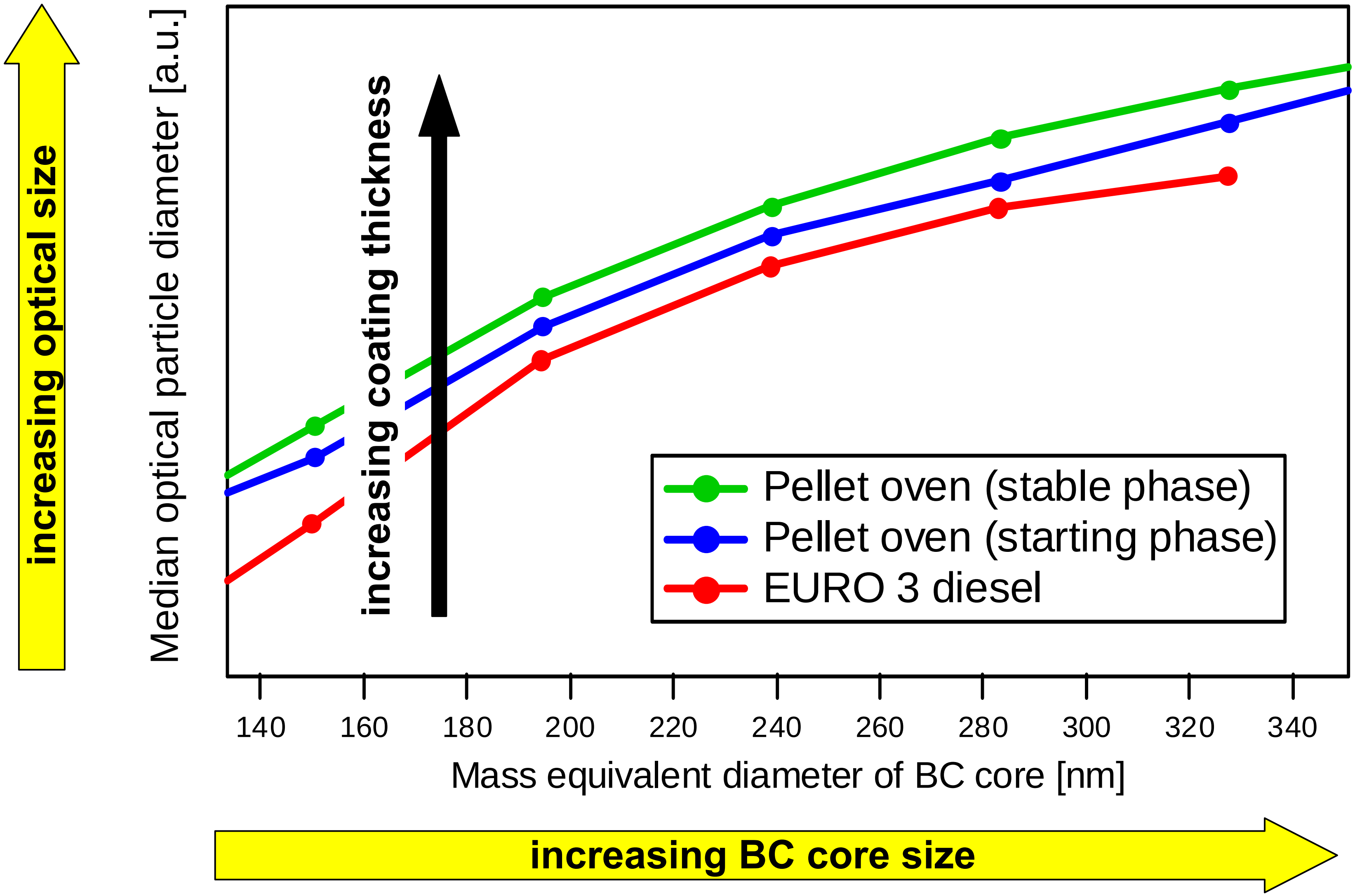


- **EURO 3 diesel (60 km/h): BC + hydrocarbon-like organic matter.**
- **Pellet oven (starting): remains to be ascertained.**
- **Pellet oven (stable): inorganic salts (~50%) + OM + BC.**

Mixing state determination (continued)

EURO 3 diesel (60 km/h)	pellet oven (starting phase)	pellet oven (stable phase)
X	X	X
X		
	X	X

Coating thickness of BC from SP2 data



⇒ coating thickness: pellet stable >> pellet starting >> diesel at 60 km/h

Ascertain pellet oven starting phase: employ HTDMA+SP2 in series

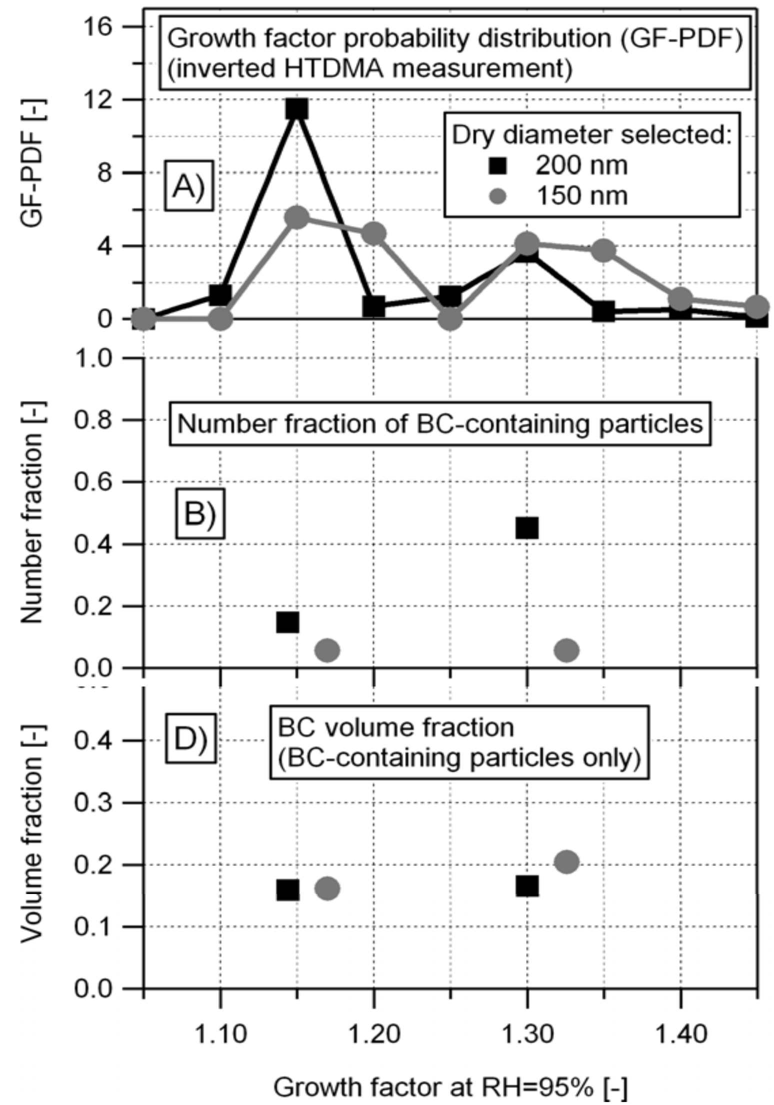
HTDMA:

Mode at GF≈1.15-1.20:
⇒ not pure BC, <5% inorganic salt

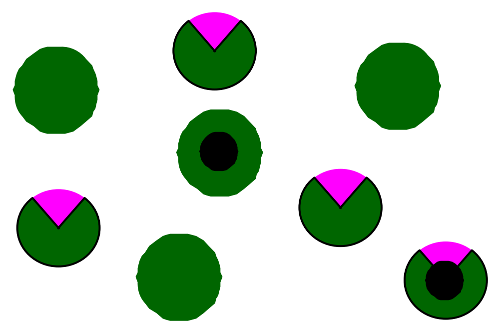
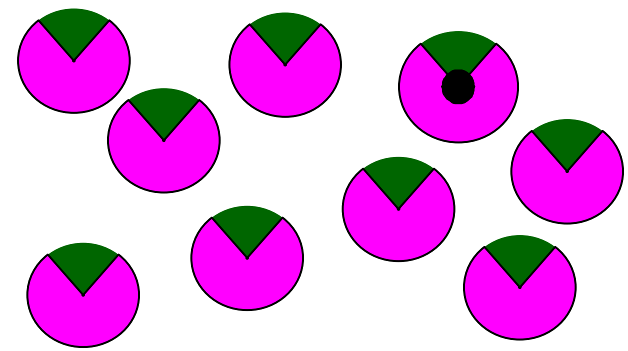
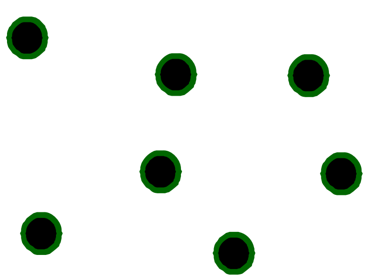
Mode at GF≈1.30-1.35:
⇒ mainly organics and/or BC; ~5-10% inorganic salt likely

SP2 (number of BC cores):
⇒ only minor fraction of particles contains detectable BC
⇒ BC cores found in either growth mode!

