Strengths and Limitations of the Single Particle Soot Photometer (SP2)
–
Black Carbon (BC) in Paris

M. Gysel[1], M. Laborde[1], M. Crippa[1], T. Tritscher[1,2], Z. Jurányi[1,3], P. DeCarlo[1,4], B. Temime-Roussel[5], N. Marchand[5], S. Eckhardt[6], A. Stohl[6], U. Baltensperger[1], A. Prévôt[1] and E. Weingartner[1]

[1]Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[2]Now at TSI GmbH, Particle Instruments, Aachen, Germany
[3]Now at Institute of Aerosol and Sensor Technology, University of Applied Sciences Northwestern Switzerland, Windisch, Switzerland
[4]Now at Department of Civil, Architectural, and Environmental Engineering, Drexel University, Philadelphia, PA, USA
[5]Aix-Marseille Université, Laboratoire Chimie Environnement, Marseille, France
[6]NILU - Norwegian Institute for Air Research, Kjeller, Norway

The single-particle soot photometer (SP2; Stephens et al., 2003; Schwarz et al., 2006) uses laser-induced incandescence combined with optical sizing to quantitatively measure the BC mass in single particles along with their optical size with a detection efficiency of 100% above the respective lower detection limits. This makes it an extremely sensitive method to determine the BC mass without interference from non-refractory coatings (e.g. Moteki and Kondo, 2007). The optical sizing provides additional information on the mixing state of individual particles (e.g. Gao et al., 2007). The reader of this abstract is kindly referred to literature for further strengths and limitations of the SP2 (e.g. Moteki and Kondo, 2010; Schwarz et al., 2010; Gysel et al., 2011; Gysel et al., 2012; Laborde et al., 2012b; Laborde et al., 2012c).

Here we report results from a measurement campaign that was carried out in Paris as part of the MEGAPOLI European project (Megacity: Emission, urban, regional and global atmospheric pollution and climate effects, and integrated tools for assessment and mitigation; www.megapoli.info) where the physical properties, mixing state and hygroscopicity of atmospheric BC-containing particles were characterised (see Laborde et al., 2012a for details). The measurements presented here were made in Winter 2010 at the site instrumental de recherche par télédetection atmosphérique (SIRTA), situated ~30 km south-west of Paris city centre. The applied experimental techniques include the SP2, a hygroscopicity tandem differential mobility analyzer (HTDMA; Swietlicki et al., 2008) and a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; DeCarlo et al., 2006).

Figure 1 shows that the diurnal patterns of the BC mass concentration, the number fraction of BC-containing particles and the hydrocarbon-like organic aerosol (HOA; a "traffic marker") mass concentration peak during the morning and evening traffic hours (left panels). In contrast to this the biomass burning organic aerosol (BBOA) mass concentration remains low during rush hours but peaks in the late evening instead (right panel). These diurnal patterns indicate a dominant influence of traffic emissions on BC loadings, while biomass burning only gives a minor contribution, which is consistent with an independent assessment using single particle aerosol mass spectrometry (Healy et al., 2012).

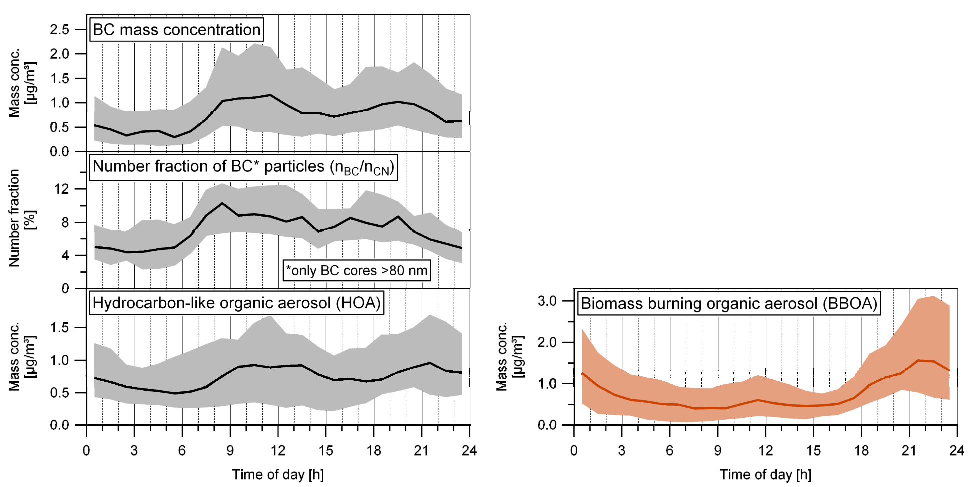

Fig. 1: Diurnal patterns of various aerosol parameters.

Different episodes with air mass types representing influence from traffic (diesel exhaust) and biomass burning (domestic heating) as well as aged aerosol (under westerly wind conditions as well as from continental Europe) were encountered during this field experiment. The distributions of hygroscopic growth factors (GF-PDF) at 90% RH of particles with a dry mobility diameter (D_0) of 265 nm are shown in Fig. 2 for these four air mass types. The background aerosol is strongly hygroscopic with a distinct mode in the GF-PDF at GF≈1.6. This background aerosol is also present under the influence of traffic and biomass burning emissions, though less prominent. Fresh traffic emissions are non-hygroscopic with a GF of ~1.0. Biomass burning emissions are slightly hygroscopic with a GF of ~1.1.

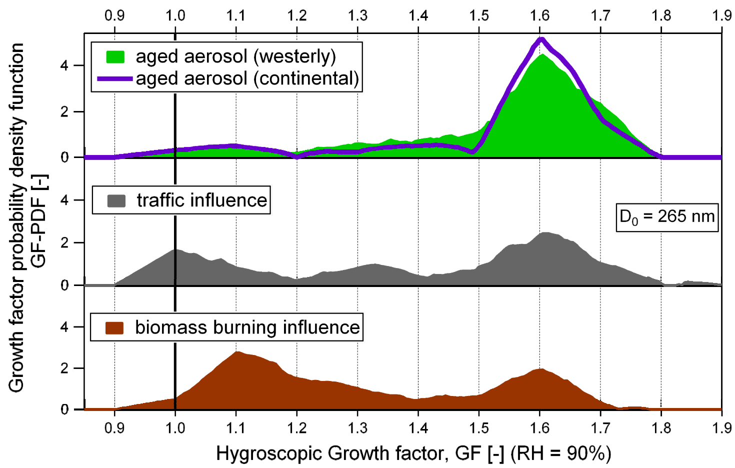

Fig. 2: Distributions of hygroscopic growth factors (GF-PDF) at 90% RH of particles with a dry mobility diameter of D_0=265 nm for different air mass types.

The growth factor distributions presented in Fig. 2 represent all aerosol particles with a dry mobility diameter of D_0=265 nm. The comparison of the different air mass types shows that the HTDMA allows separating particles from different sources or age. Further insight into the mixing state of BC was obtained by operating the SP2 in series behind the HTDMA. The results of these measurements, which happened to coincide with strong biomass burning influence, reveal that most particles of the aged background aerosol (GF>1.4) do not contain a detectable BC core. In contrast to this, all non-hygroscopic particles from traffic emissions with GF<1.05 contain a BC core. A substantial fraction of the slightly hygroscopic particles (1.05 < GF < 1.3) from biomass burning emissions do not contain a BC core. The observation that, even under strong influence from biomass burning emissions, most BC particles are from traffic emissions is consistent with above result, that traffic emissions give the dominant contribution to BC in Paris. The different properties of traffic and biomass burning emissions can be explained by differences in the emission ratios of organic carbon to black carbon. The organic carbon mass fraction in primary traffic emissions is small (Chirico et al., 2010), essentially resulting in uncoated BC particles. This was confirmed by the coating thickness measurement of the SP2. In contrast, the biomass burning emissions contain relatively high organic mass fractions and also some inorganic salts, resulting in a medium coating of the BC particles emitted from biomass burning.

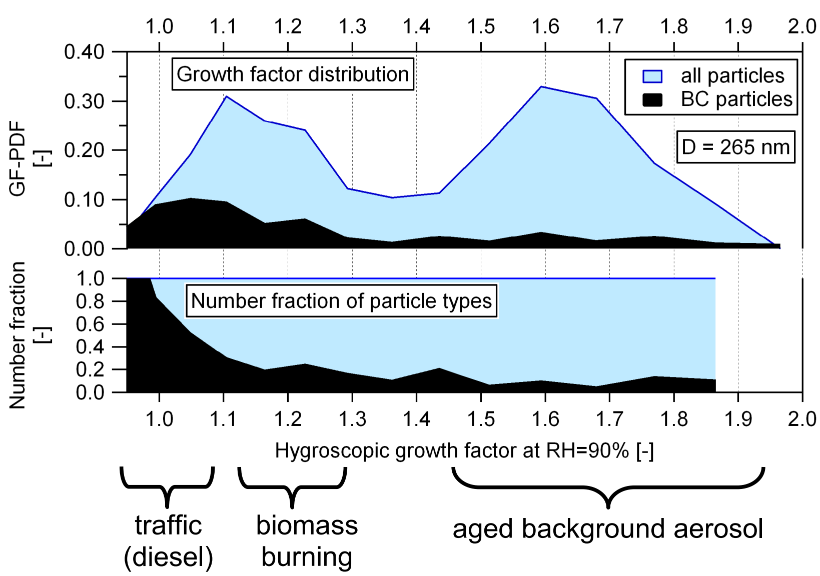

Fig. 3: Growth factor distributions (GF-PDF) of all particles and BC-containing particles during an episode with strong biomass burning influence.

The fact that traffic BC is non-hygroscopic and uncoated while biomass burning is slightly hygroscopic with medium coatings is important for several reasons. Non-refractory coatings increase the mass specific absorption coefficient of the BC particles, which increases their direct climate impact caused by absorption of solar radiation. Non-refractory coatings also decrease the critical supersaturation required to form a cloud condensation nuclei, which is important for the life-cycle of BC particles and their impact on liquid clouds.

Acknowledgements

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References

Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prévôt, A. S. H., Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, M., and Baltensperger, U.: Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments. *Atmos. Chem. Phys.*, **10**, 11545-11563, doi:10.5194/acp-10-11545-2010, 2010.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.*, **78**, 8281-8289, 2006.

Gao, R. S., Schwarz, J. P., Kelly, K. K., Fahey, D. W., Watts, L. A., Thompson, T. L., Spackman, J. R., Slowik, J. G., Cross, E. S., Han, J.-H., Davidovits, P., Onasch, T. B., and Worsnop, D. R.: A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer. *Aerosol Sci. Technol.*, **41**, 125-135, 2007.

Gysel, M., Laborde, M., Corbin, J. C., Mensah, A. A., Keller, A., Kim, J., Petzold, A., and Sierau, B.: Technical Note: The single particle soot photometer fails to detect PALAS soot nanoparticles. *Atmos. Meas. Tech. Discuss.*, **5**, 4905-4925, doi:10.5194/amtd-5-4905-2012, 2012.

Gysel, M., Laborde, M., Olfert, J. S., Subramanian, R., and Gröhn, A. J.: Effective density of Aquadag and fullerene soot black carbon reference materials used for SP2 calibration. *Atmos. Meas. Tech.*, **4**, 2851-2858, doi:10.5194/amt-4-2851-2011, 2011.

Healy, R. M., Sciare, J., Poulain, L., Kamili, K., Merkel, M., Müller, T., Wiedensohler, A., Eckhardt, S., Stohl, A., Sarda-Estève, R., McGillicuddy, E., O'Connor, I. P., Sodeau, J. R., and Wenger, J. C.: Sources and mixing state of size-resolved elemental carbon particles in a European megacity: Paris. *Atmos. Chem. Phys.*, **12**, 1681-1700, doi:10.5194/acp-12-1681-2012, 2012.

Laborde, M., Crippa, M., Tritscher, T., Jurányi, Z., DeCarlo, P. F., Temime-Roussel, B., Marchand, N., Eckhardt, S., Stohl, A., Baltensperger, U., Prévôt, A. S. H., Weingartner, E., and Gysel, M.: Black carbon physical properties and mixing state in the European megacity Paris. *Atmos. Chem. Phys. Discuss.*, manuscript in preparation, 2012a.

Laborde, M., Mertes, P., Zieger, P., Dommen, J., Baltensperger, U., and Gysel, M.: Sensitivity of the Single Particle Soot Photometer to different black carbon types. *Atmos. Meas. Tech.*, **5**, 1031-1043, doi:10.5194/amt-5-1031-2012, 2012b.

Laborde, M., Schnaiter, M., Linke, C., Saathoff, H., Naumann, K.-H., Möhler, O., Berlenz, S., Wagner, U., Taylor, J. W., Liu, D., Flynn, M., Allan, J. D., Coe, H., Heimerl, K., Dahlkötter, F., Weinzierl, B., Wollny, A. G., Zanatta, M., Cozic, J., Laj, P., Hitzenberger, R., Schwarz, J. P., and Gysel, M.: Single Particle Soot Photometer intercomparison at the AIDA chamber. *Atmos. Meas. Tech. Discuss.*, **5**, 3519-3573, doi:10.5194/amtd-5-3519-2012, 2012c.

Moteki, N. and Kondo, Y.: Effects of mixing state on black carbon measurements by laser-induced incandescence. *Aerosol Sci. Technol.*, **41**, 398-417, doi:10.1080/02786820701199728, 2007.

Moteki, N. and Kondo, Y.: Dependence of laser-induced incandescence on physical properties of black carbon aerosols: measurements and theoretical interpretation. *Aerosol Sci. Technol.*, **44**, 663-675, doi:10.1080/02786826.2010.484450, 2010.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Darbeheshti, M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Loewenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere. *J. Geophys. Res.*, **111**, D16207, doi:10.1029/2006JD007076, 2006.

Schwarz, J. P., Spackman, J. R., Gao, R. S., Perring, A. E., Cross, E., Onasch, T. B., Ahern, A., Wrobel, W., Davidovits, P., Olfert, J., Dubey, M. K., Mazzoleni, C., and Fahey, D. W.: The detection efficiency of the single particle soot photometer. *Aerosol Sci. Technol.*, **44**, 612-628, doi:10.1080/02786826.2010.481298, 2010.

Stephens, M., Turner, N., and Sandberg, J.: Particle identification by laser-induced incandescence in a solid-state laser cavity. *Appl. Opt.*, **42**, 3726-3736, doi:10.1364/AO.42.003726, 2003.

Swietlicki, E., Hansson, H.-C., Hämeri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P. H., Petäjä, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments - a review. *Tellus*, **60B**, 432-469, doi:10.1111/j.1600-0889.2008.00350.x, 2008.

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Strengths and Limitations of the Single Particle Soot Photometer (SP2) – Black Carbon (BC) in Paris

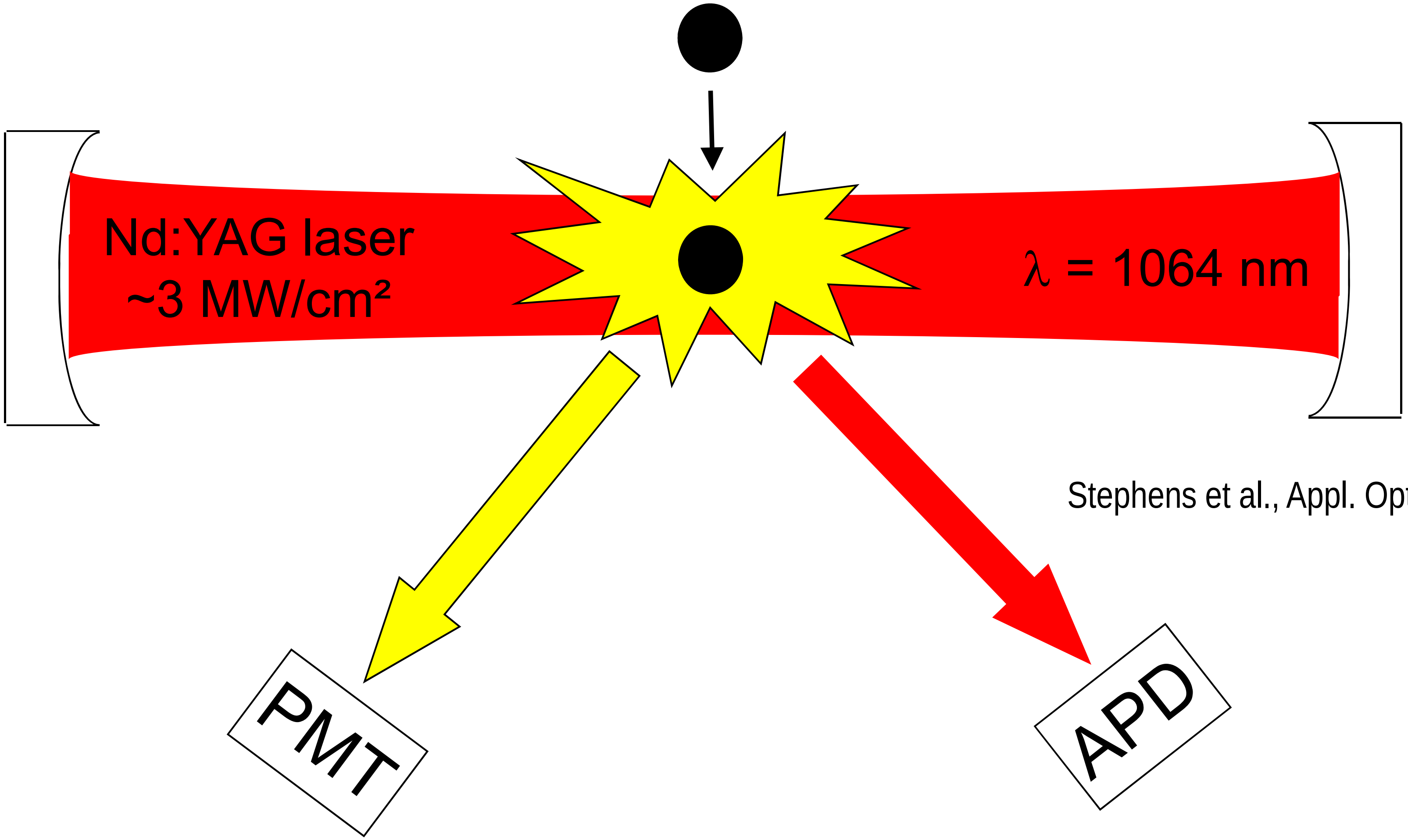
Martin Gysel[1], Marie Laborde, Monica Crippa, Torsten Tritscher, Zsófia Jurányi, Peter DeCarlo, Brice Temime-Roussel, Nicolas Marchand, Sabine Eckhardt, Andreas Stohl, Urs Baltensperger, André Prévôt and Ernest Weingartner

[1]Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI

16th ETH Conference on Combustion Generated Particles

Zurich, 26/06/2012

Single Particle Soot Photometer (SP2)