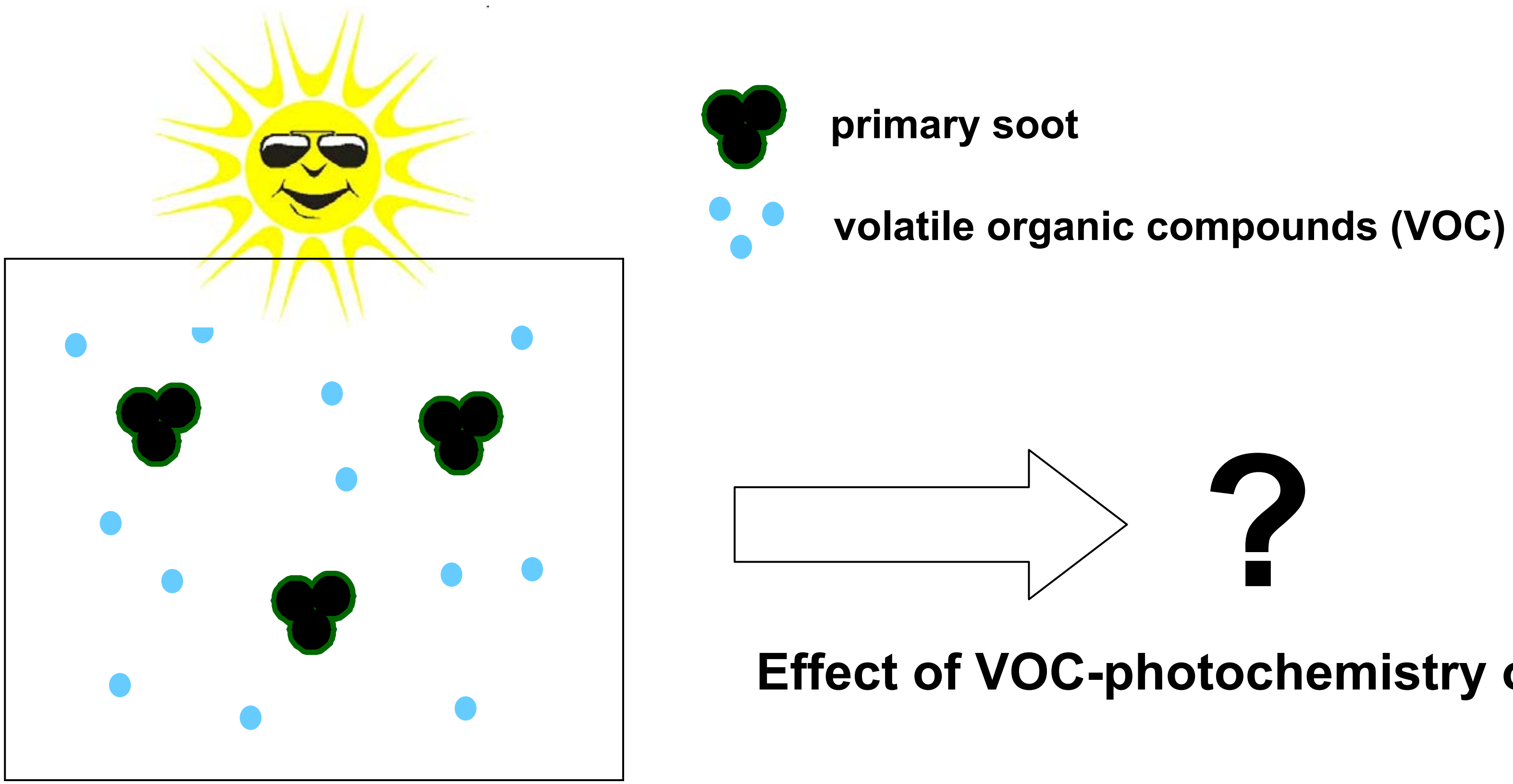
SP2 (mean BC core size):
⇒ at most ~20 vol-% is BC
⇒ all BC cores have a thick coating



Final result of mixing state determination

EURO 3 diesel (60 km/h)	pellet oven (starting phase)	pellet oven (stable phase)
X	X	X
X		
	X	X

Simulating atmospheric aging process in the lab



Effect of VOC-photochemistry on BC?

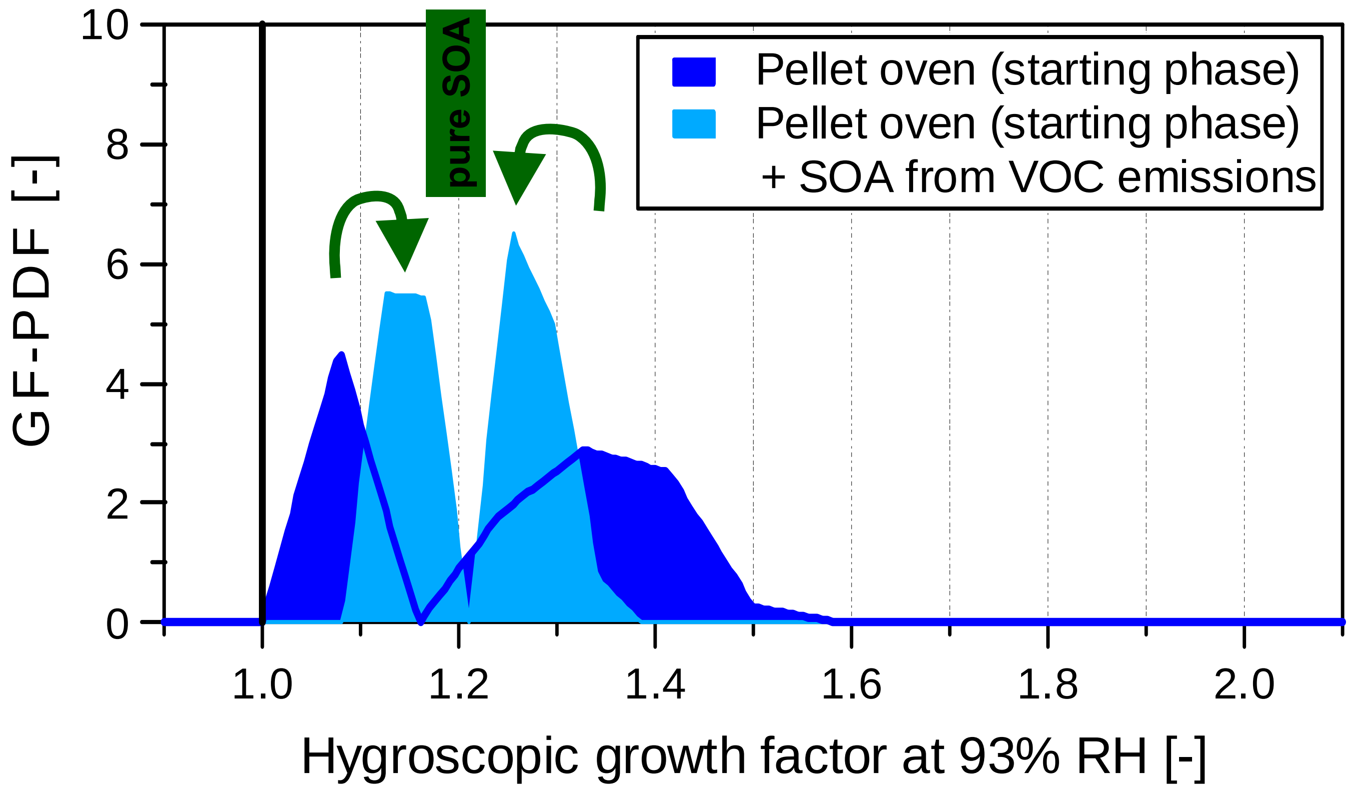
More on the aerosol formation potential from VOC emissions of diesel and wood combustion exhaust in:

Session 2: “Primary organic aerosol and secondary aerosol formation potential from a Euro 3 diesel passenger car” (R. Chirico)

Session 6A: “Investigation of primary and secondary organic aerosols from wood combustion with a high resolution time of flight aerosol mass spectrometer” (M. Heringa)

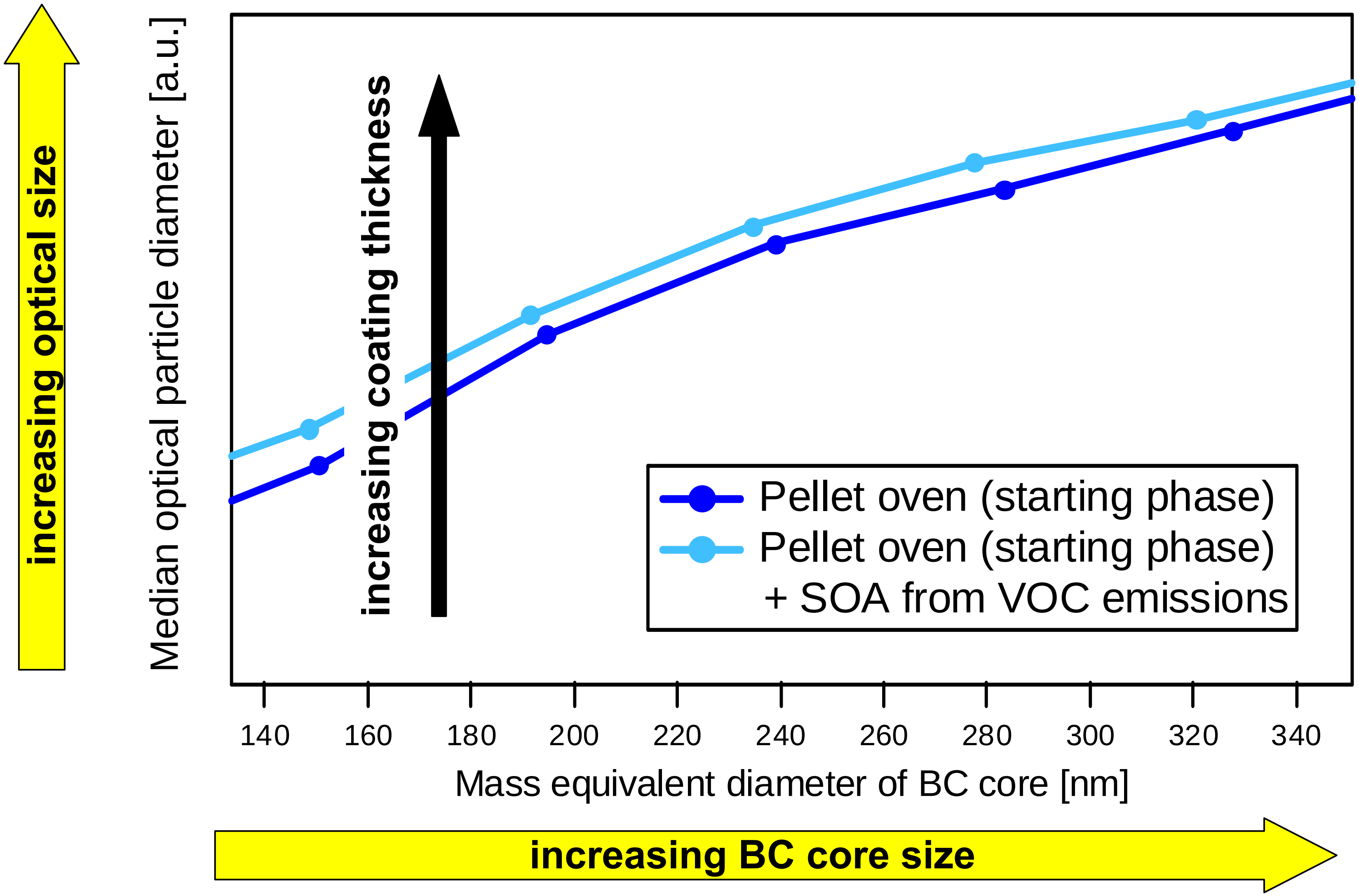
Atmospheric aging: effect of SOA on hygroscopicity

condensation of secondary organic aerosol (SOA) produced from photochemical reactions of volatile organic (VOC) emissions



HTDMA indicates condensation of SOA ⇒ increased coating thickness

Atmospheric aging: effect of SOA on coating thickness



⇒ increase of coating thickness confirmed by SP2 measurement

Conclusions and outlook

This presentation aimed at showing that:

- **mixing state of BC is important for its climate effects.**
- **a substantial fraction of freshly emitted BC is externally mixed.**
- **atmospheric aging processes lead towards internally mixed BC.**

Furthermore:

- **Recent developments of single particle detection techniques and aerosol mass spectrometry will – hopefully – allow us to better understand the properties and evolution of atmospheric BC during its live-cycle and its interactions with clouds.**

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Acknowledgement

LABOR FÜR ATMOSPHÄREN-CHEMIE

Particular thanks to my co-workers

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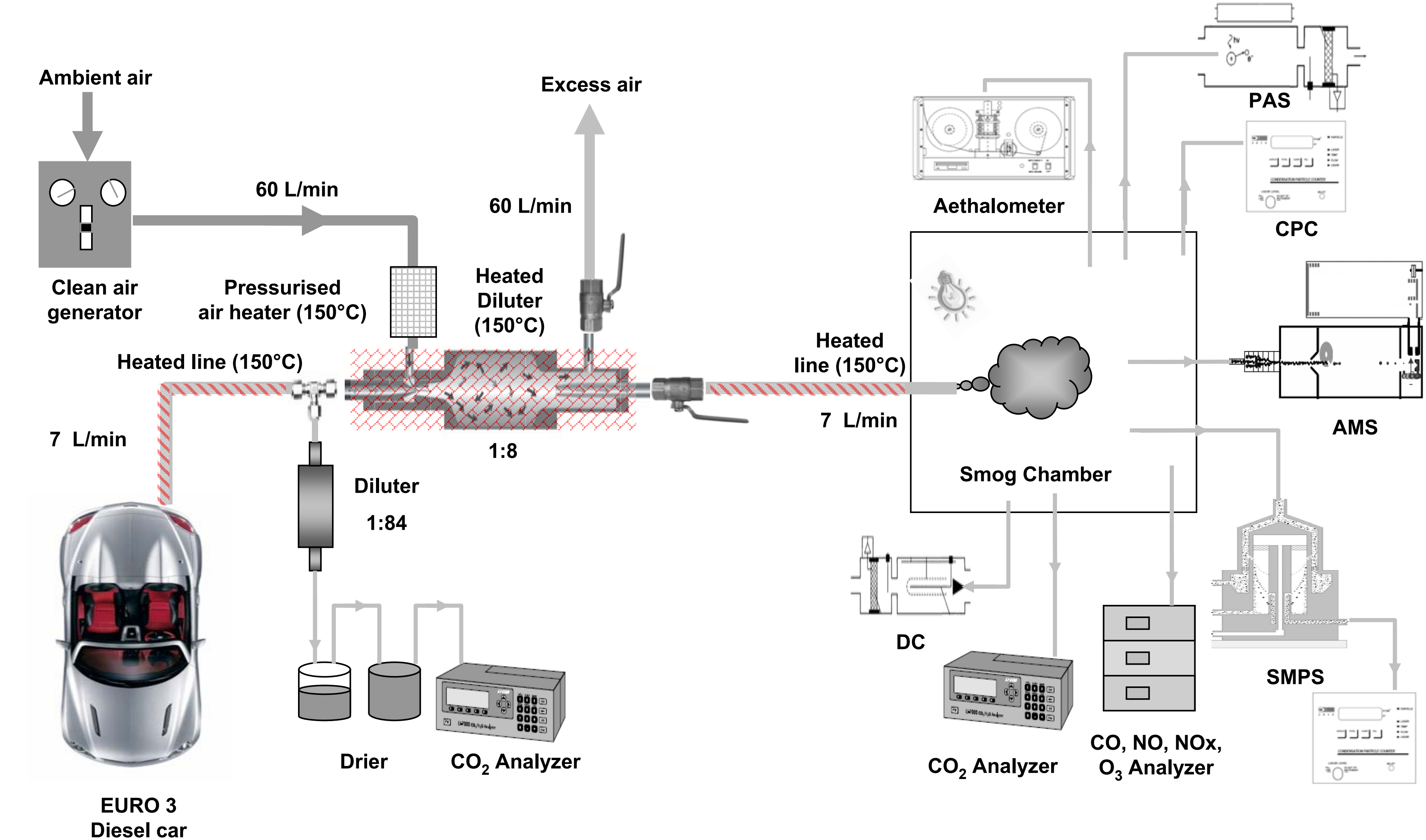
Josef Dommen
René Richter
Günther Wehrle
Jun Noda,
Torbjörn Gustafsson
Jan Pettersson
Ernest Weingartner
André Prévôt
Urs Baltensperger

for their tremendous efforts in
- running the diesel and wood combustion smogchamber experiments
- analysing experimental data and providing their results
- maintaining the infrastructure
- providing input and feedback in many discussion
- …

Financial support was received from:
- Swiss National Science Foundation
- Competence Center Energy and Mobility
- ESF-programme INTROP