Stephens et al., Appl. Opt., 2003

detection of incandescent light
⇒ BC mass

detection of scattered light
⇒ optical sizing

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SP2 specifications

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Strengths of the SP2:

- Quantitative detection of BC in single particles
- 100% detection efficiency*
  (*above the lower detection limit)

$\Rightarrow$ extremely sensitive

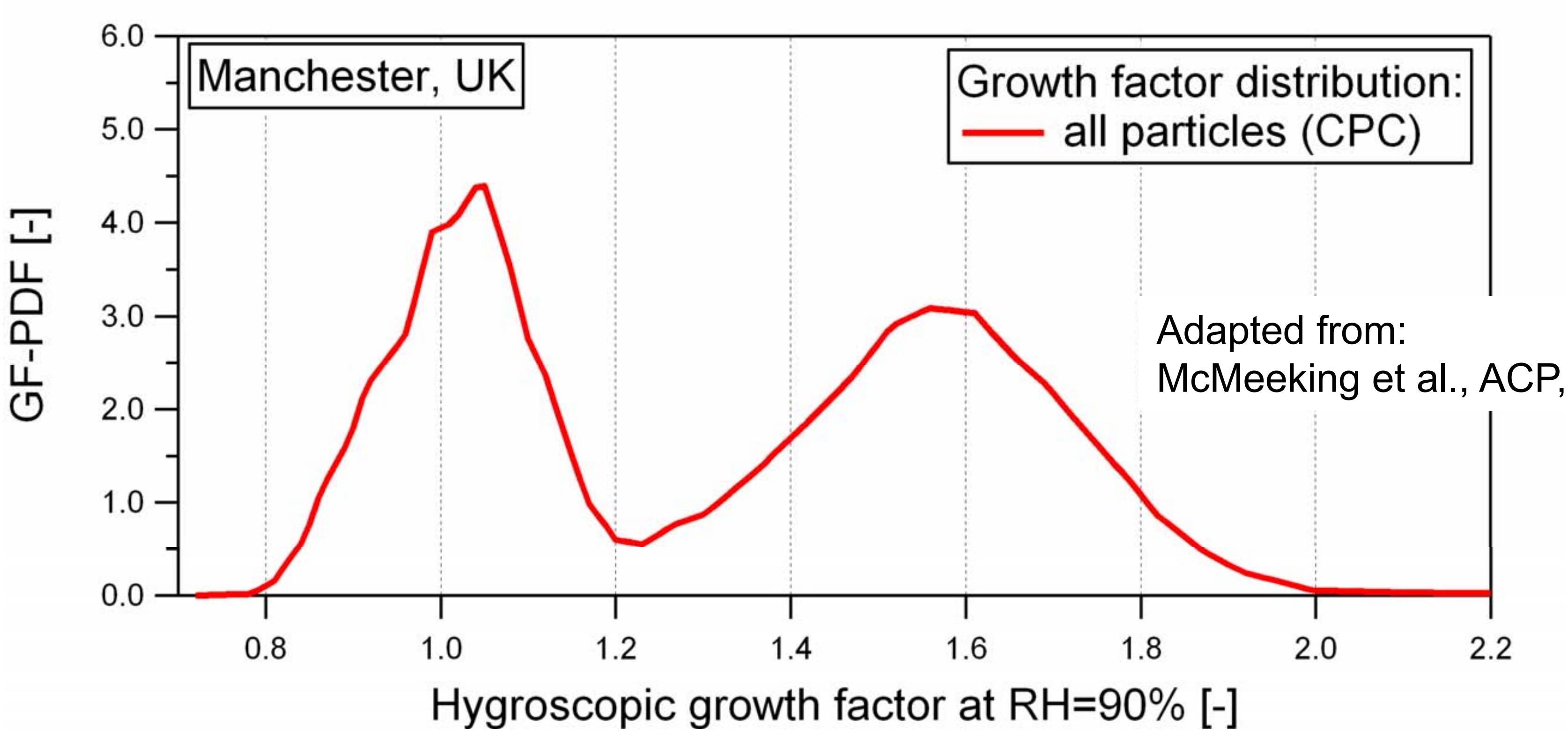
- BC mass measurement is independent of non-refractory coatings
- Optical sizing provides information on the mixing state of individual BC particles.

Limitations of the SP2:

- Lower detection limit: ~0.3-1.0 fg BC per particle ($D_{BC} \approx 70\text{-}100$ nm)
  (loosely-packed agglomerates of very small primary particles such as PALAS soot remain undetected)
- Coincidence problems can already occur at atmospheric particle number concentrations (polluted locations).
- Not really a “plug and play” instrument
- Sensitivity of SP2 to different BC types differs by up to ~35%

Aerosol mixing state in urban Manchester (summer)

ambient aerosol → HTDMA → CPC

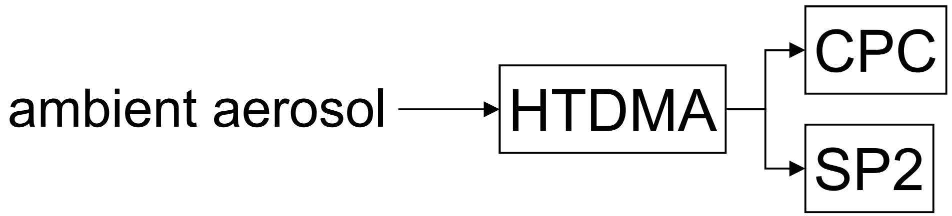


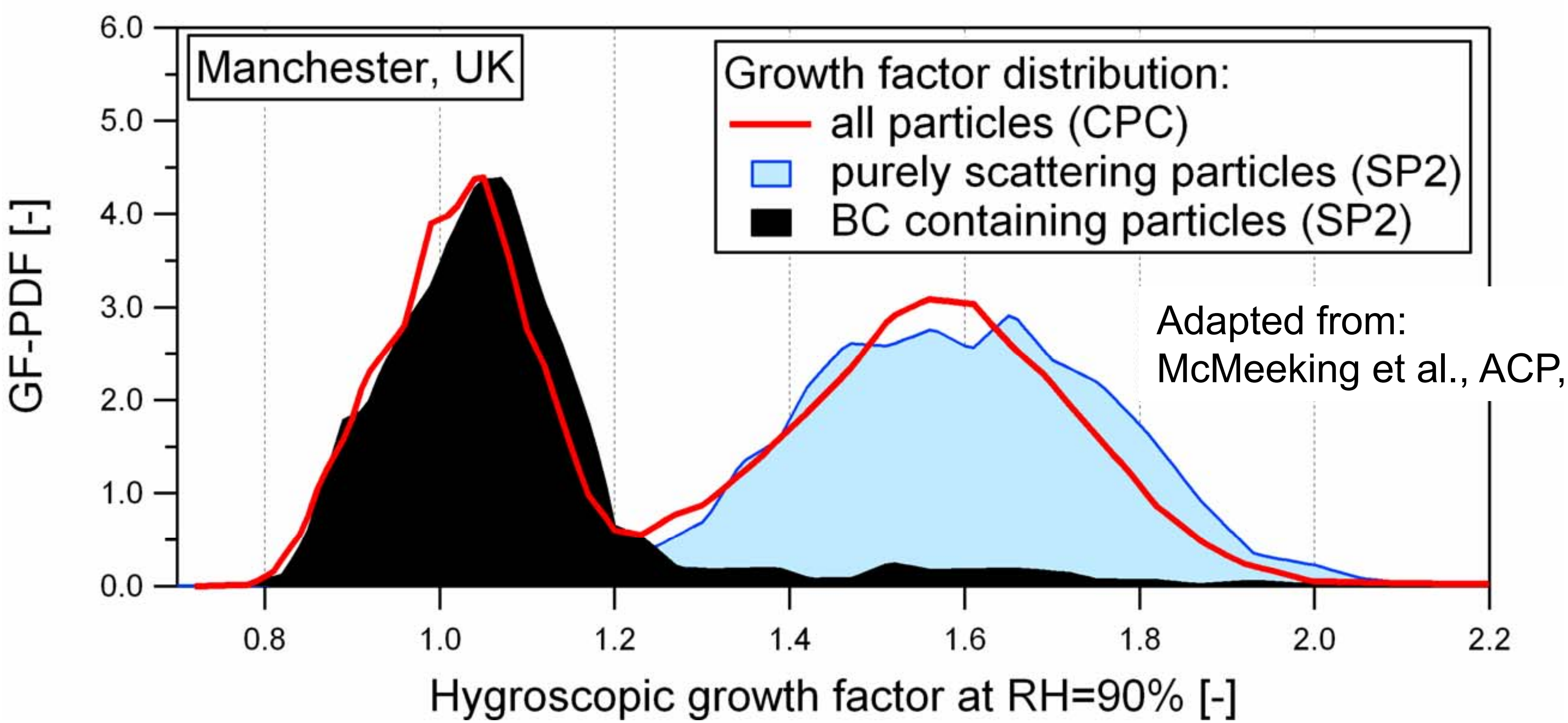
Adapted from:
McMeeking et al., ACP, 2011

fresh emissions

aged background aerosol

Aerosol mixing state in urban Manchester (summer)





Adapted from:
McMeeking et al., ACP, 2011

- Fresh emissions are non-hygroscopic and all particles contain BC (at D = 193 nm).
- Background aerosol is strongly hygroscopic and most particles do not contain a detectable BC core.

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Aerosol measurements in Paris (MEGAPOLI project)

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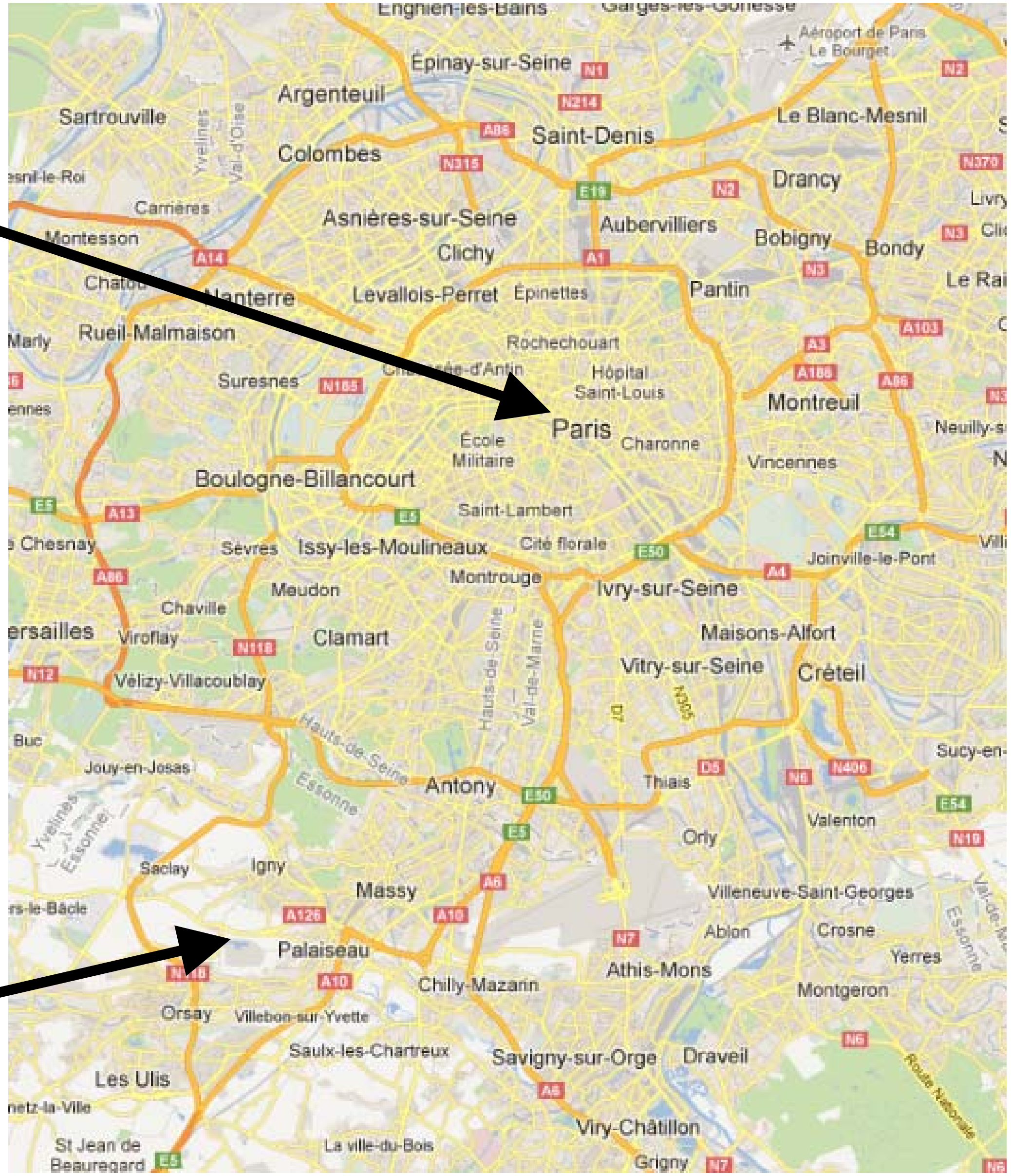
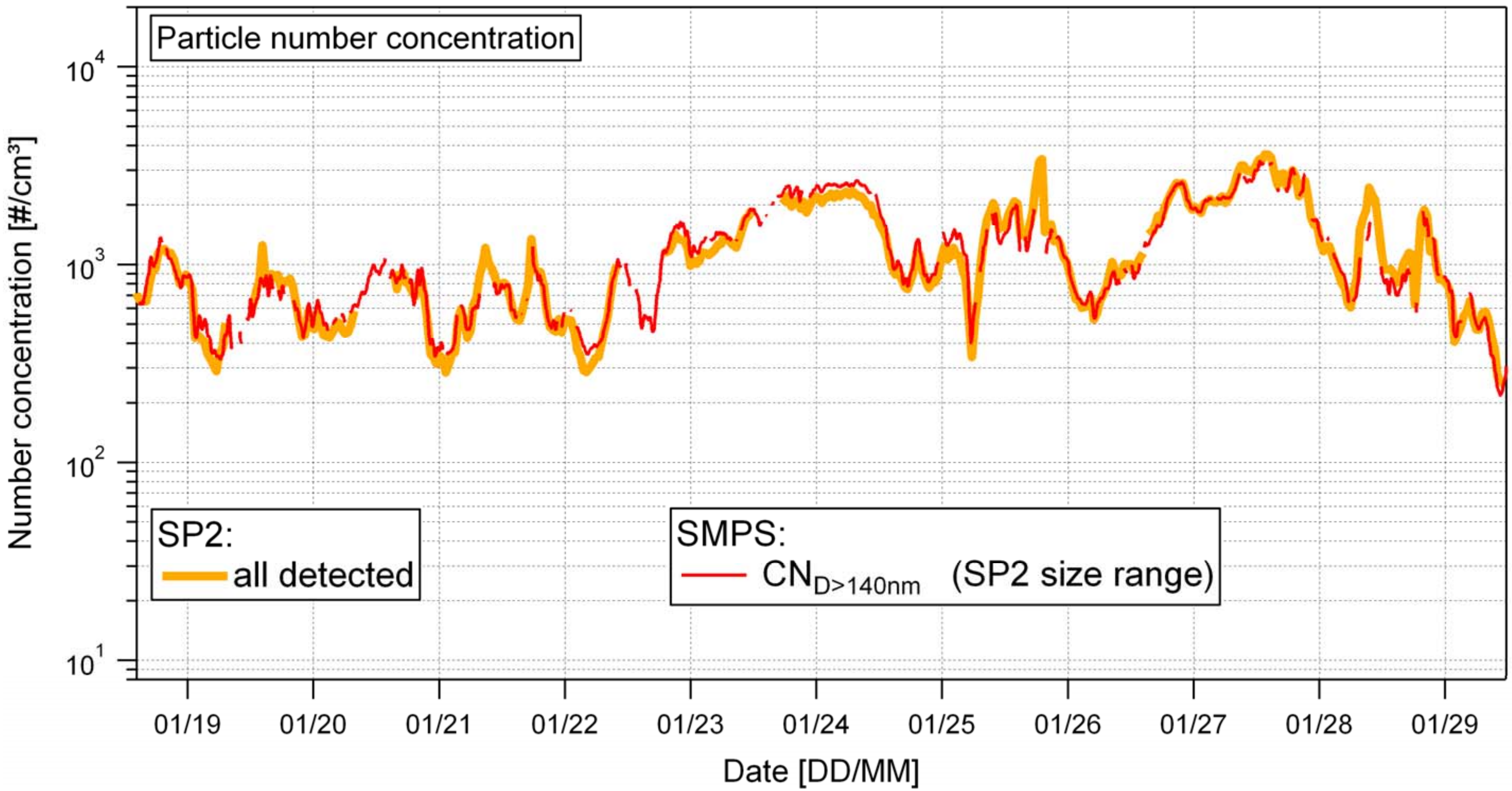
Paris city centre

Measurement site (SIRTA)

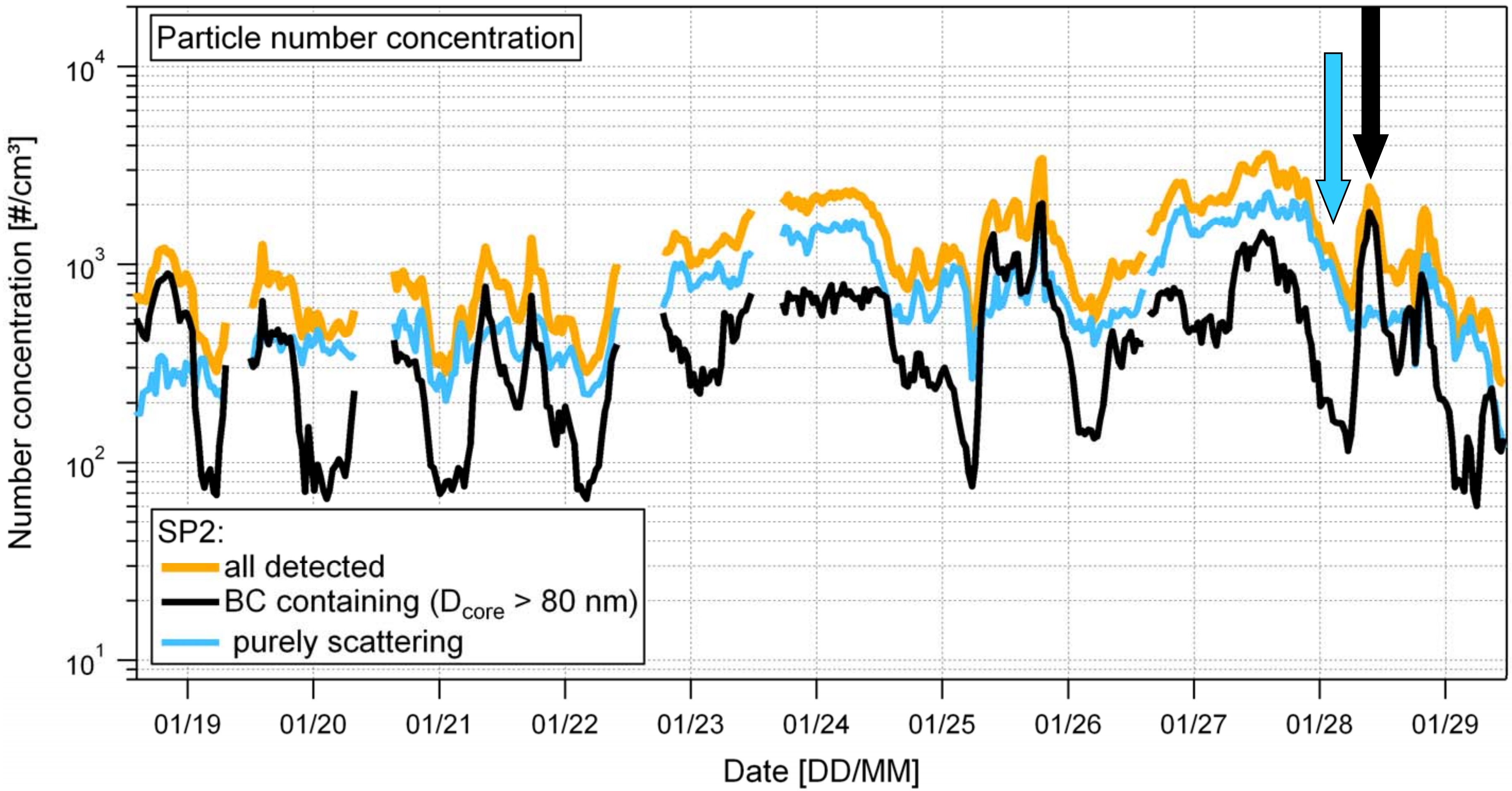


Comparison of SP2 and SMPS



⇒ Excellent agreement between SP2 and SMPS.

SP2 can distinguish between BC containing and purely scattering particles



Number concentration of BC particles varies more than that of purely scattering particles.

⇒ This indicates strong influence of local sources on BC.

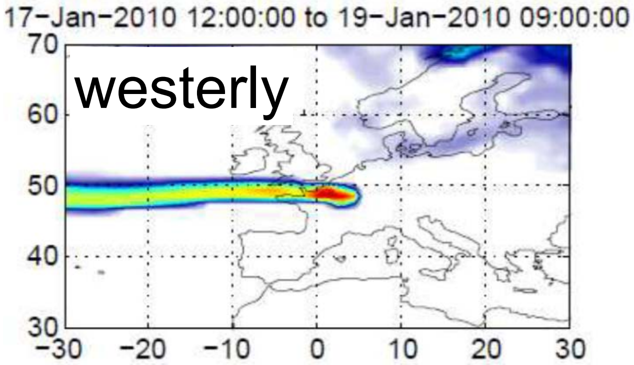
Different aerosol types

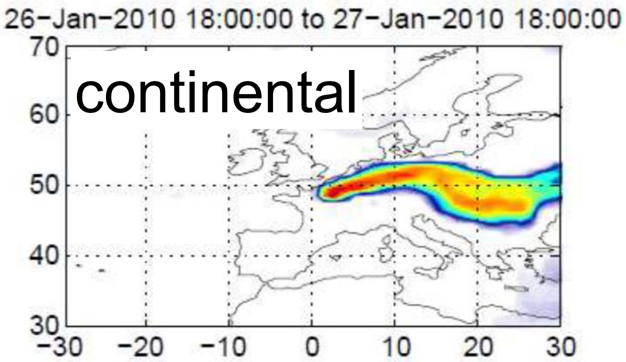
strong or dominant influence from:

fresh
traffic
emissions

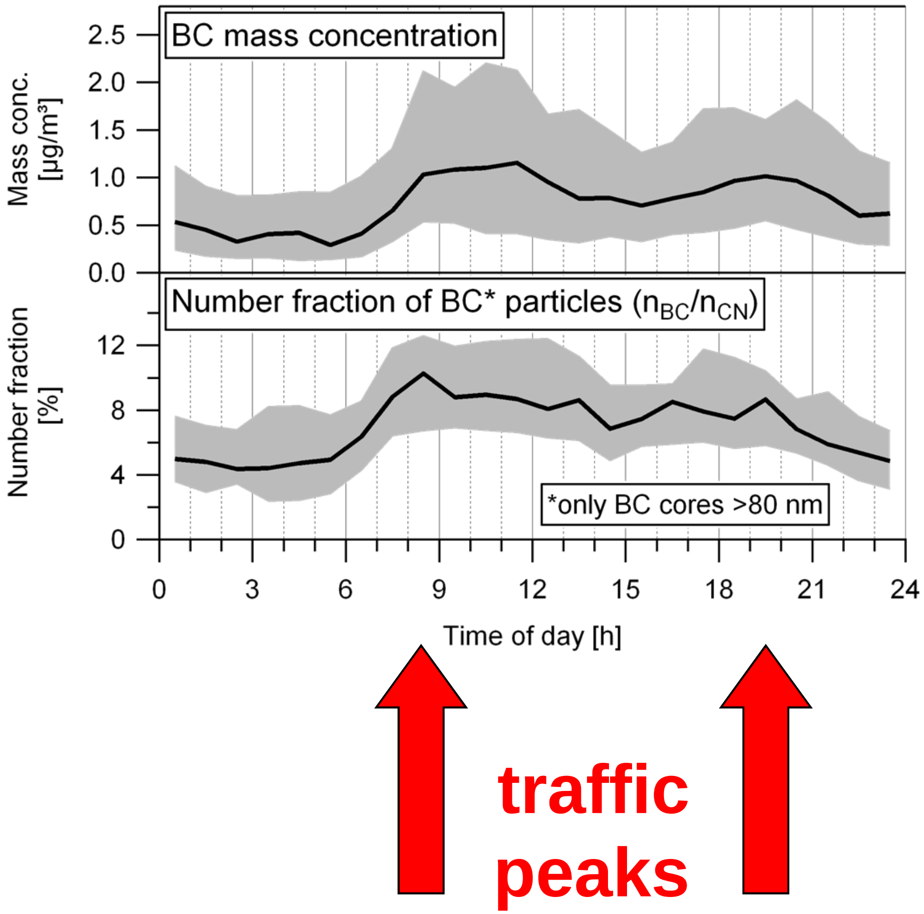
fresh
biomass burning
emissions

aged
background
aerosol



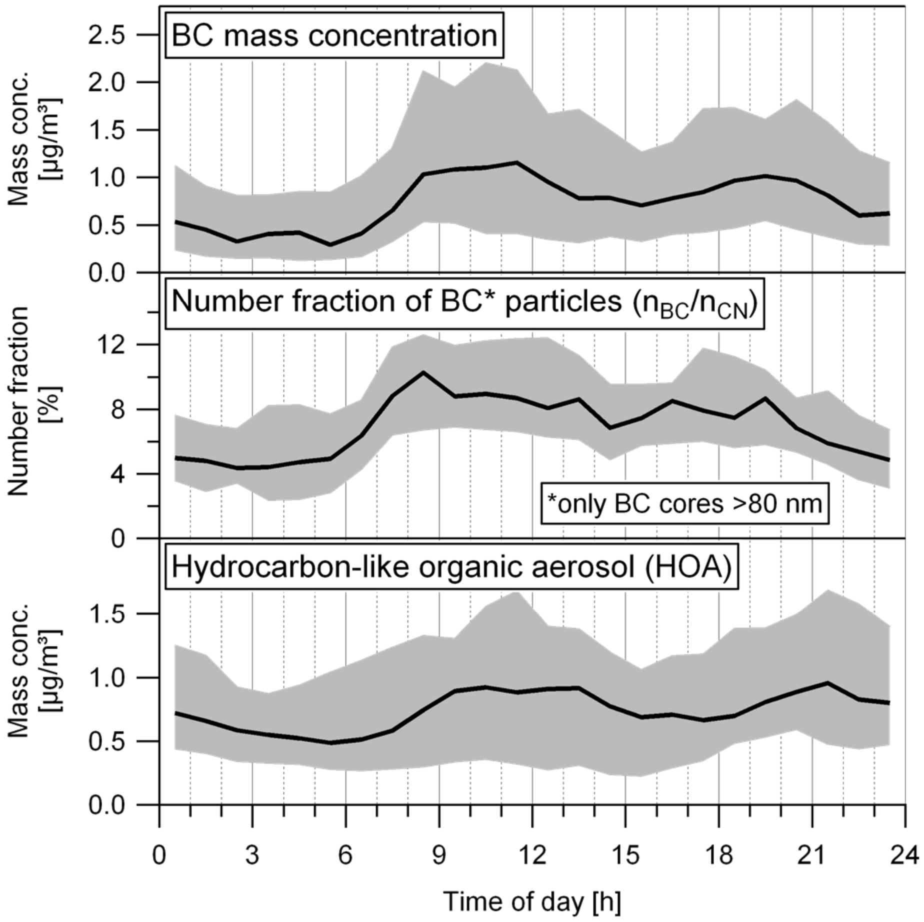


Diurnal cycles

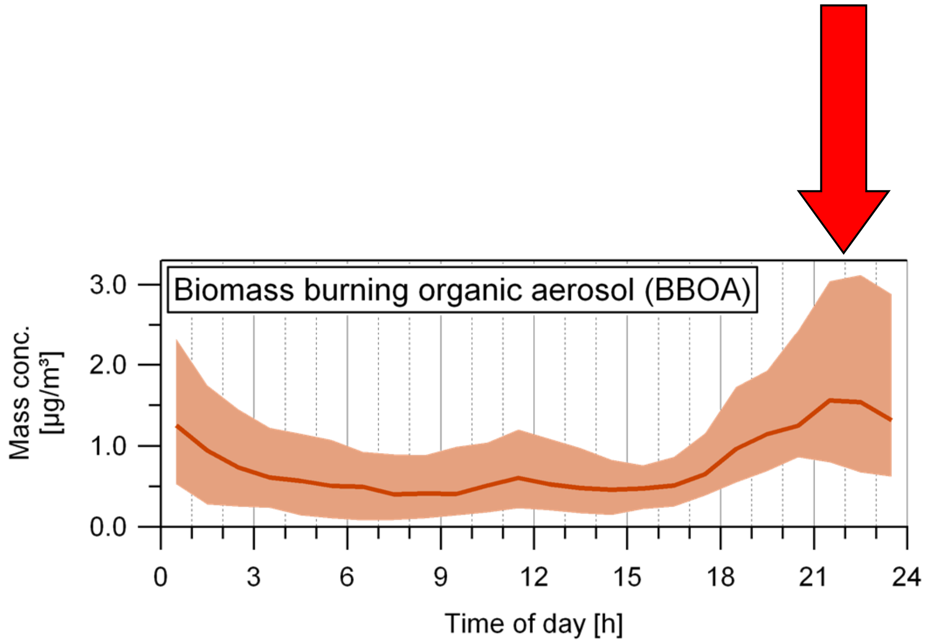


⇒ Distinct peaks in diurnal cycles of BC are from traffic emissions.

Diurnal cycles



domestic heating



- Different diurnal patterns of "traffic marker" (HOA) and "biomass burning marker" (BBOA).
- Diurnal patterns of BC and "traffic marker" (HOA) are similar.

⇒ Clear evidence that dominant fraction of BC mass is from fresh traffic emissions.

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Hygroscopic properties of the aerosol

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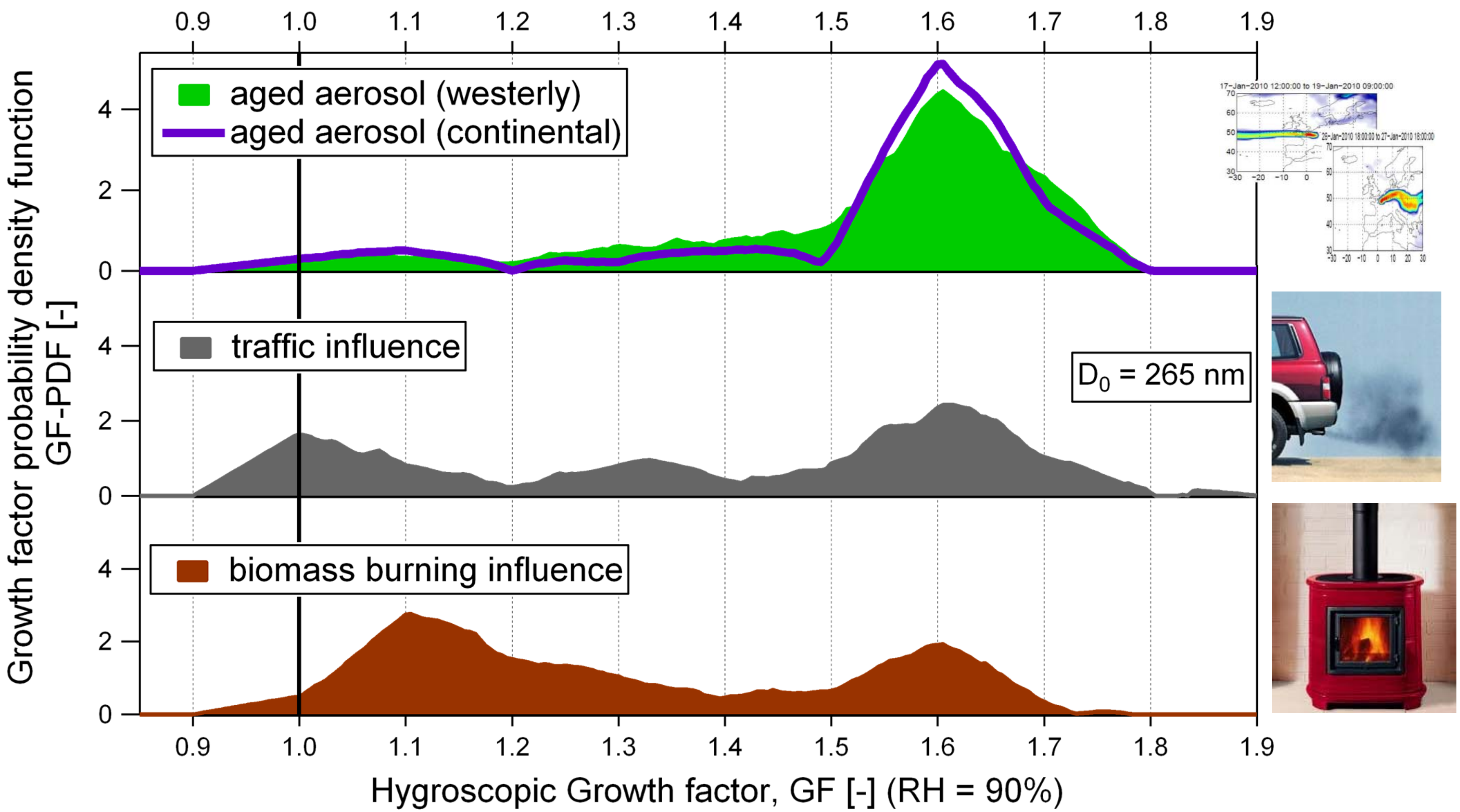

- background aerosol is strongly hygroscopic
- traffic emissions are non-hygroscopic
- biomass burning emissions are slightly hygroscopic

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Hygroscopicity of BC particles

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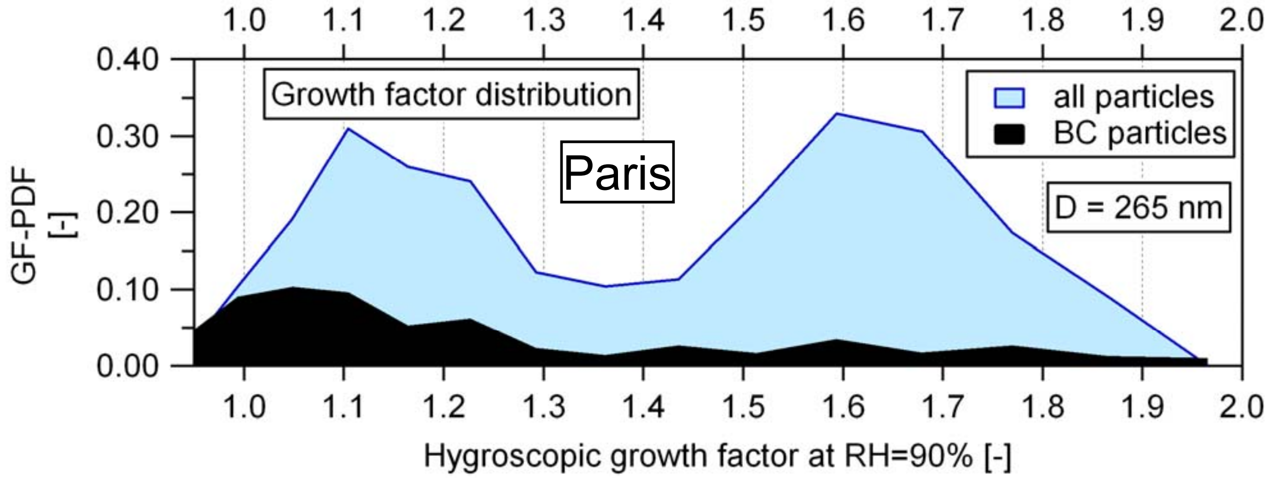
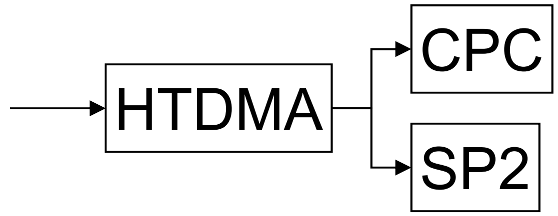
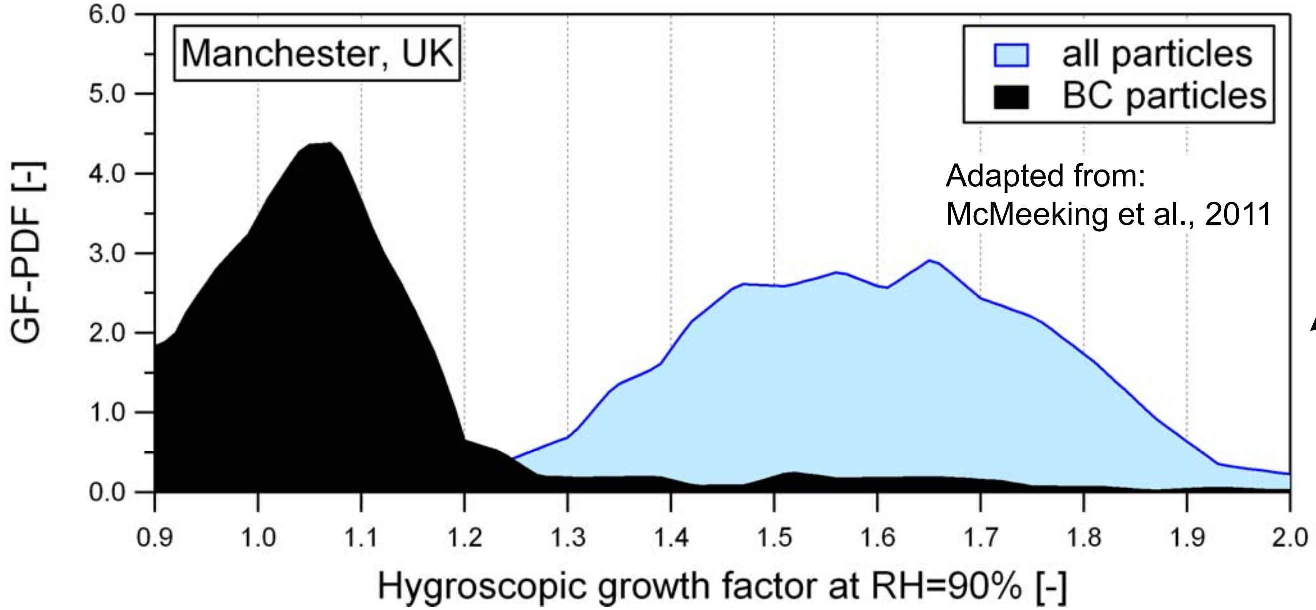