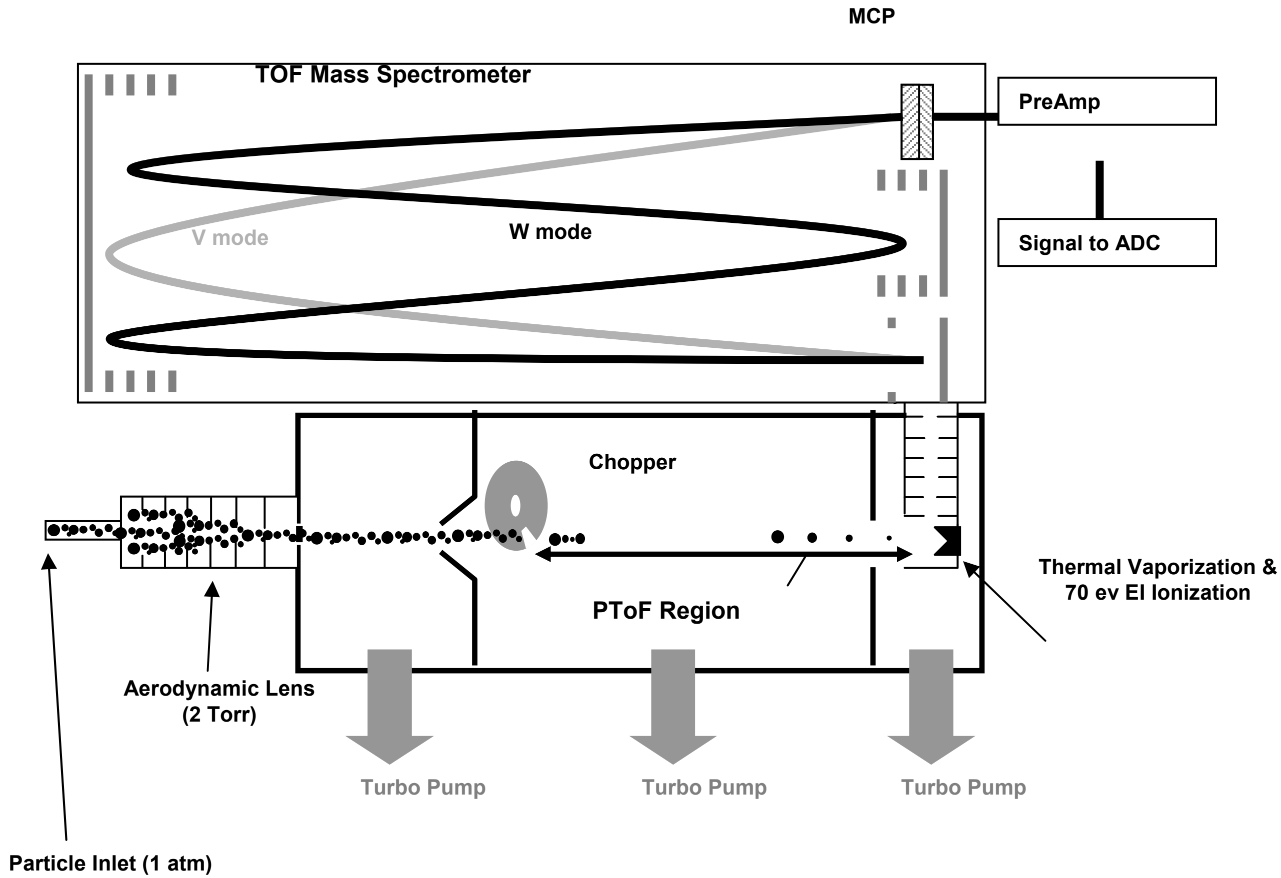
Set up for smog chamber experiments



Dilution factors: 300-1200

Idle – 60 km/h

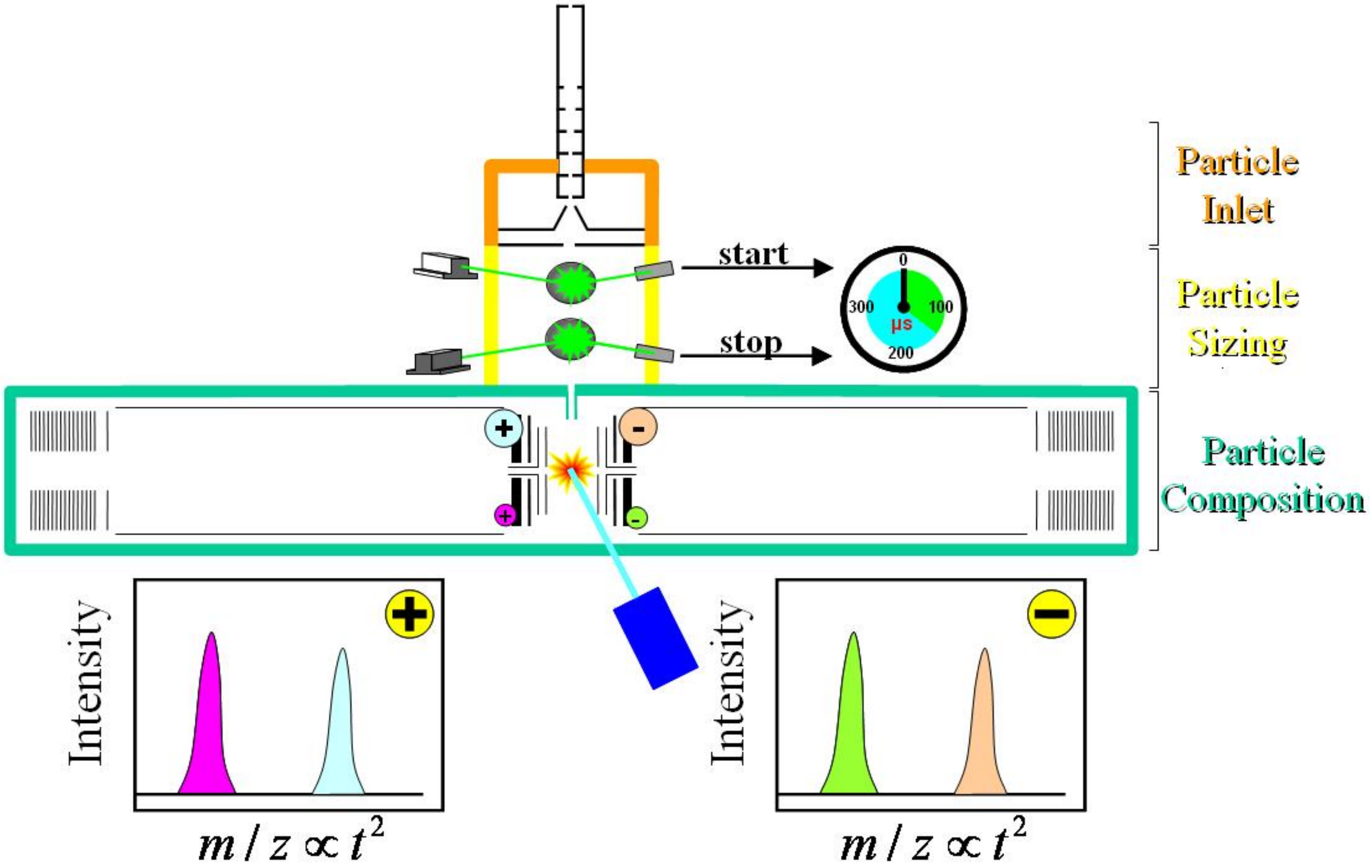
Organic Matter and Non-Refractory Inorganic Salts: Aerodyne HR-ToF-AMS



Aerosol mass spectrometer here mainly used for quantitative detection of organic matter.

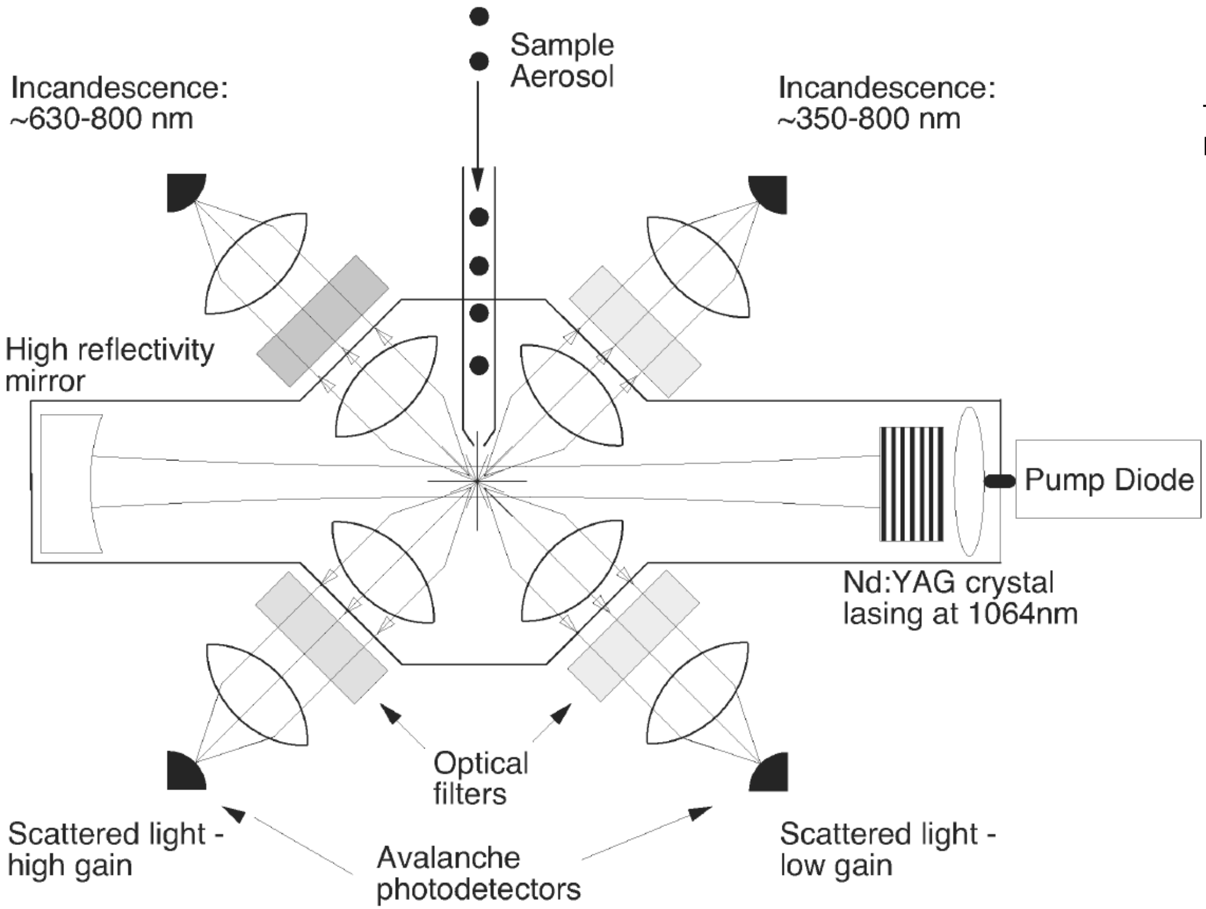
TSI ATOFMS

ATOFMS: Bipolar Time-of-flight mass spectrometer
Chemical composition of single particles (qualitative)
Nd-YAG solid state laser, λ = 266 nm



D. Gross, Carleton College, Based on TSI, Inc. schematic.

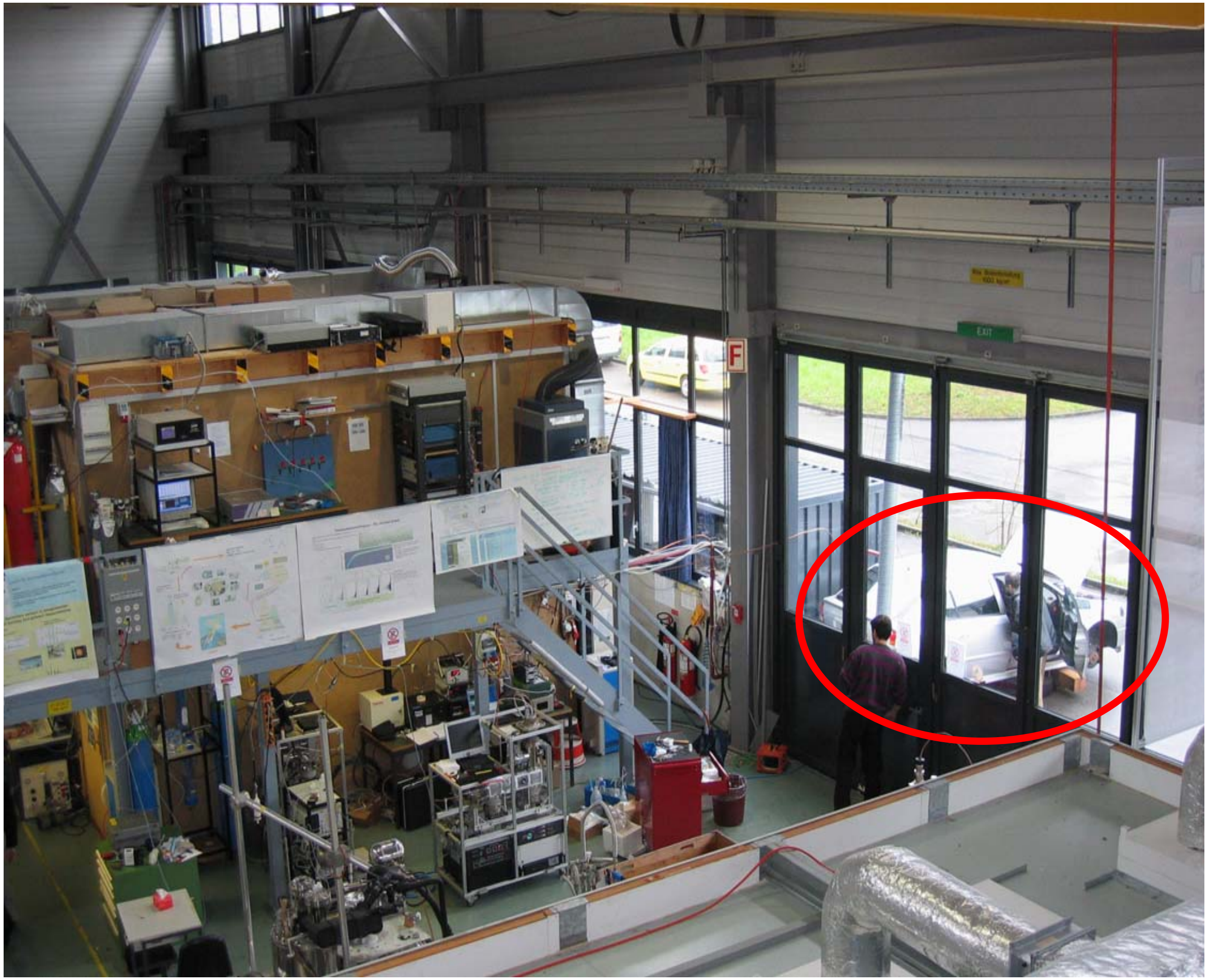
BC Characterization: Single Particle Soot Photometer



Technical paper: Stephens et al., J. *Appl. Opt.,* 2003.
Figure: Gao et al., *Aerosol Sci. Technol.,* 2007.

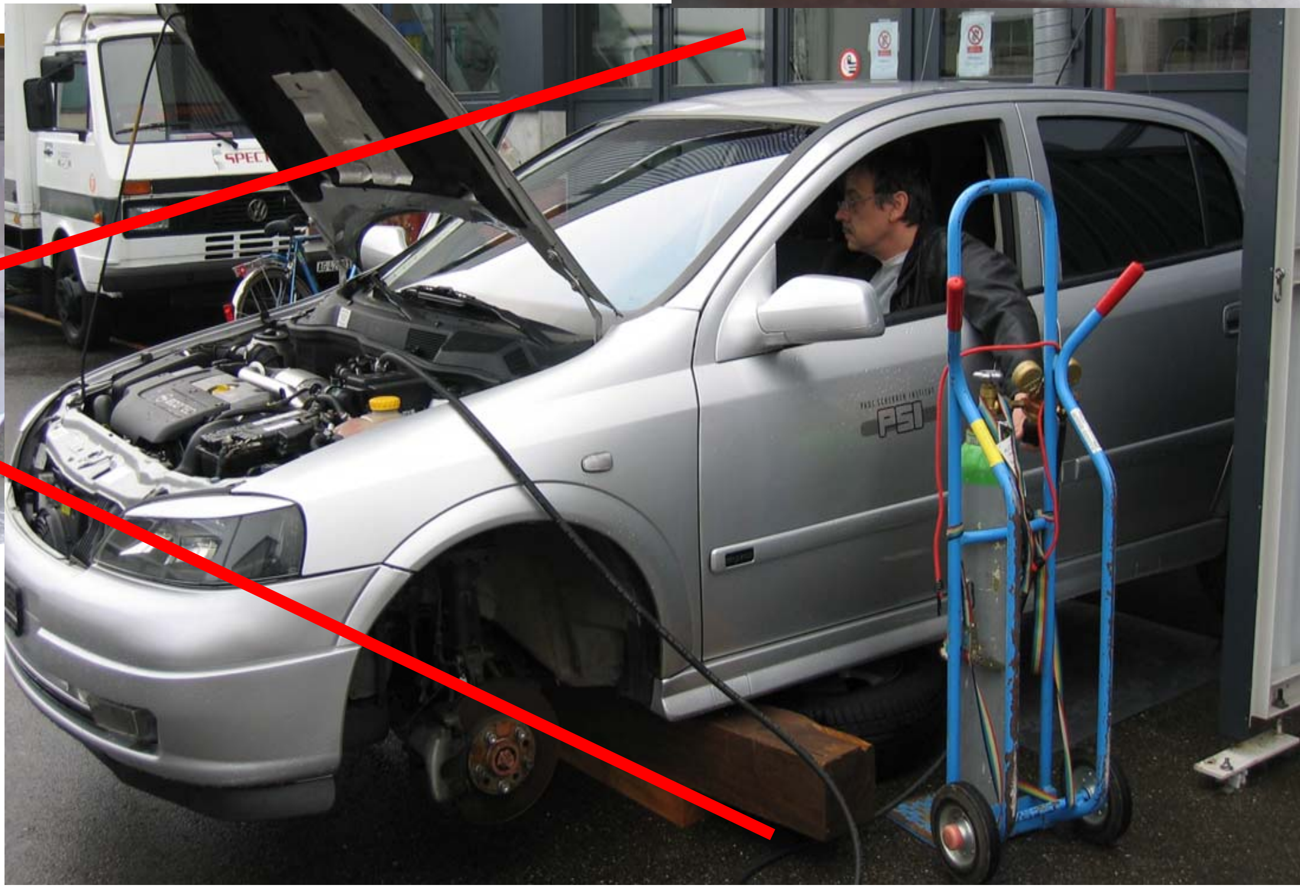
- Detection of single particles.
- Quantitative measurement of BC uninfluenced by other material in the particle.
- Qualitative information on the mixing state of BC.

Diesel Exhaust Processing in the PSI Smog Chamber



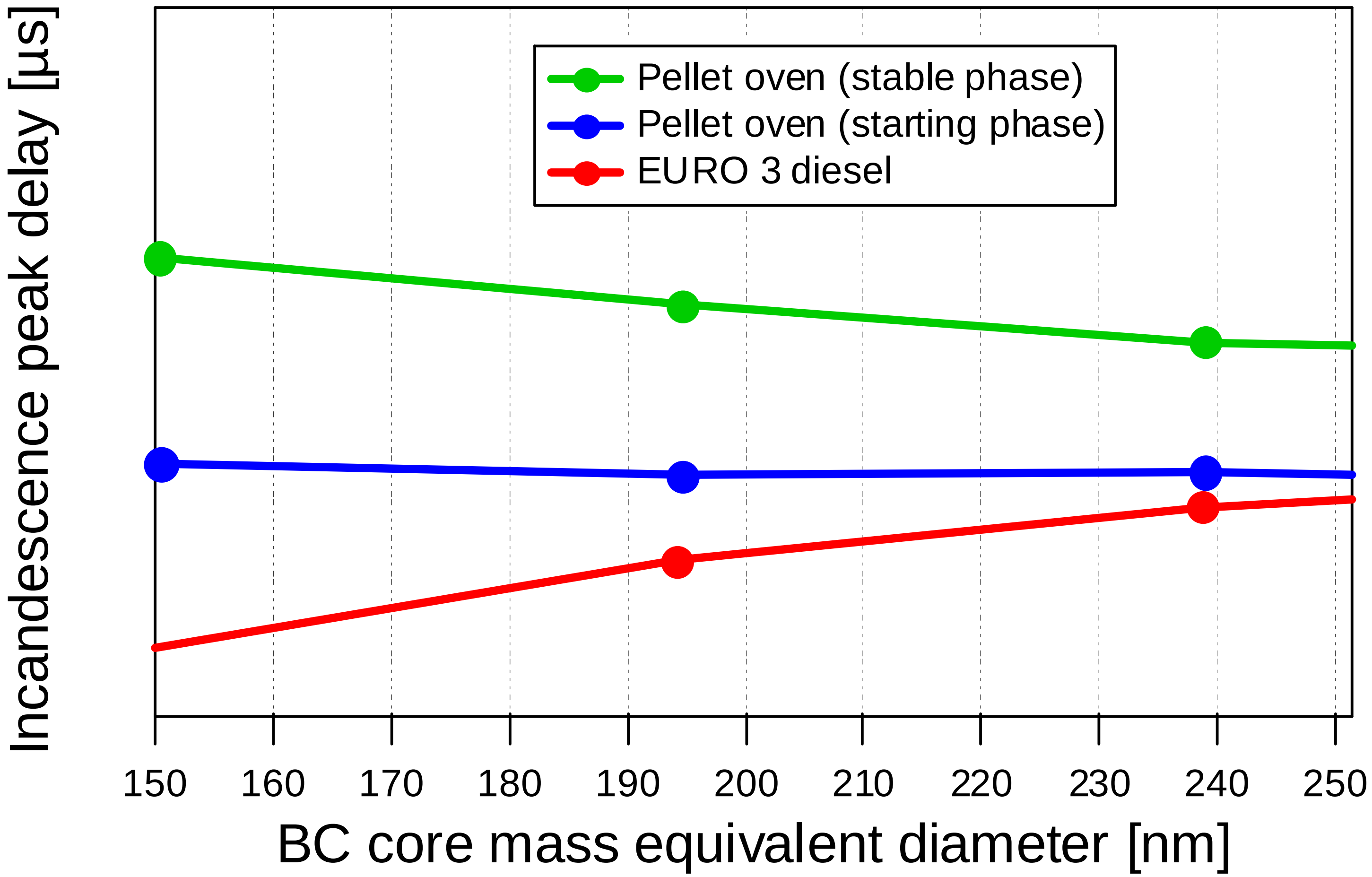
Diesel Exhaust Processing in the PSI Smog Chamber