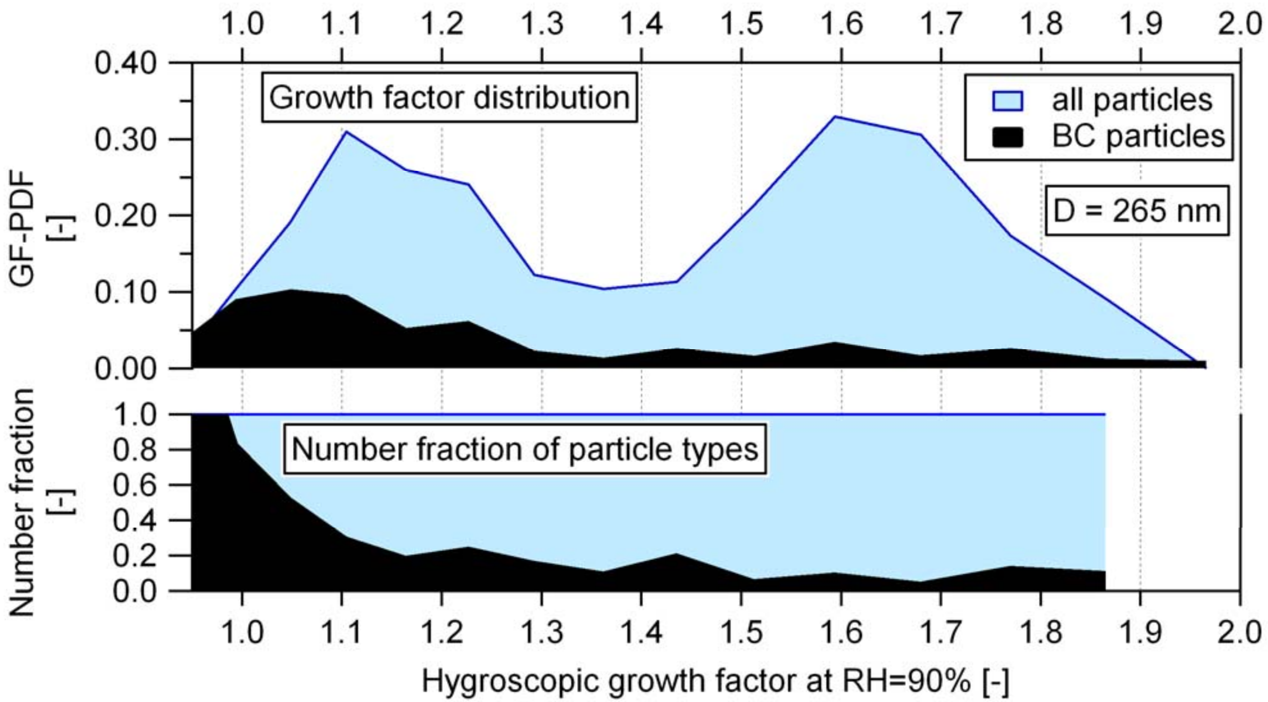
Paris in winter

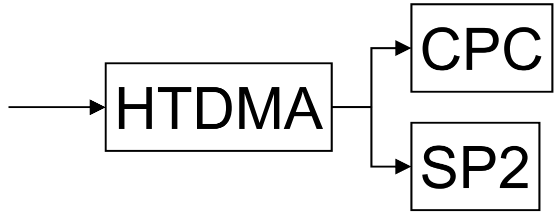
≠

Manchester in summer



Hygroscopicity of BC particles





traffic (diesel)

biomass burning

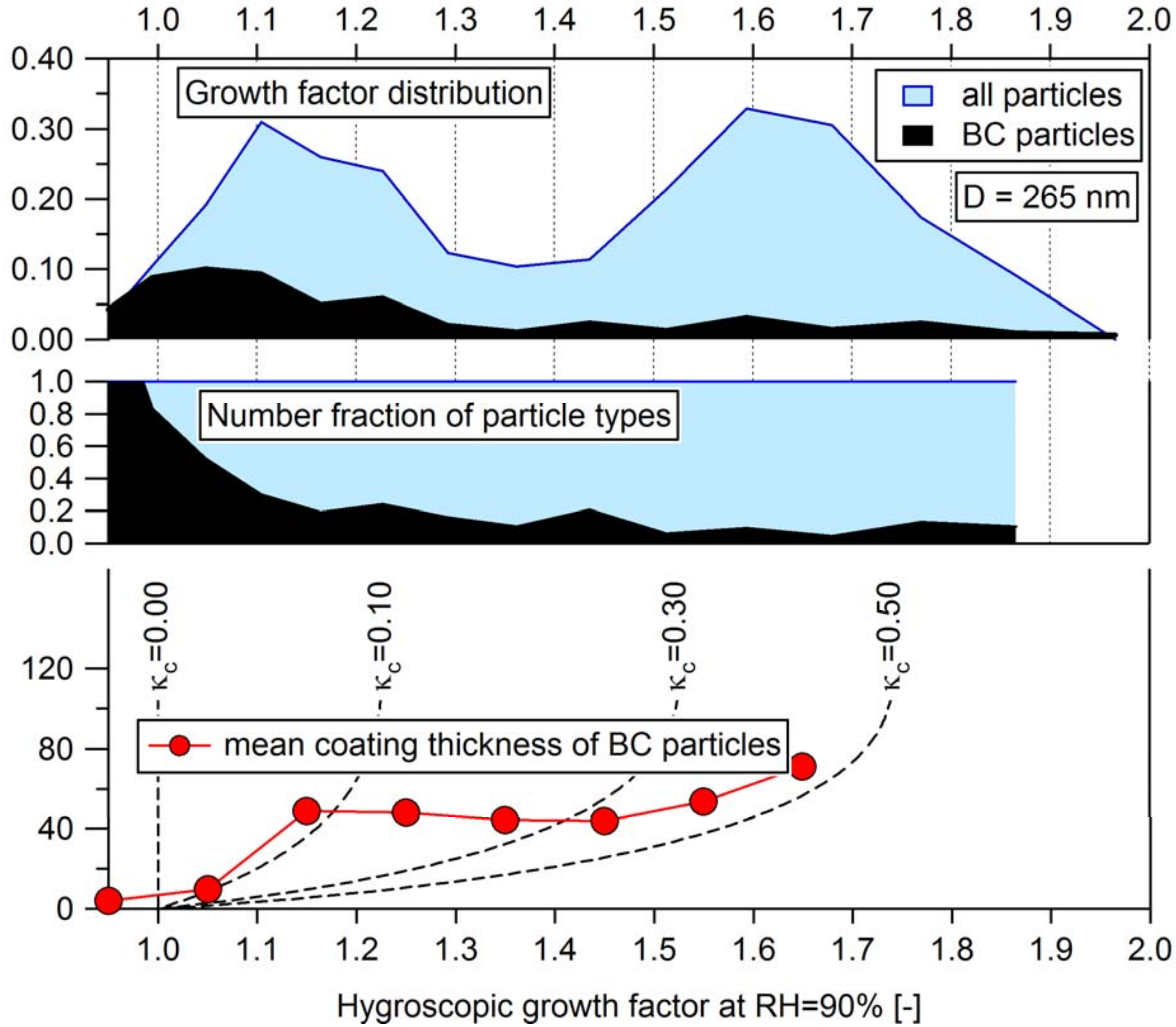
aged background aerosol

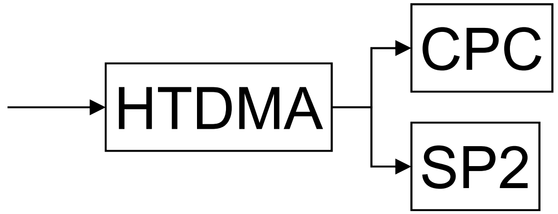
very few particles contain a detectable BC core

majority of particles without a detectable BC core

all particles contain BC

Coating of BC particles



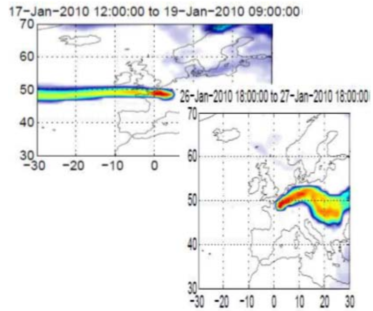


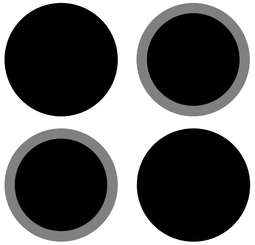
no coating

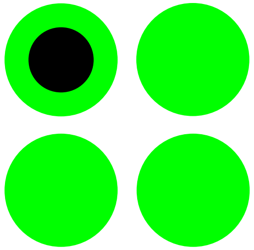
organic coating

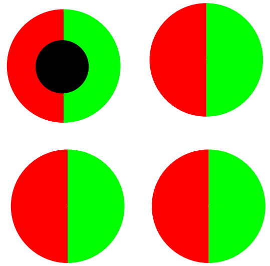
mixed organic/inorganic coating

Conclusions for BC in Paris (winter season)









Traffic BC:

- almost uncoated
- non-hygroscopic
- major BC source

Biomass burning BC:

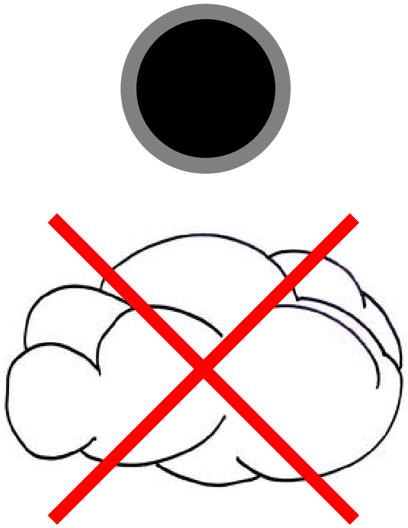
- medium coating (**organic**)
- slightly hygroscopic
- minor BC source

Aged BC:

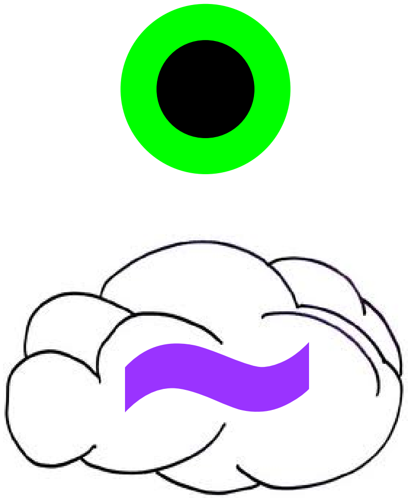
- medium to thick coating (**organic/inorganic**)
- strongly hygroscopic
- minor contribution to total BC

Importance of BC mixing state

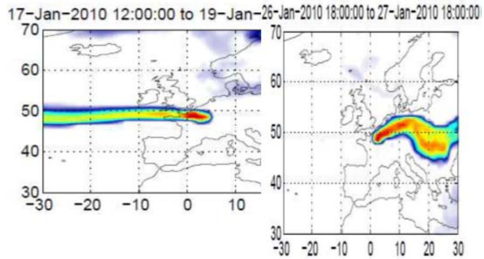
traffic emissions

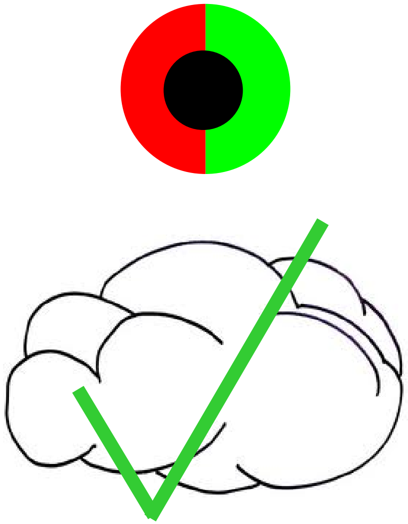


biomass burning



aged aerosol





mass specific light absorption efficiency

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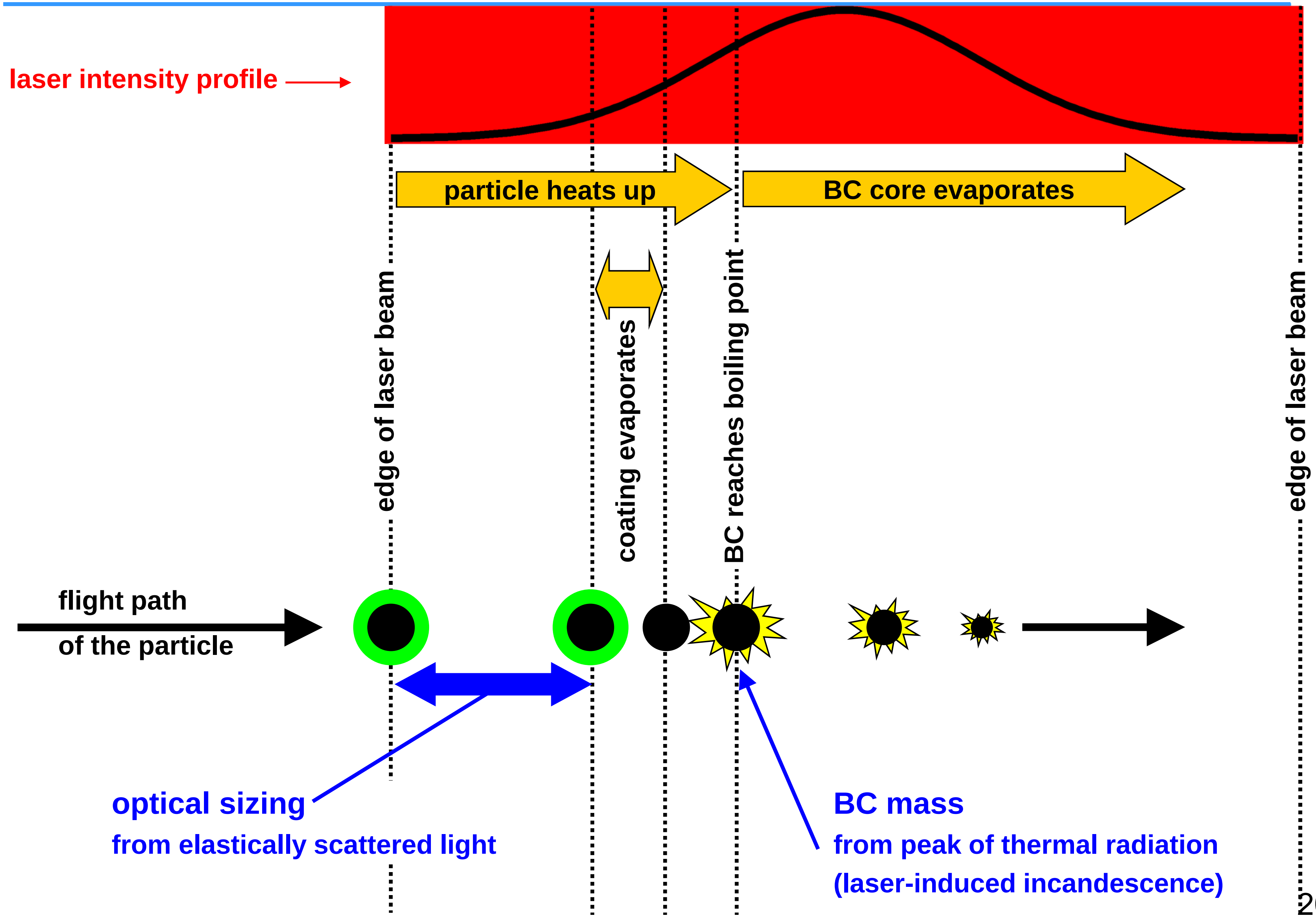
- The MEGAPOLI project
  (European Community's Framework Program FP/2007-2011)
- The Swiss National Science Foundation

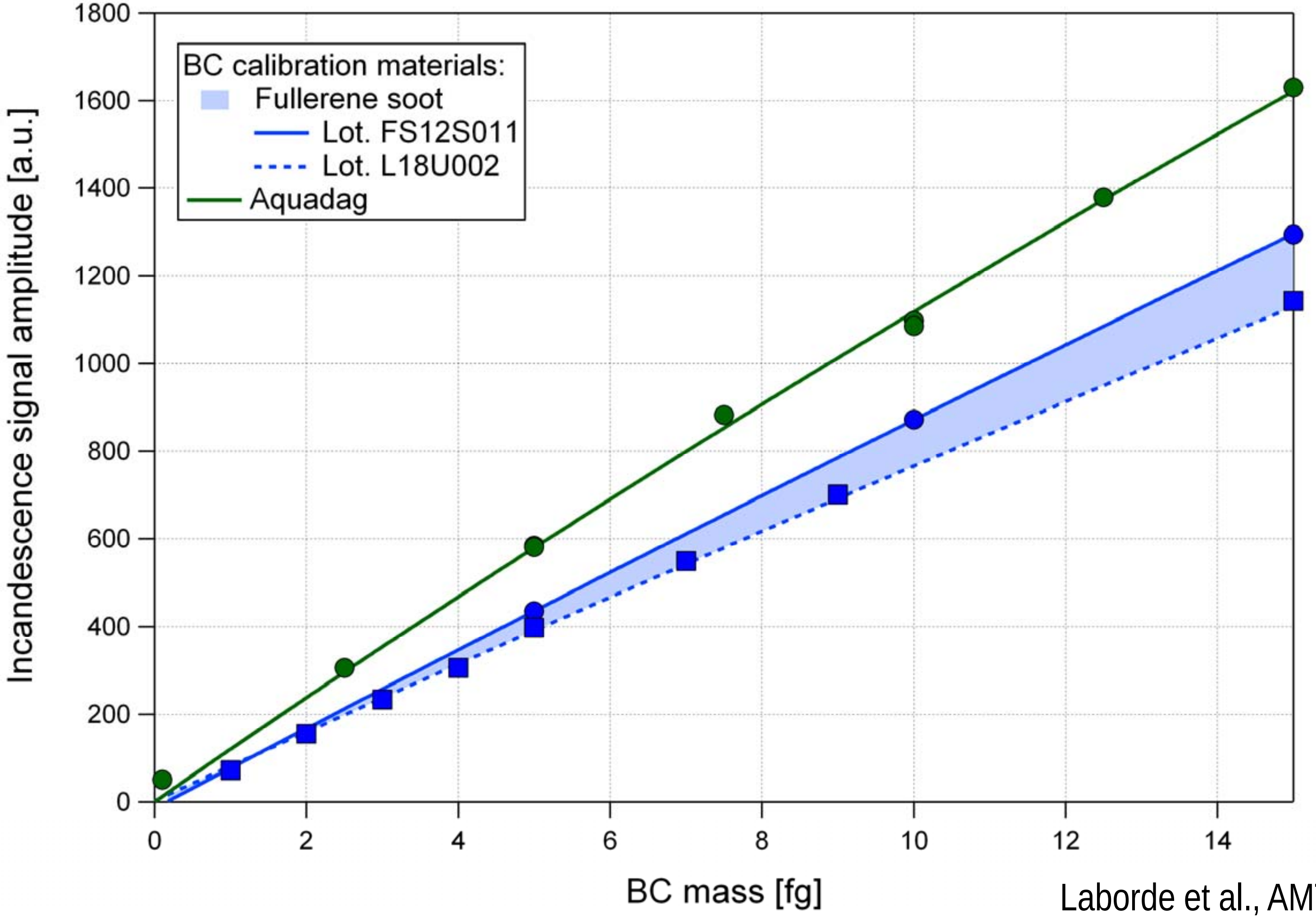
And last but not least:

- Thank you for your attention!