Euro 3 diesel car running at 60 km per hour

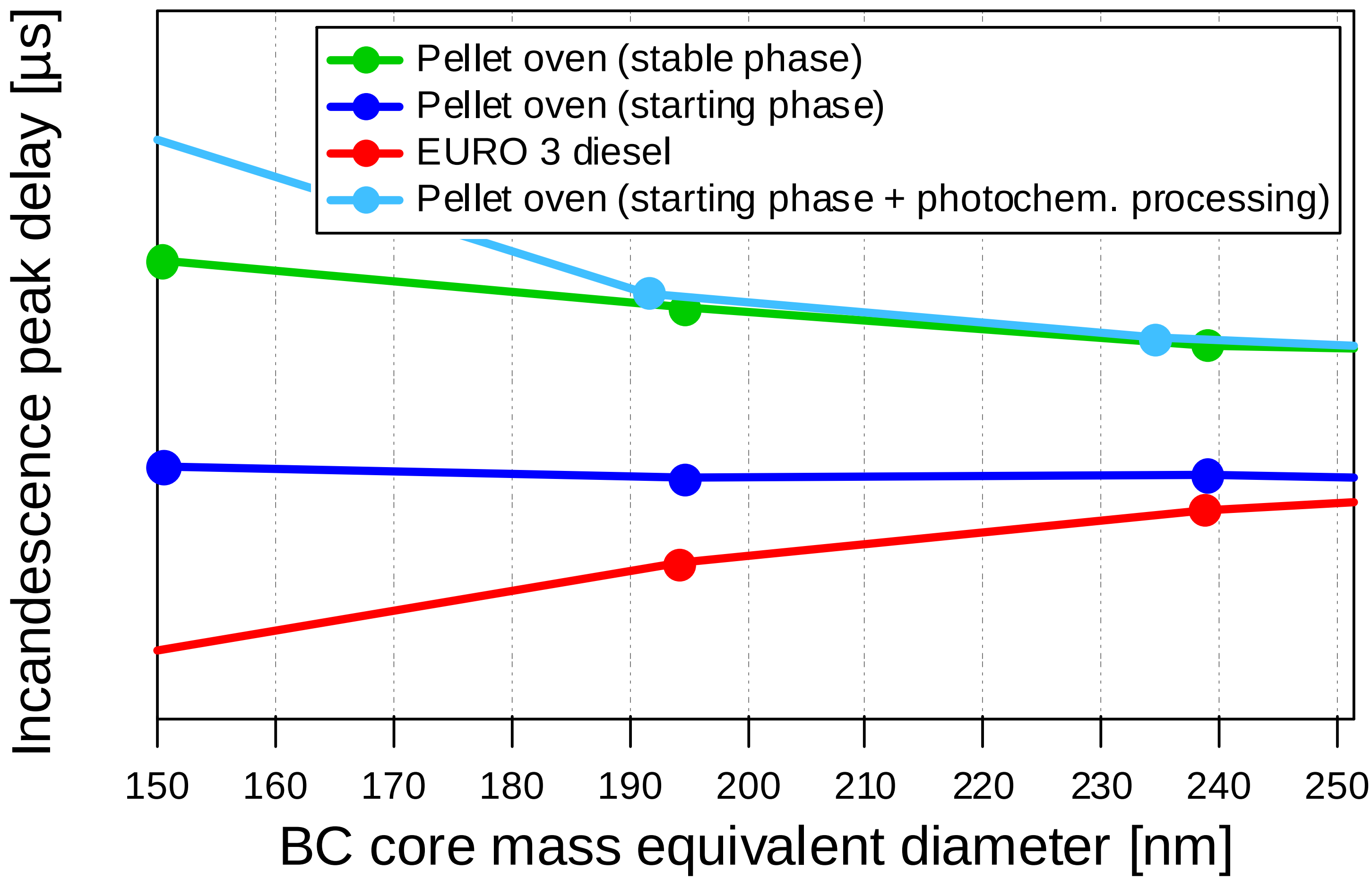


Filling the chamber in ~15 min

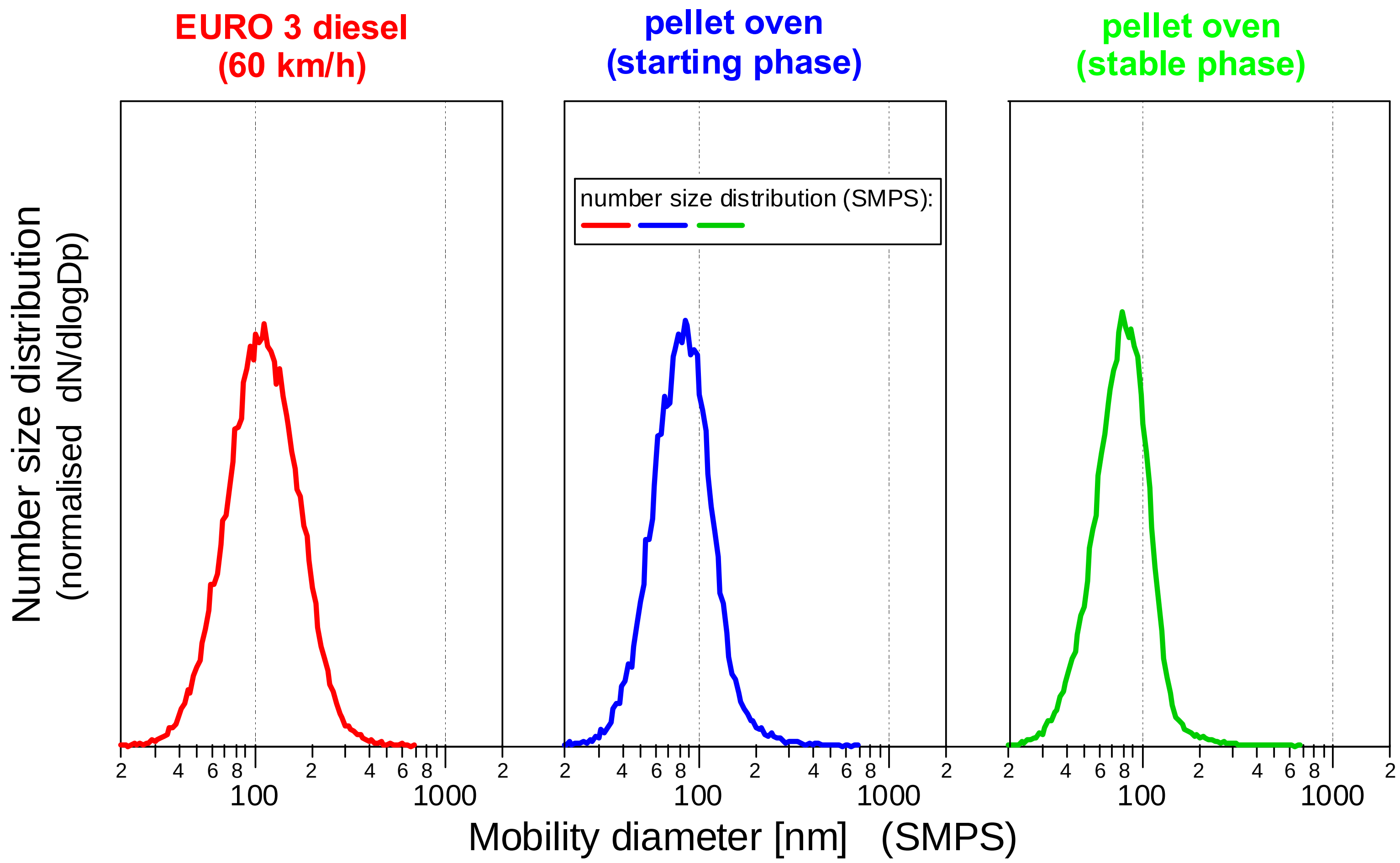
Qualitative Measurement of Coating Thickness (SP2)



Qualitative Measurement of Coating Thickness



Number Size Distributions (SMPS)