SP2 signals of a coated BC particle



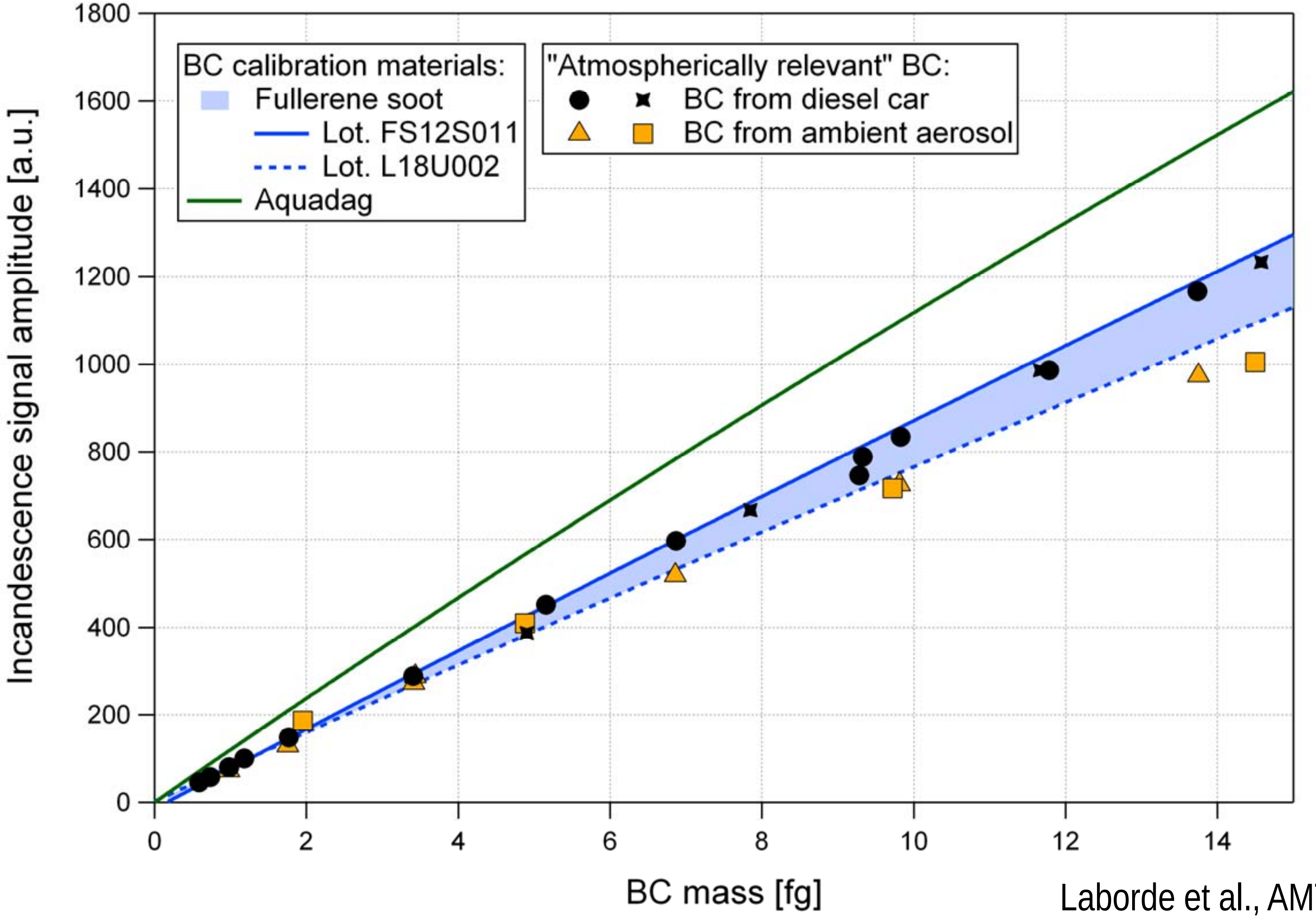
SP2 calibration for BC mass



Laborde et al., AMT, 2012

SP2 is about 35% more sensitive to Aquadag and fullerene soot
⇒ What about the sensitivity to atmospheric BC?

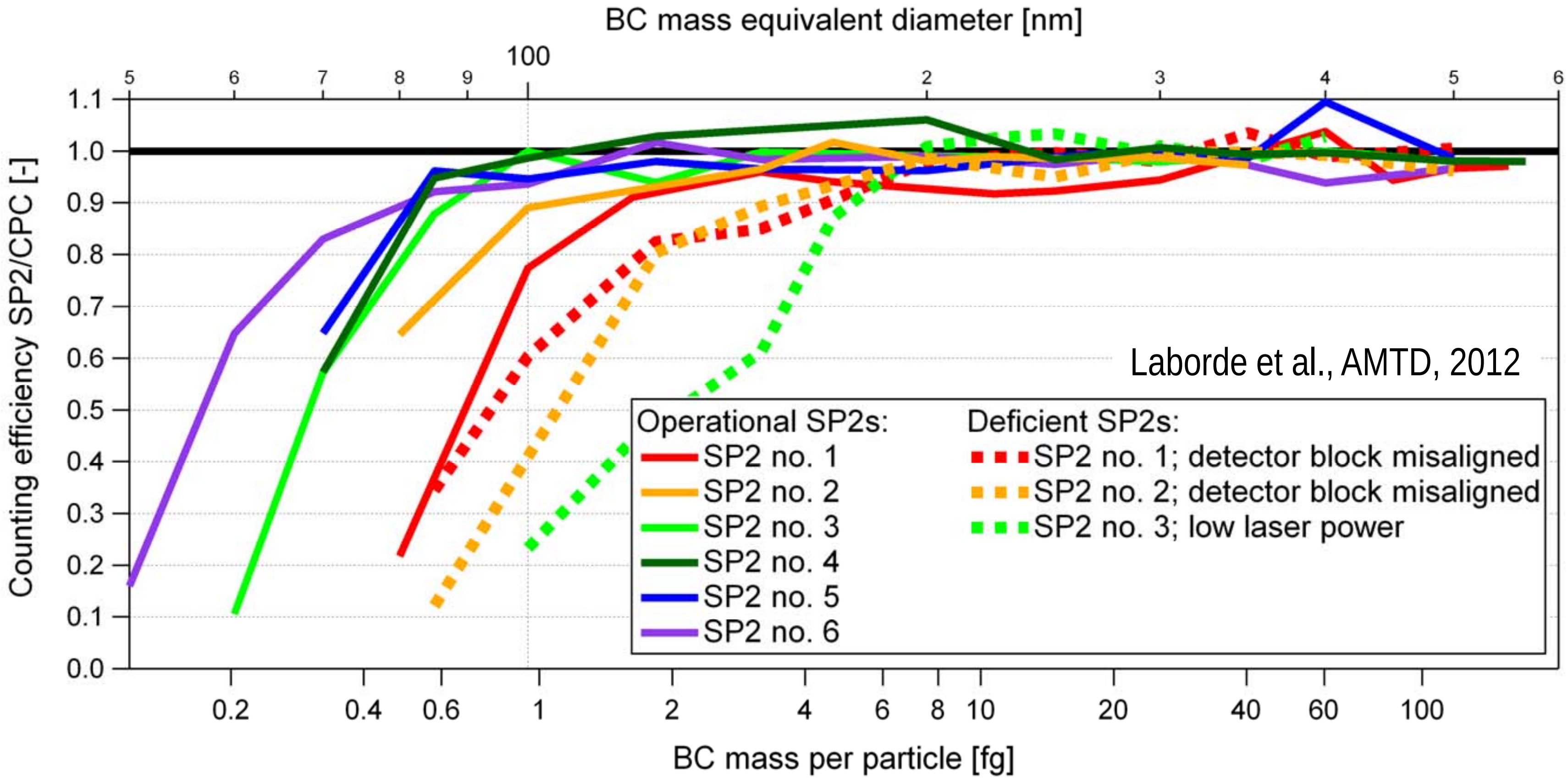
SP2 calibration for BC mass



Laborde et al., AMT, 2012

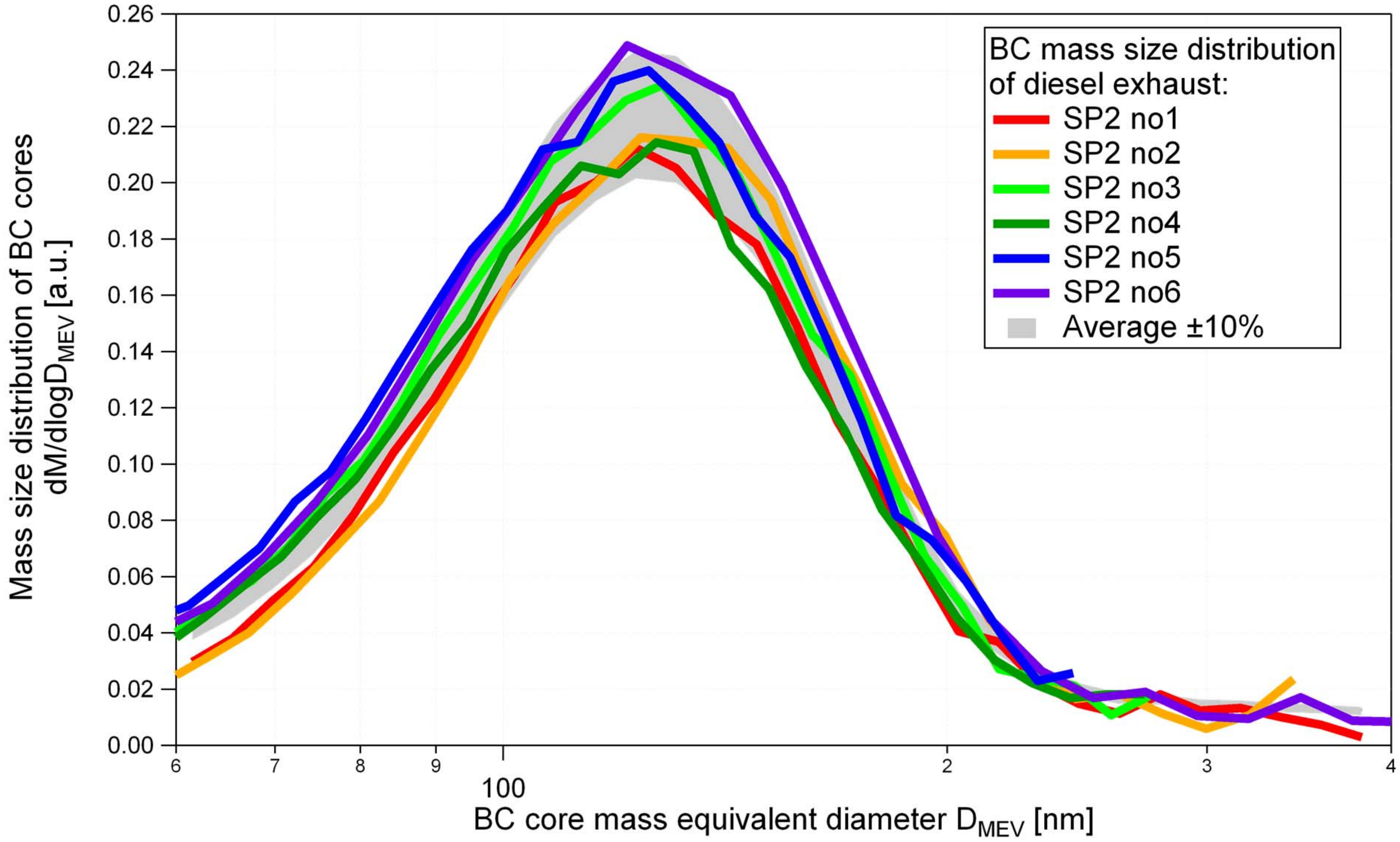
⇒ **Fullerene soot is recommended as calibration material for atmospheric purposes**
(see Moteki and Kondo, AS&T, 2010; Laborde et al., AMT 2012; Baumgardner et al., AMTD, 2012)

Detection efficiency of the SP2



- Lower detection limit: ~0.3-1.0 fg BC (D_{BC}~70-100 nm)
  (see Schwarz et al., AS&T, 2010; Laborde et al., AMTD, 2012).
- Careful preparation of SP2 is critical for detection of particles with small BC mass.
- The above detection limit applies for sufficiently compact particles. PALAS soot is not detected by the SP2 even at 2 fg BC per particles! (Gysel et al., submitted to AMTD).