⇒ normalised number size distributions are similar in all three cases

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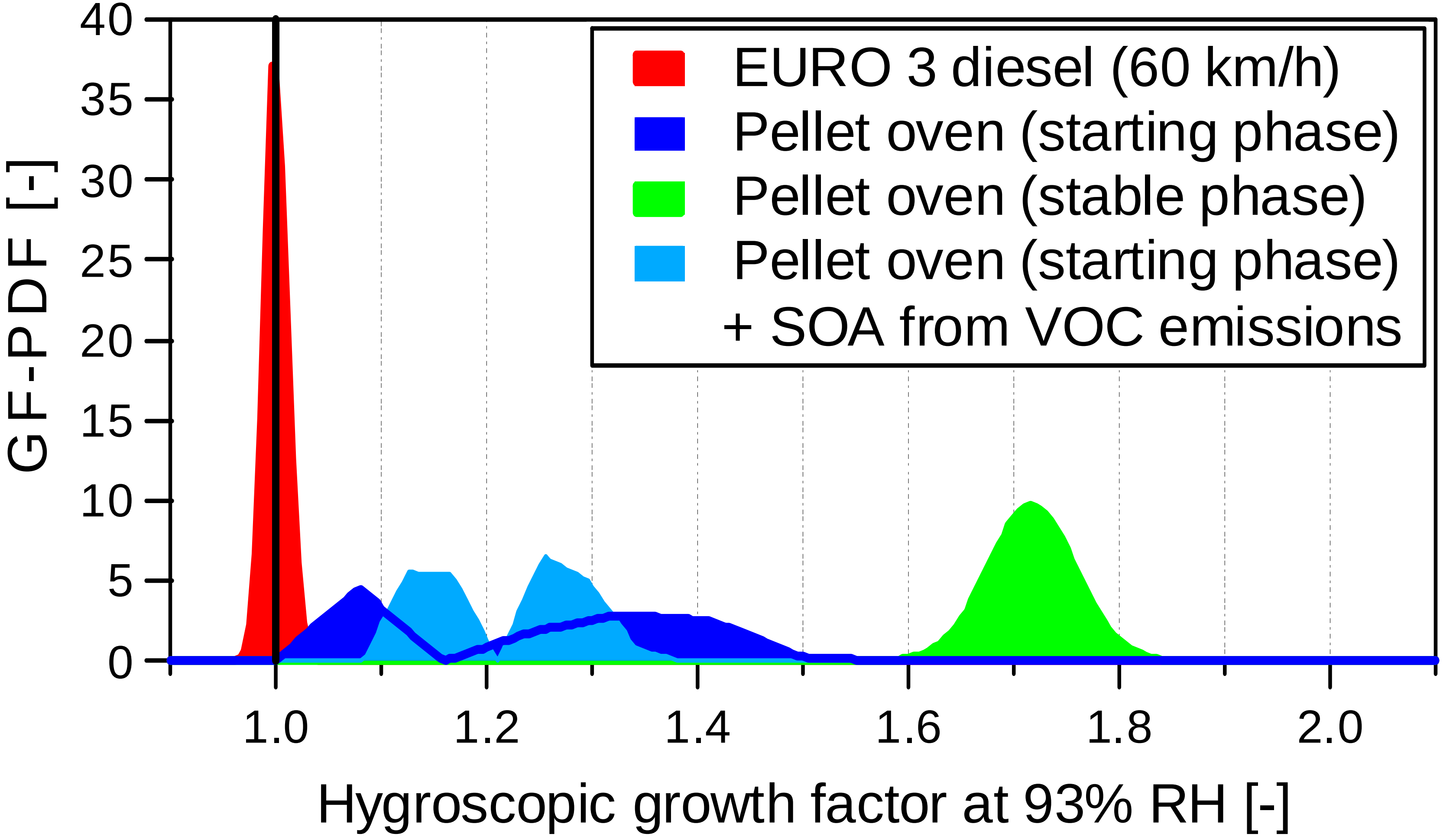


Scavenging of Black Carbon

Aging effect

Close to sources

Far from sources

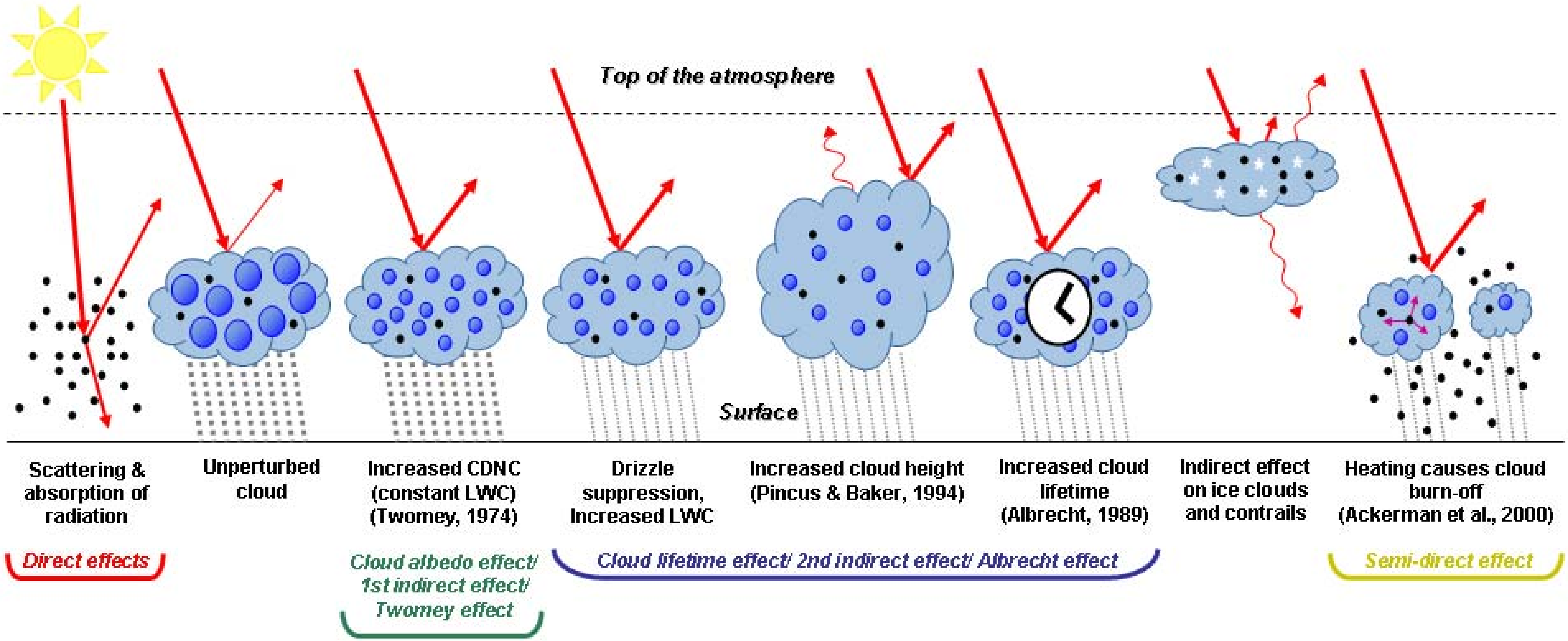
Sampling site	$F_{scav,BC}$	Type of site	Reference
Po Valley (Italy)	0.06	Urban	Hallberg et al. (1992)
Kleiner Feldberg (Germany)	0.15	Rural	Hallberg et al. (1994)
Puy de Dôme (France)	0.33	Mid altitude (1465m)	Sellegri et al. (2003)
Mt Sonnblick (Austria)	0.45	High altitude (3106m)	Kasper-Gielb et al. (2000)
Rax (Austria)	0.54	Mid altitude (1644m)	Hitzenberger et al. (2001)
Great Dun Fell (U.K.)	0.57	Rural - Coastal	Gieray et al. (1997)
Jungfraujoch (Switzerland)	0.61	High altitude (3580m)	Cozic et al. (2007)
Mt Sonnblick (Austria)	0.74	High altitude (3106m)	Hitzenberger et al. (2000)
Spitzbergen (Norway)	0.80	Artic	Heintzenberg and Leck (1994)

Cozic J. et al., ACP, 7, 1797–1807, 2007

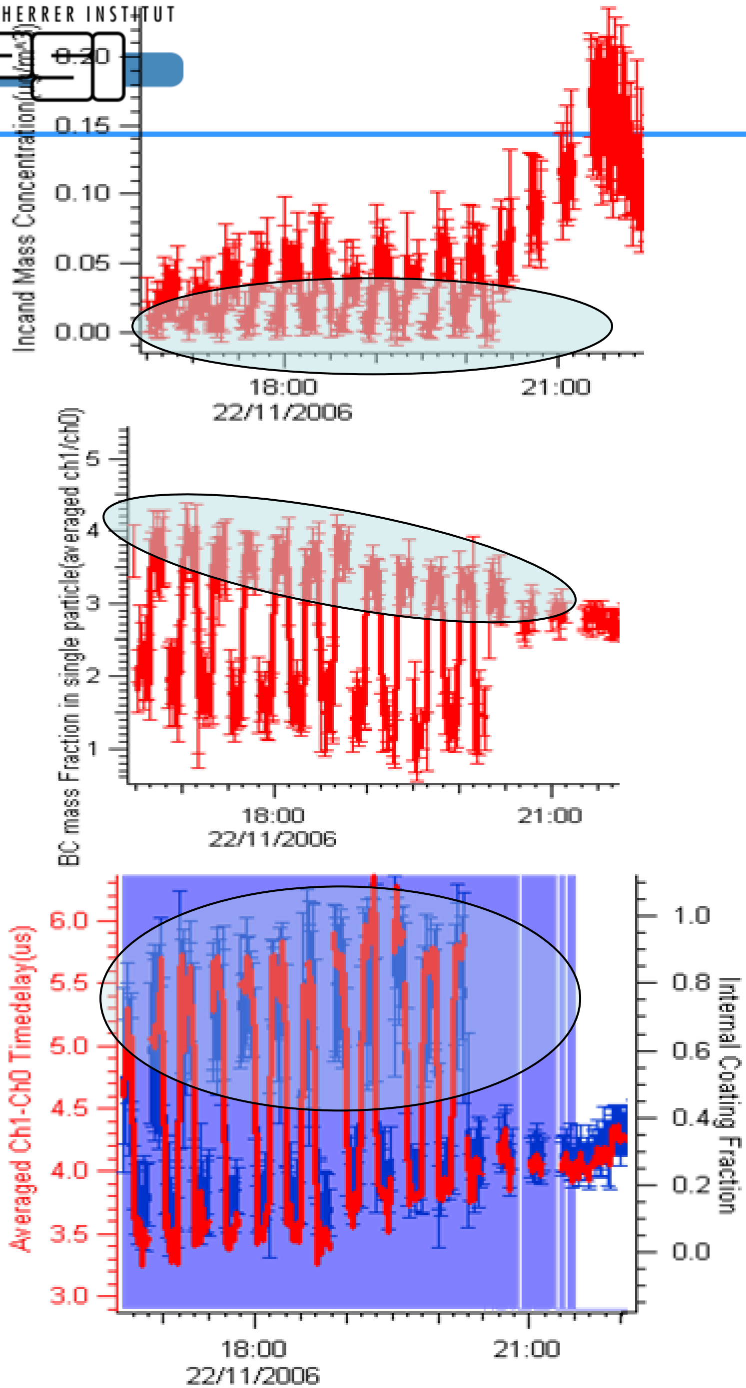
Follow up U.S. six cities study:

Increase in daily mortality with increase of PM2.5 by 10 mg/m3 (Laden et al., 2000):
- Mobile sources: 3.4%
- Coal combustion: 1.1%
- Mineral dust: ~0%

Aerosol direct and indirect effects



IPCC 2007


Incand Mass Concentration(ug/m^3)
0.20
0.15
0.10
0.05
0.00
18:00
22/11/2006
21:00
BC mass Fraction in single particle(averaged ch1/ch0)
5
4
3
2
1
18:00
22/11/2006
21:00
Averaged Ch1-Ch0 Timedelay(us)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Internal Coating Fraction
1.0
0.8
0.6
0.4
0.2
0.0
18:00
22/11/2006
21:00

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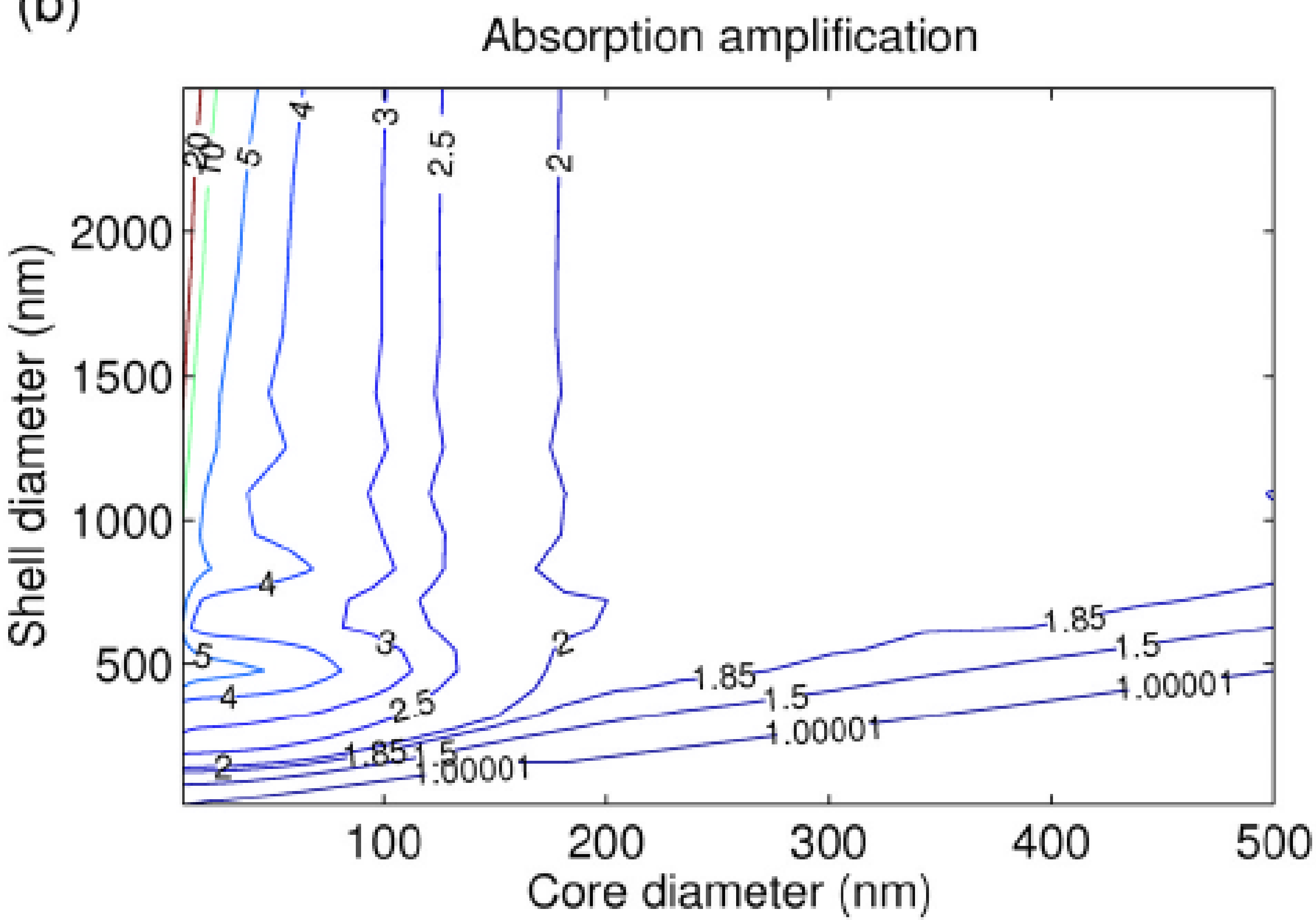
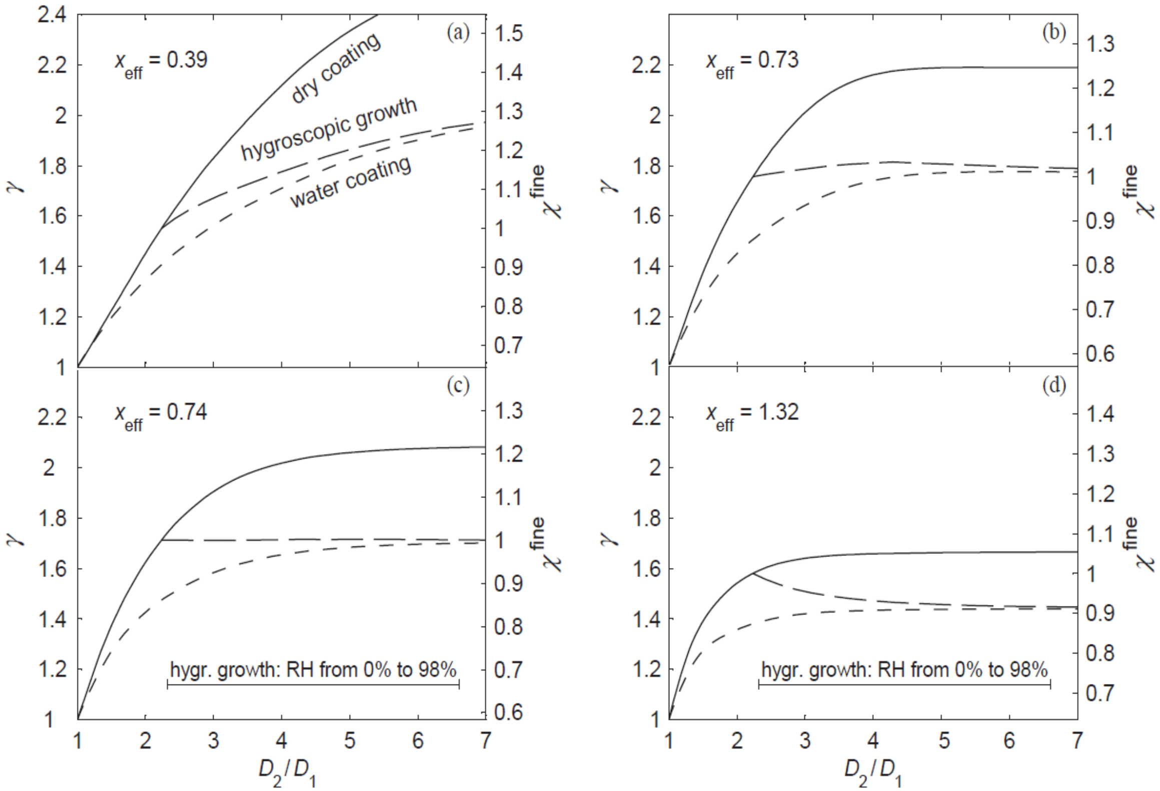
Limitations in the enhancement of visible light absorption due to mixing state

Tami C. Bond,[1] Gazala Habib,[1] and Robert W. Bergstrom[2]

(b)



Absorption Enhancement by Coating



Nessler et al., *J. Aerosol Sci.*, 2005.

Fig. 2. Coating effect for absorbing cores as present in the JFJ fine mode aerosol (winter case). Depicted are four cases for different x_{eff} values. Each sub-figure shows the evolution of the coating factor γ (left ordinates) with increasing shell thickness for coating with material corresponding to the soluble part of the dry JFJ fine mode (scenario (1), solid line), coating with water (scenario (2), short dashed line), and coating according to JFJ hygroscopic growth (scenario (3) for $D_2/D_1 \geqslant D_2^{dry}/D_1$, long dashed line). For this last scenario, fine mode RH enhancement factors for absorption, χ^{fine}, are given in the right ordinates. The dry JFJ aerosol exhibits $D_2/D_1 = D_2^{dry}/D_1 = 2.2$ (winter case).

Data evaluation overview

diesel 60 km/h / 07.11.08 / SP2 data at 11:18

pellet starting: 24.11.08; SP2 data at 10:58 and 18:00

pellet stable: 19.11.08; SP2 data at 11:31

ADDEM Data

RH=93%, D=inf

NaCl:	**2.67**
H2SO4:	**2.27**
NaNO3:	**2.26**
Na2SO4:	**2.11**
NH4NO3:	**2.09**
NH42SO4:	**1.92**
kappa=0.1:	**1.33**
kappa=0.2:	**1.54**
kappa=0.4:	**1.85**