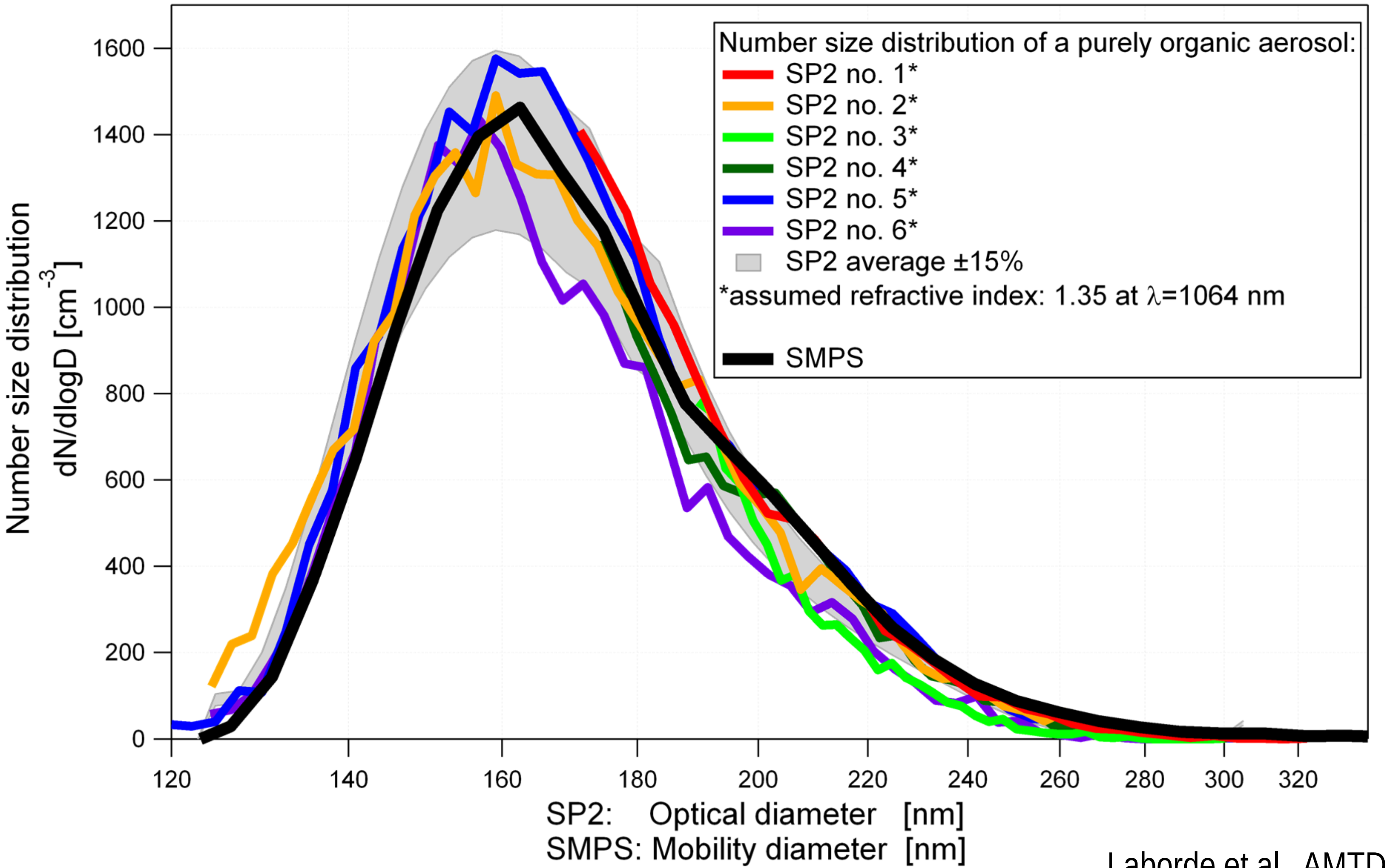
Reproducibility of BC mass measurement



Laborde et al., AMTD, 2012

Good agreement between all SP2's ⇒ precise and reproducible method

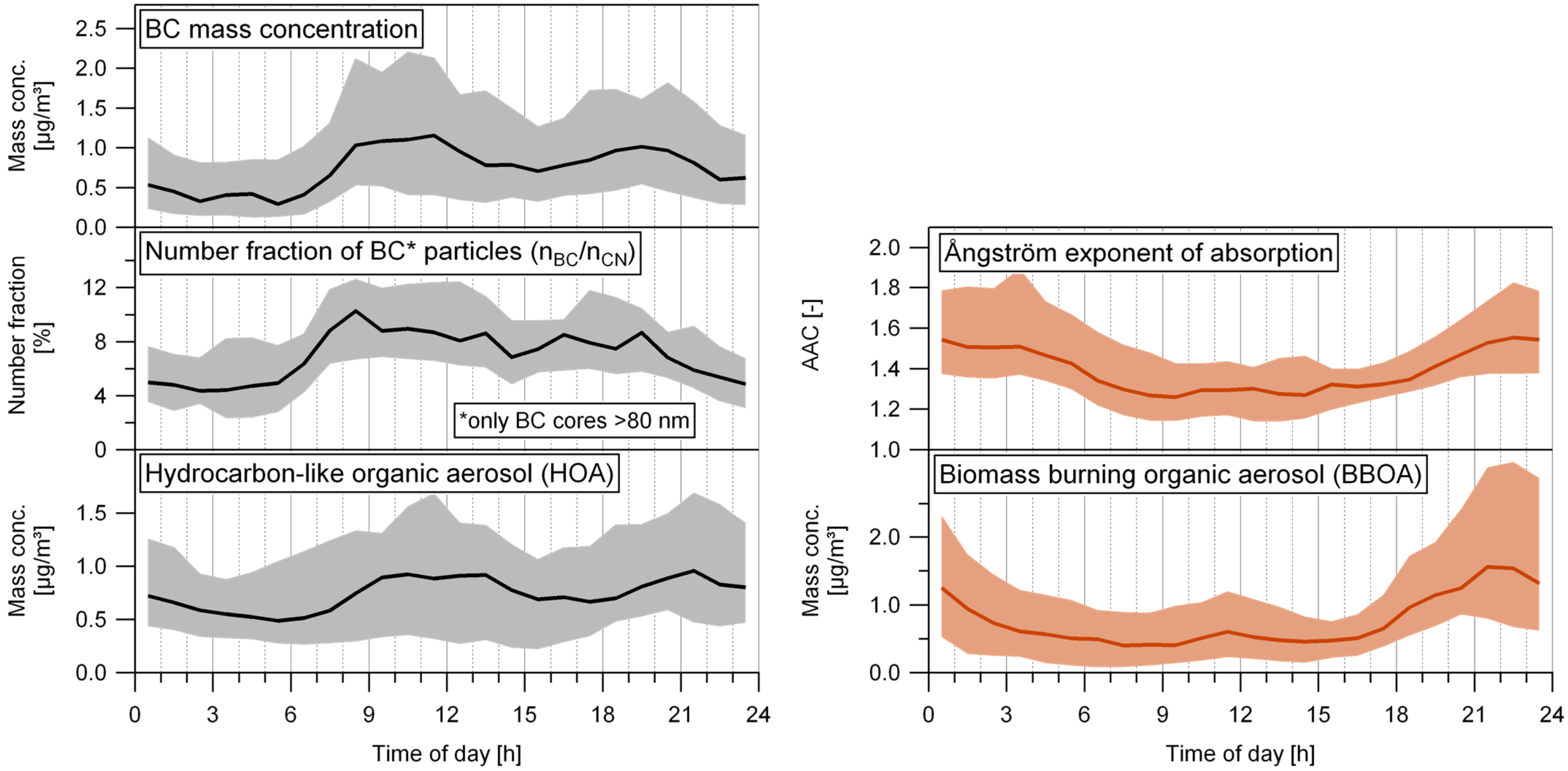
Reproducibility of optical sizing



Laborde et al., AMTD, 2012

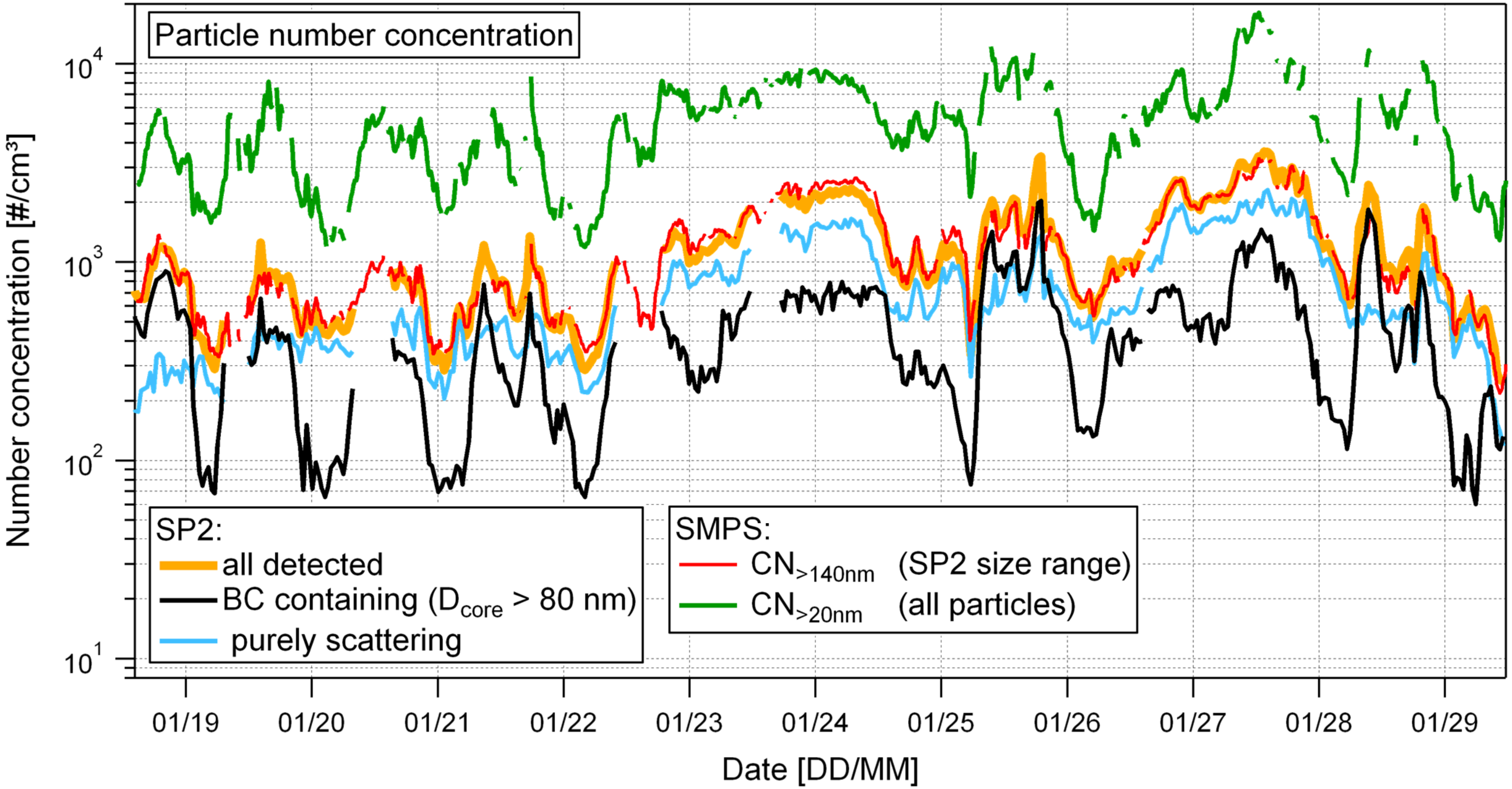
- Reliable optical sizing of purely scattering particles
- Lower detection limit: D ≈ 120 – 180 nm

Diurnal cycles



⇒ Ångström exponent of absorption is consistent with traffic influence during daytime and wood burning influence during nighttime.

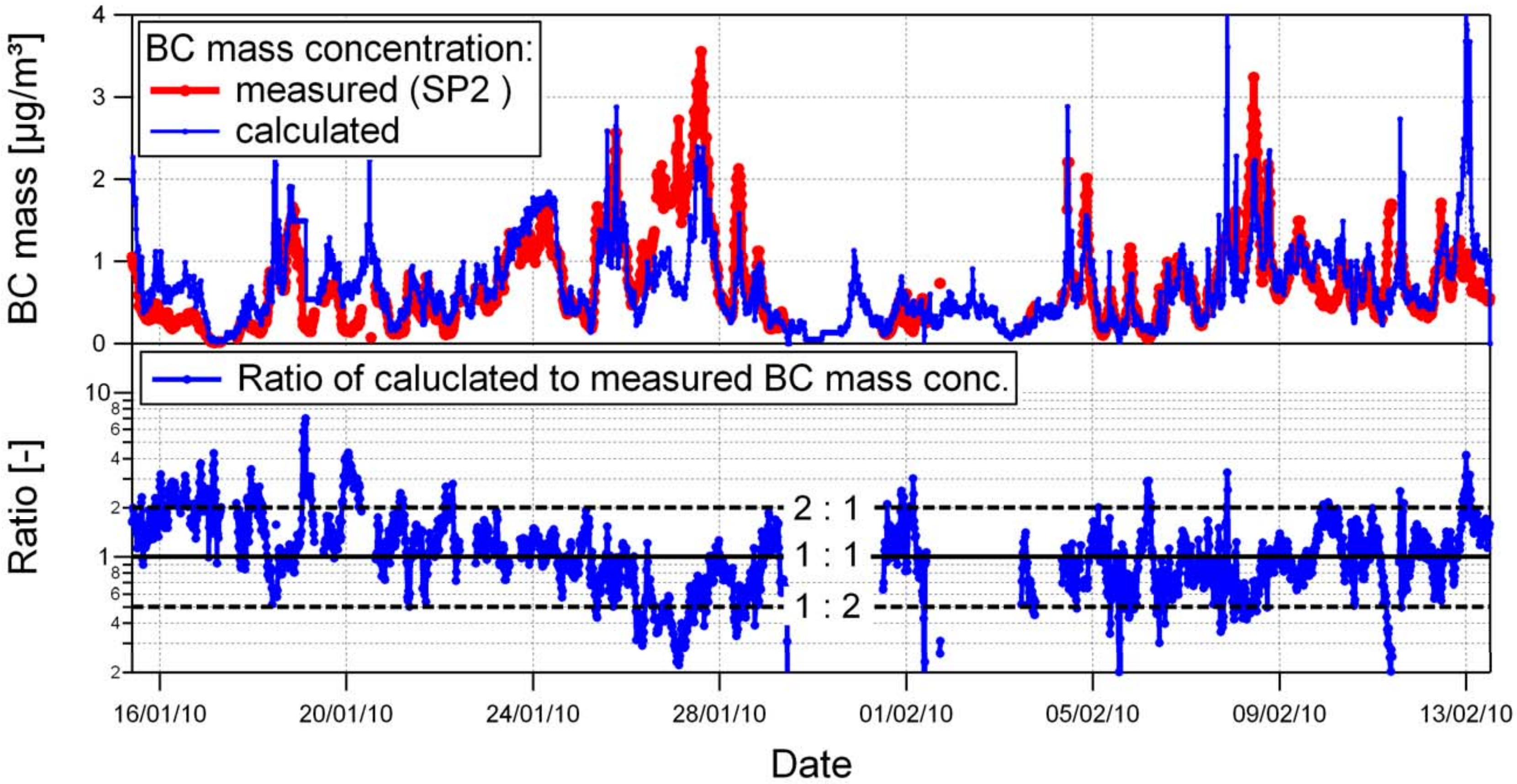
Particle number concentration



Calculation of BC mass from organic aerosol components

$$m_{\text{BC,calculated}} = a \cdot m_{\text{HOA}} + b \cdot m_{\text{BBOA}}$$

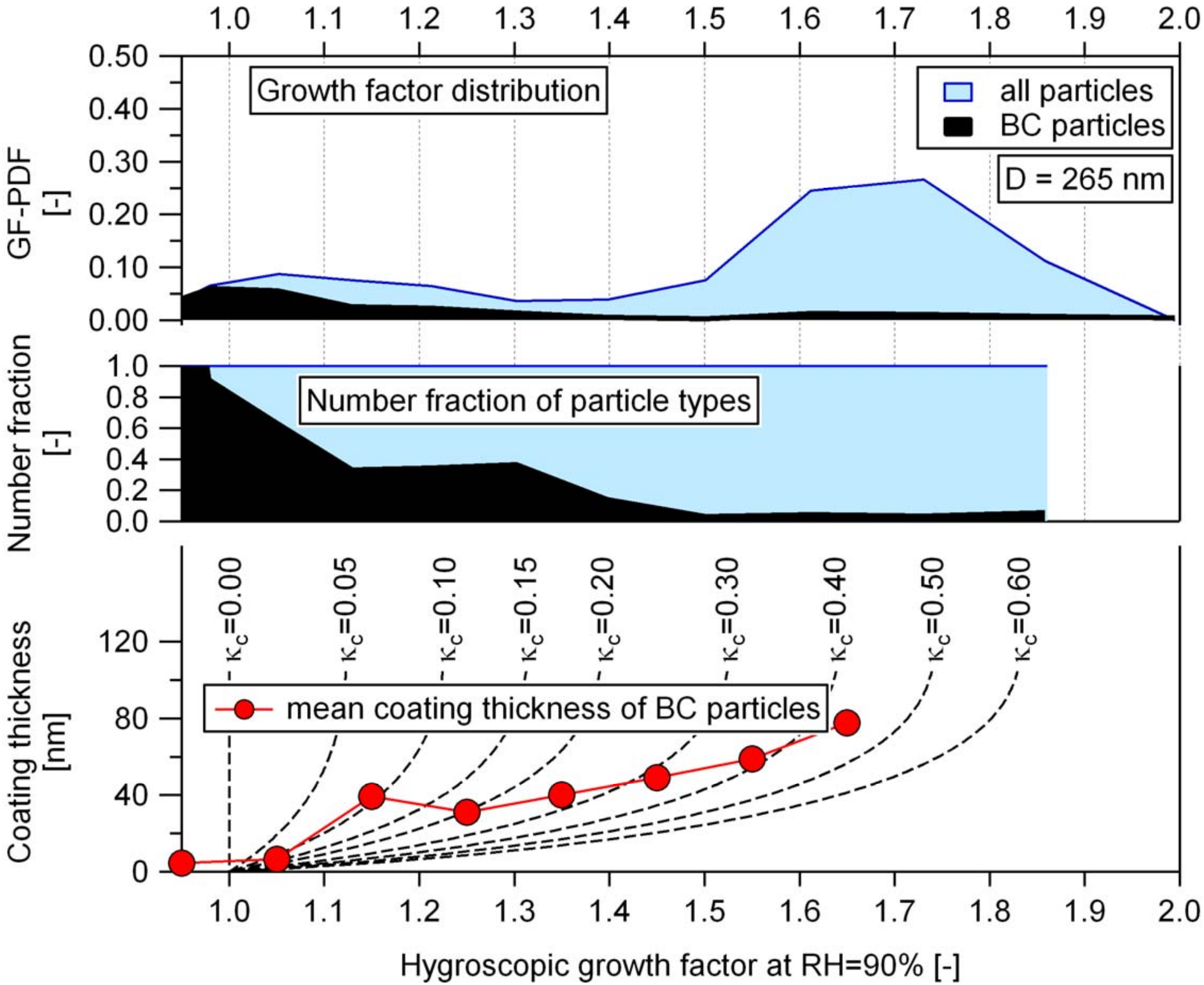
a, b: coefficients of bilinear regression



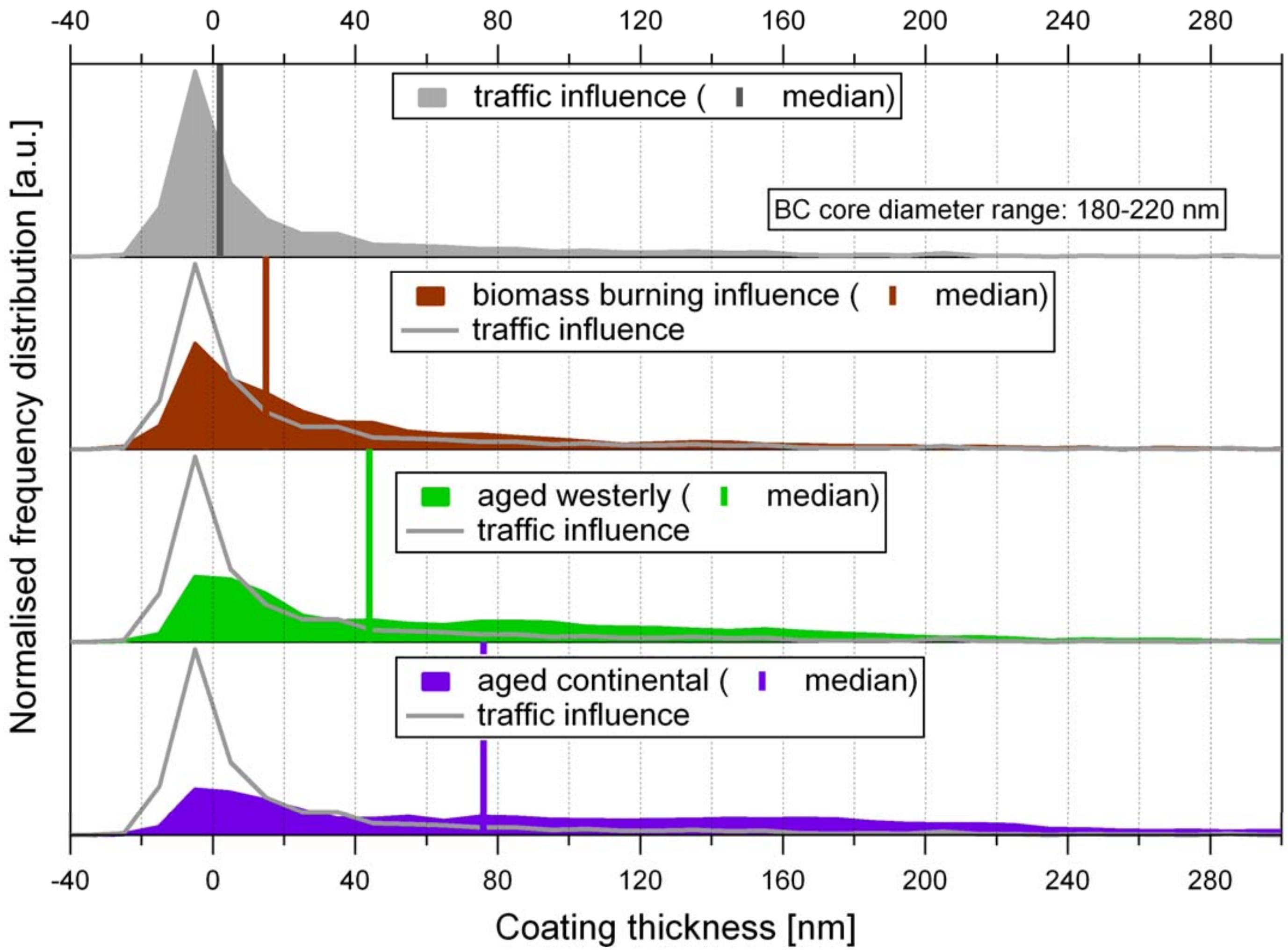
The bilinear regression indicates that dominant fraction BC is from traffic.

⇒ This is consistent with the observed diurnal cycles and the Ångström exponent of absorption, as well as with results by Healy et al., 2012.

Background aerosol

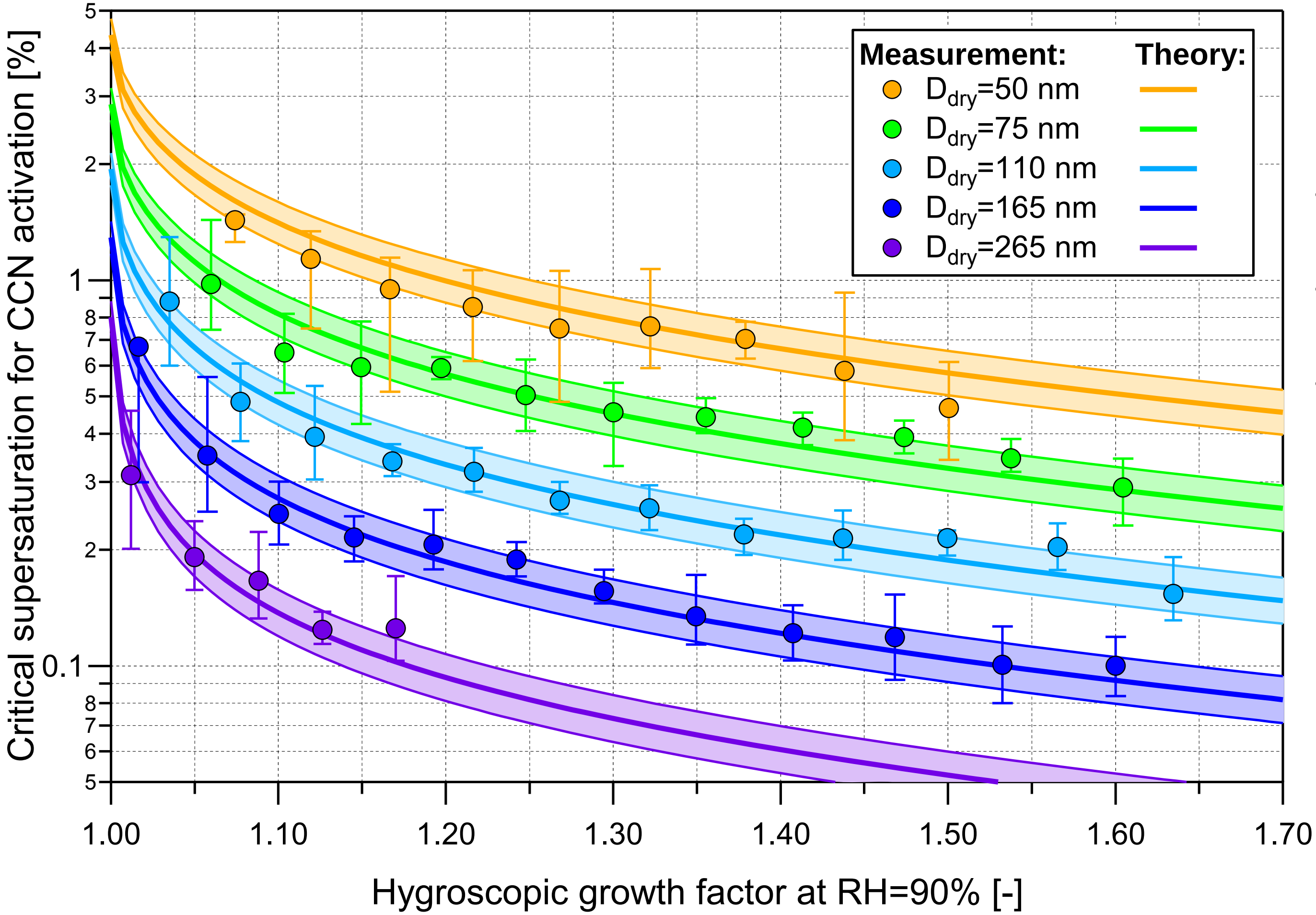


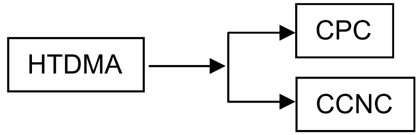
Coating thickness of BC particles



Coating thickness: traffic < biomass burning < aged

Paris: mixing state resolved hygroscopicity-CCN closure





- 5 dry sizes from 50-265 nm
- 20 SS from 0.07-1.5%
- GF from ~1.0-1.6 with ΔGF≈0.05

Successful hygroscopicity-CCN closure:

⇒ κ-Köhler theory describes the CCN activation behaviour well across the whole investigated 3-dimensional parameter space D_{dry}-SS-GF!

[redacted]

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SP2 specifications

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Strengths of the SP2:

- Quantitative detection of BC in single particles
- 100% detection efficiency*
  (*above the lower detection limit)

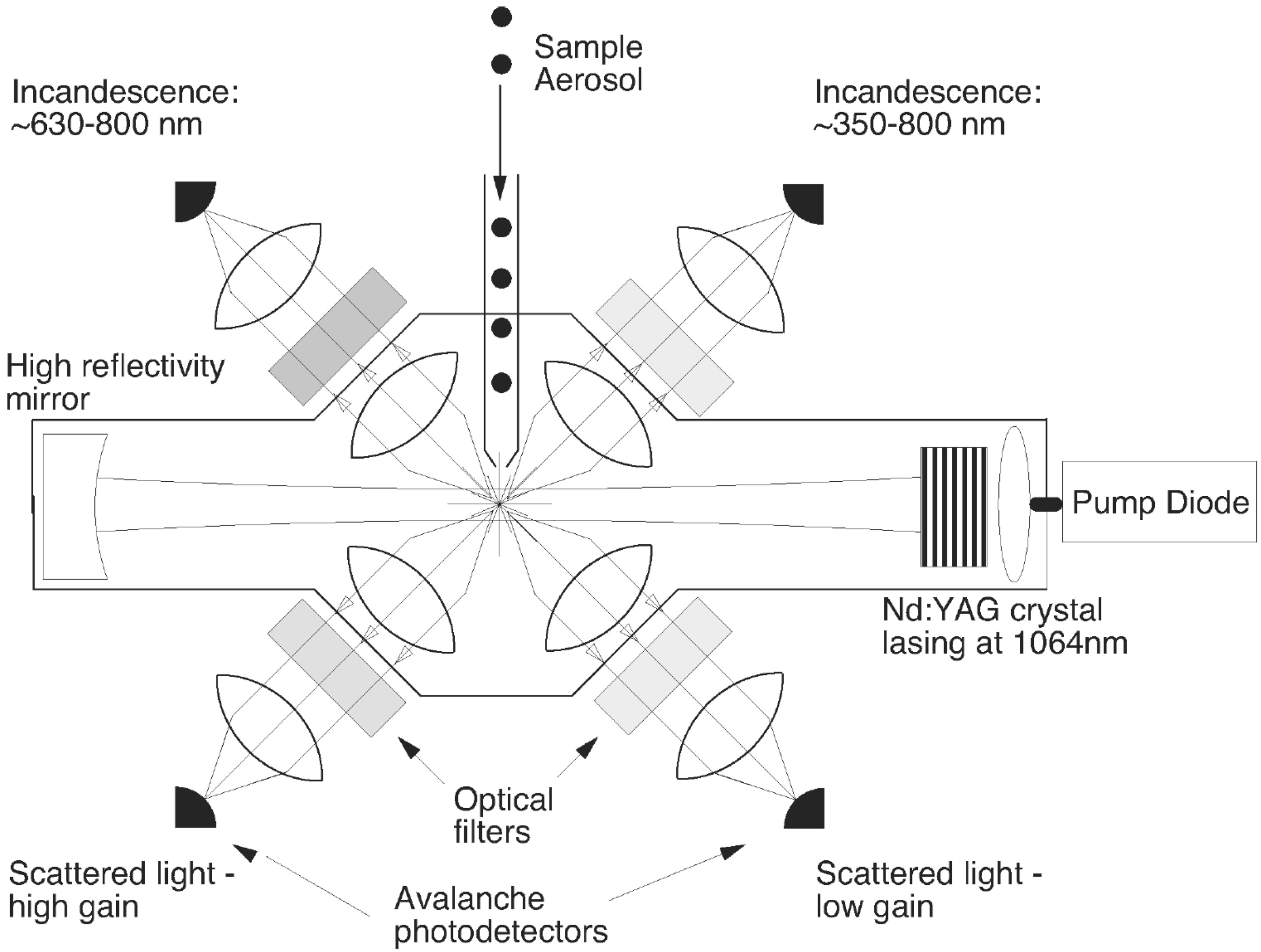
⇒ extremely sensitive

- BC mass measurement is independent of particle mixing state.
- Optical sizing provides semi-quantitative information on the mixing state of individual BC particles.

Limitations of the SP2:

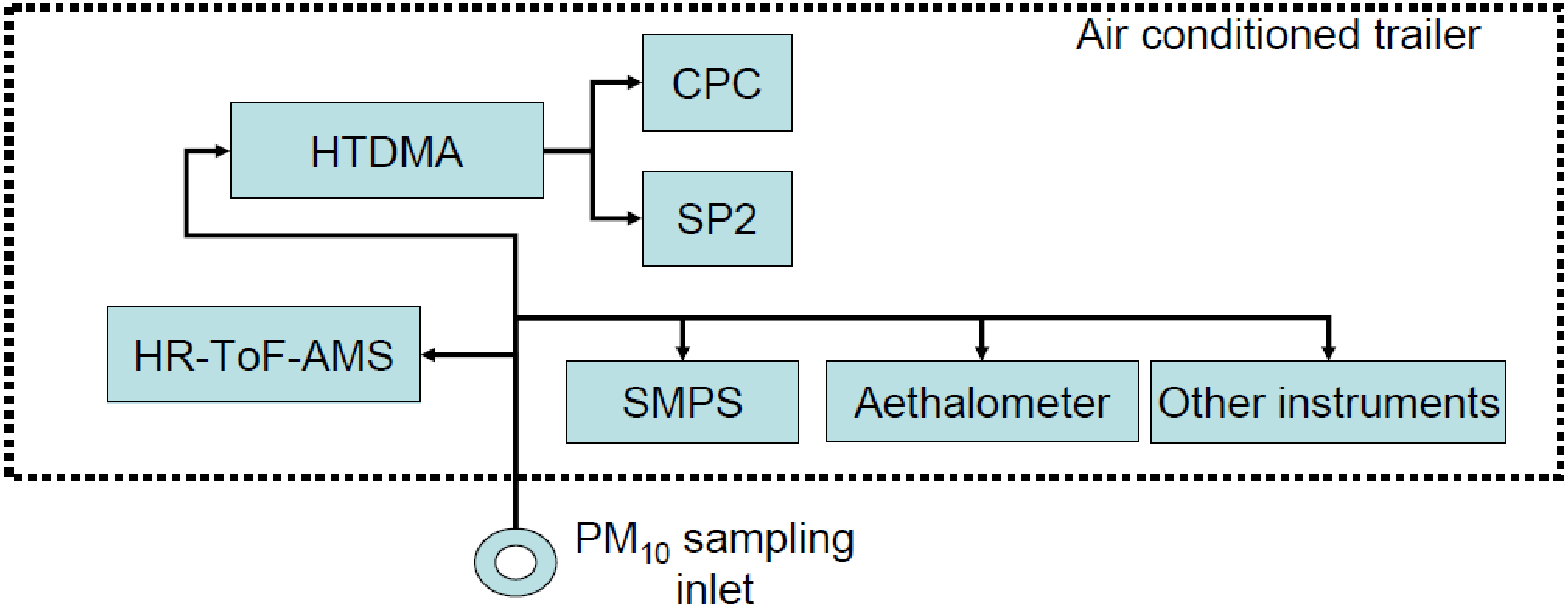
- Lower detection limit: ~0.3-1.0 fg BC per particle (D_{BC}≈70-100 nm)
- Coincidence problems can already occur at atmospheric particle numberconcentrations (polluted locations).
- Not really a “plug and play” instrument

Single Particle Soot Photometer (SP2)

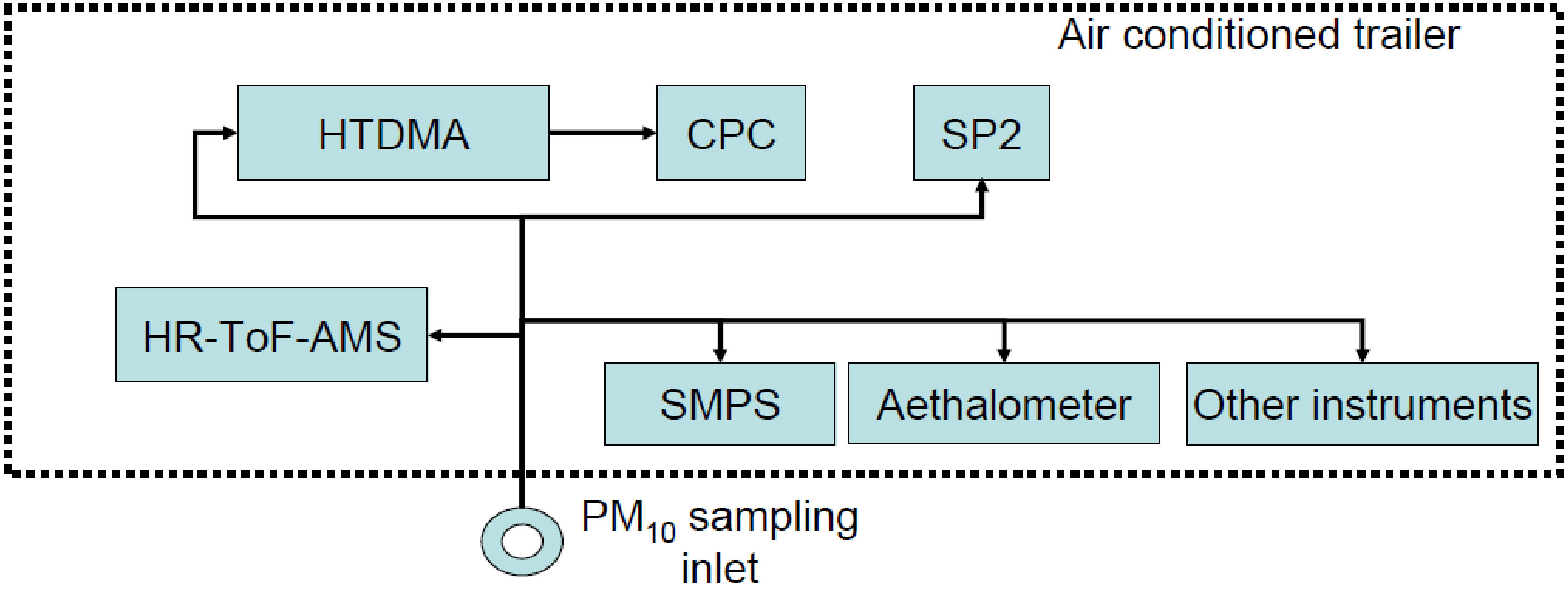


Technical paper: Stephens et al., J. *Appl. Opt.,* 2003.
Figure: Gao et al., *Aerosol Sci. Technol.,* 2007.

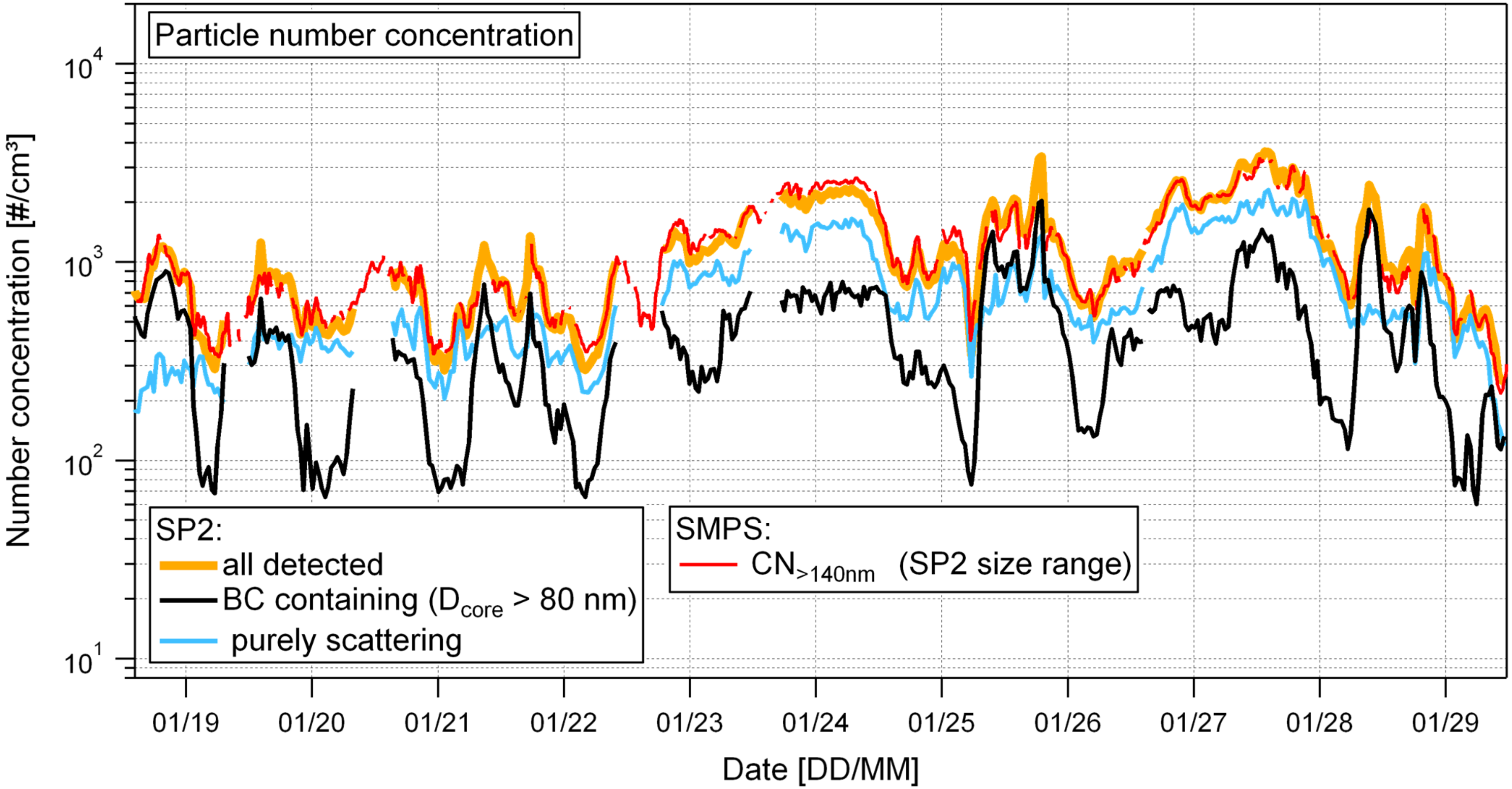
Experimental setup



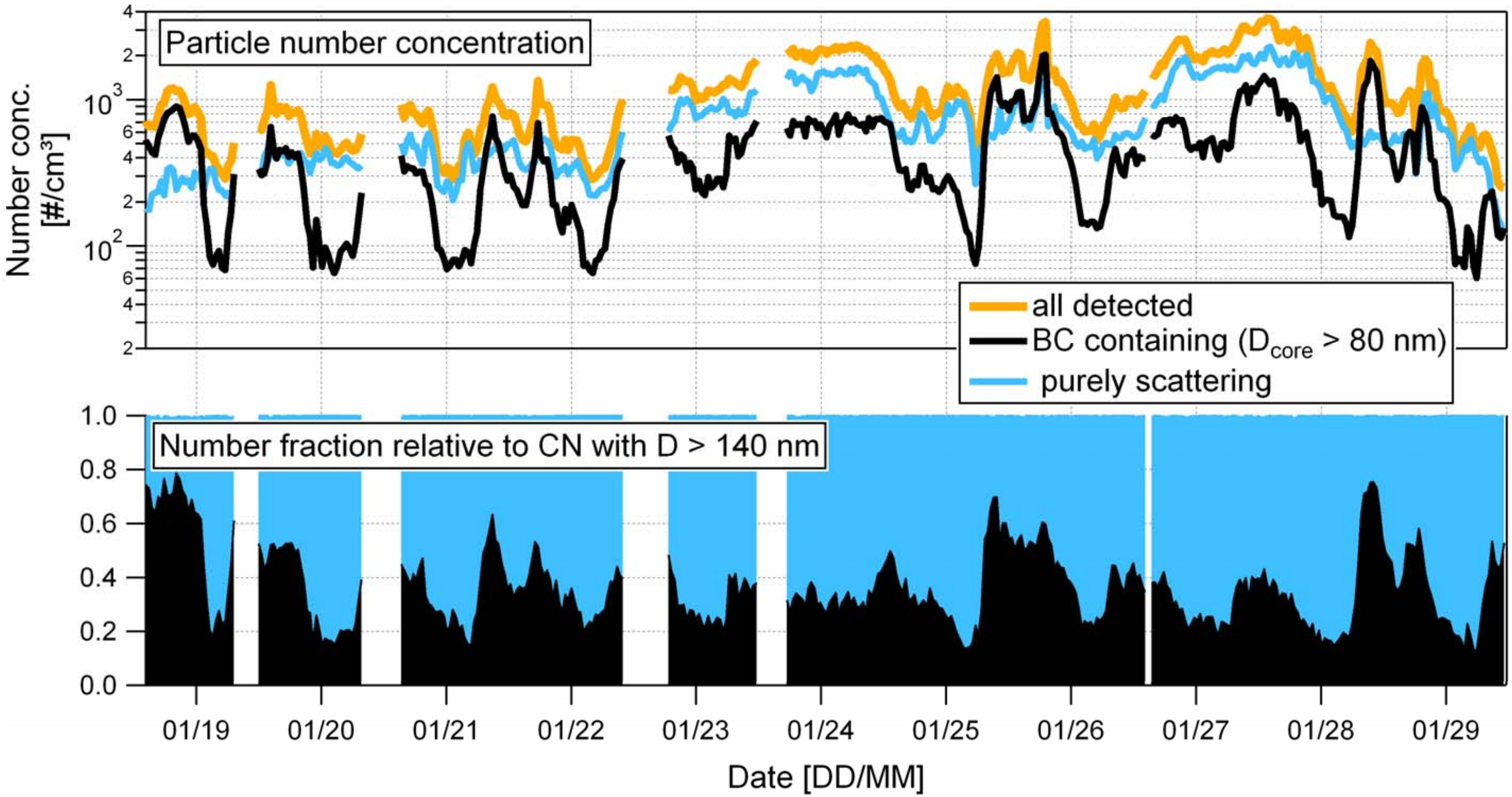
Experimental setup



Particle number concentration



SP2 can distinguish between BC particles and purely scattering particles



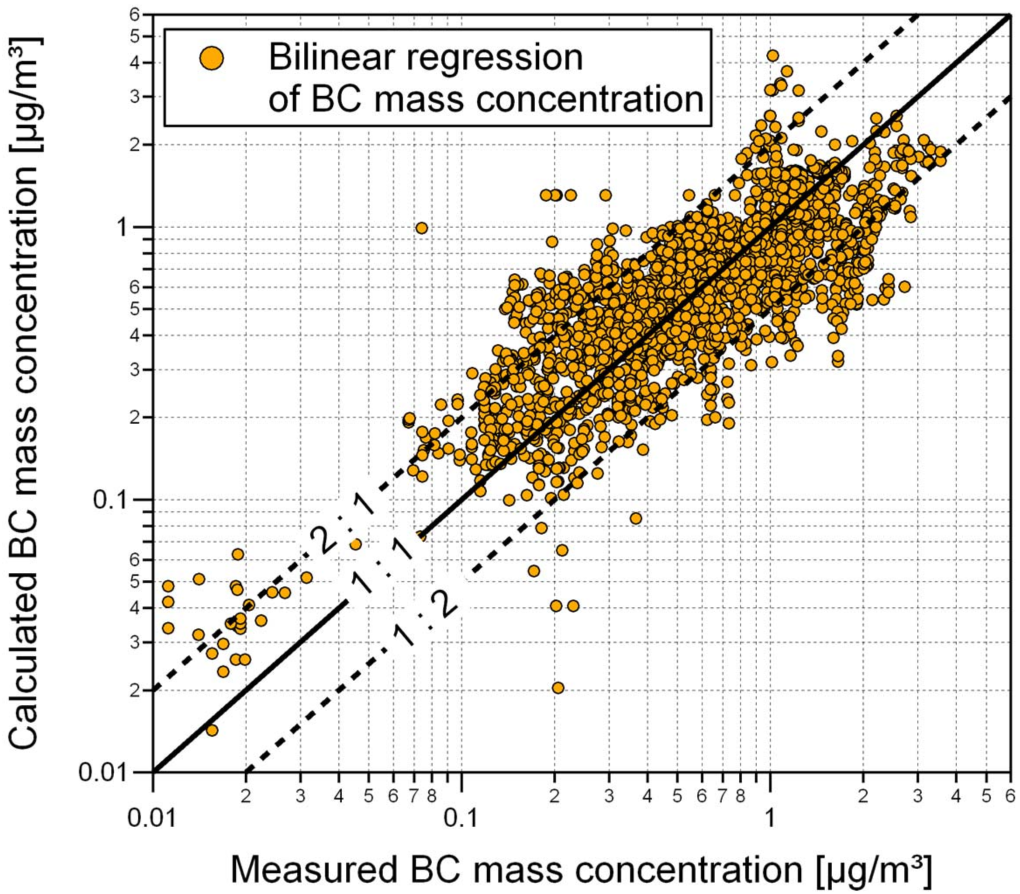
SP2 provides information on the particle type

⇒ number fraction of BC containing particles is highly variable

Calculation of BC mass from organic aerosol components

$$m_{\text{BC,calculated}} = a \cdot m_{\text{HOA}} + b \cdot m_{\text{BBOA}}$$

a, b: coefficients of bilinear regression



The bilinear regression indicates that dominant fraction BC is from traffic.

⇒ This is consistent with the observed diurnal cycles and the Ångström exponent of absorption, as well as with results by Healy et al., 2012.

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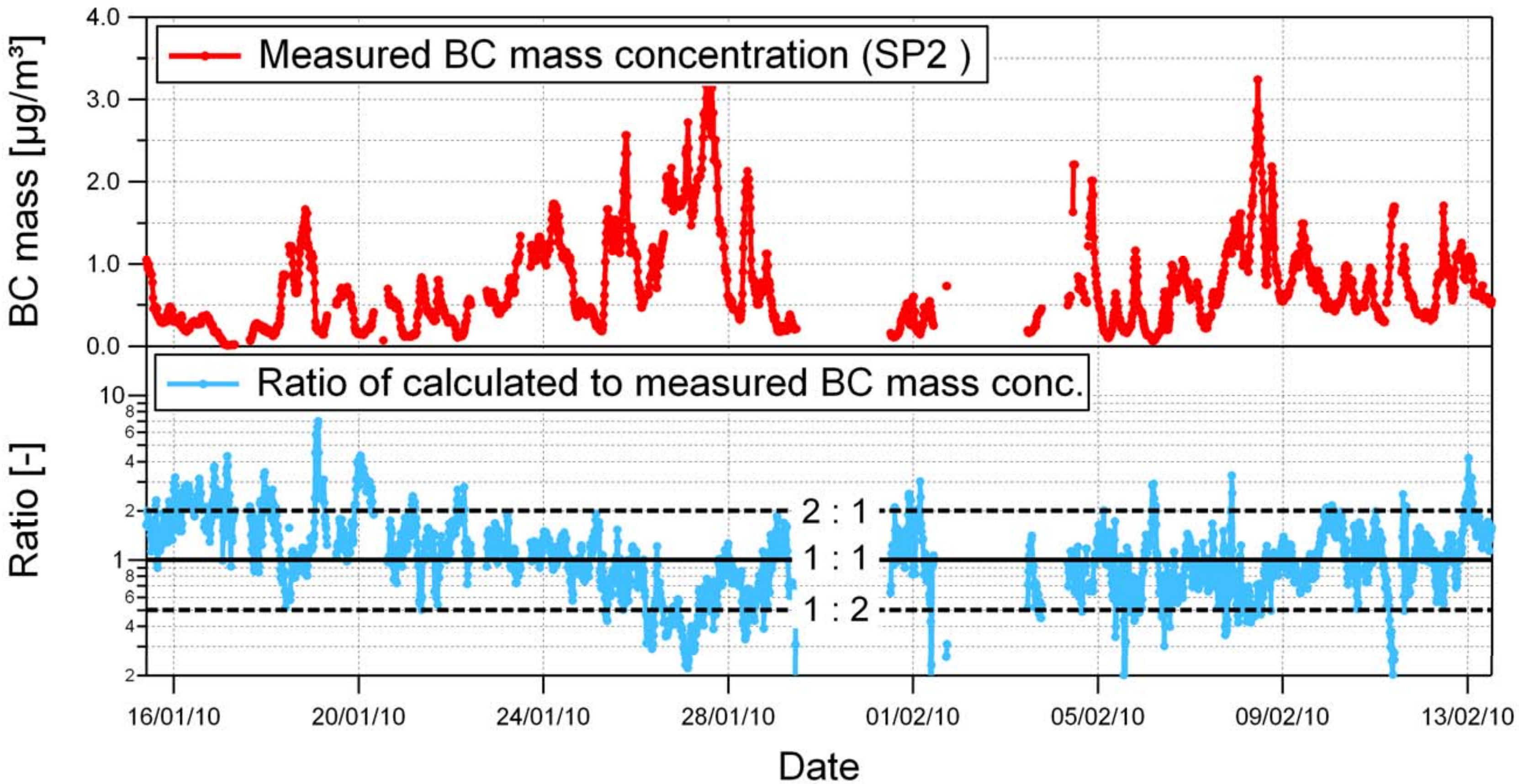

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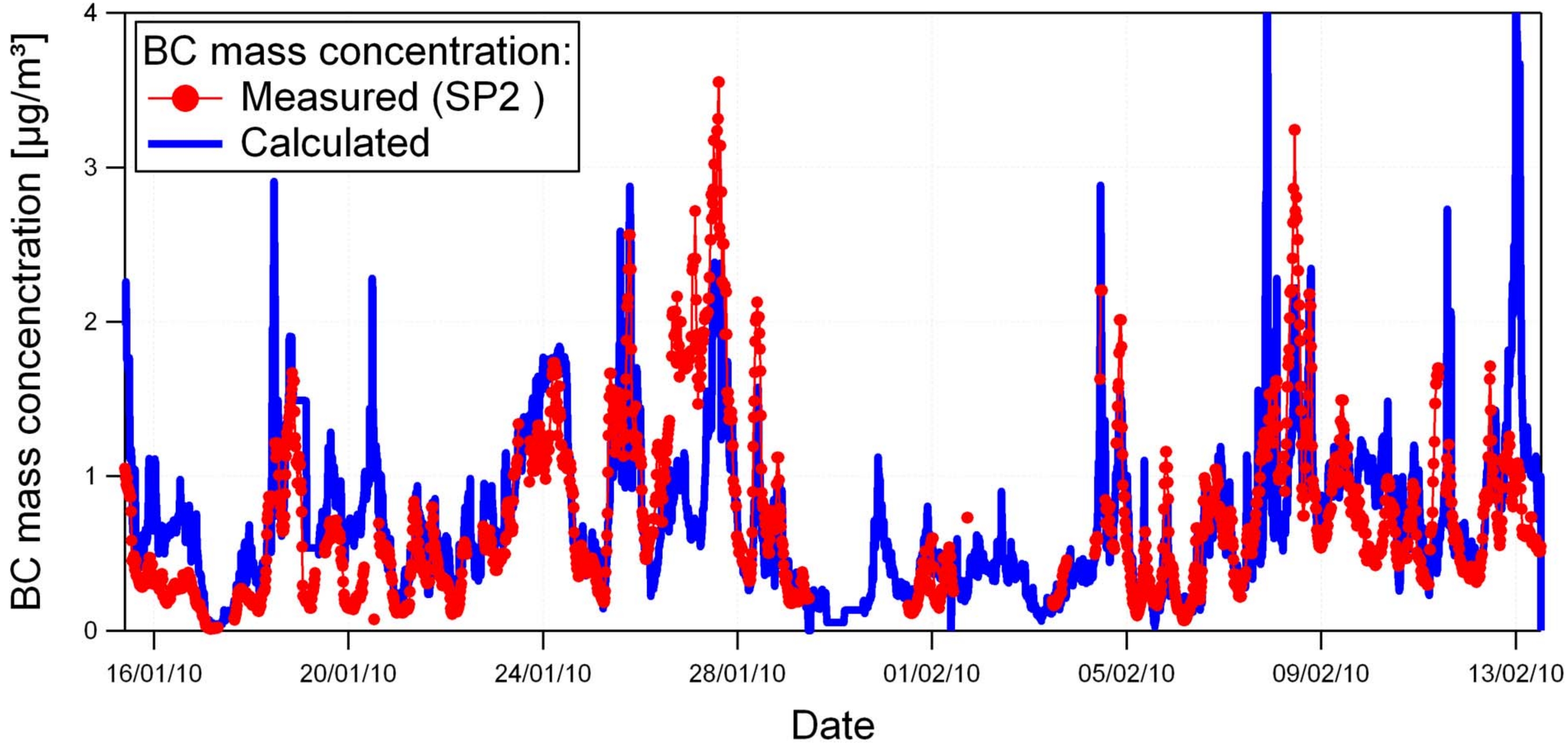

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Diurnal cycles

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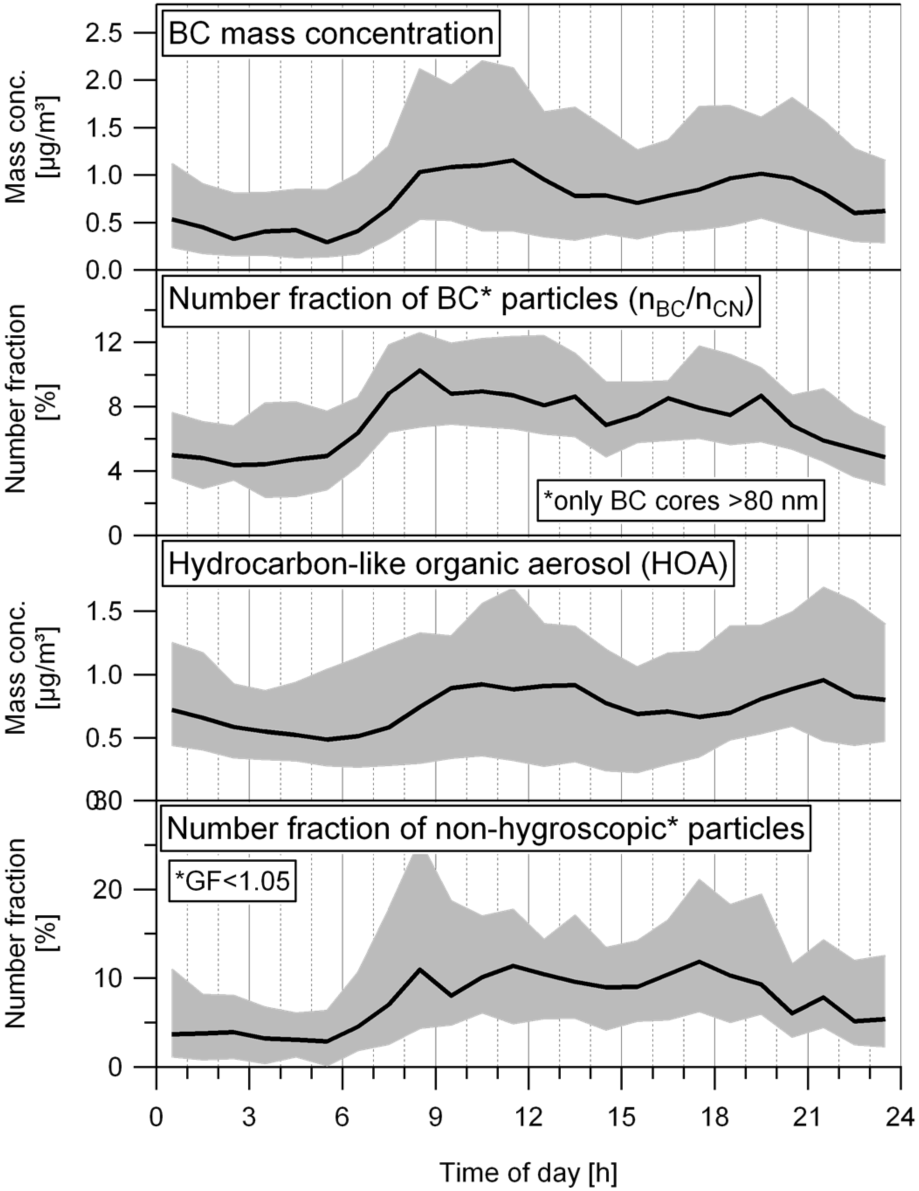
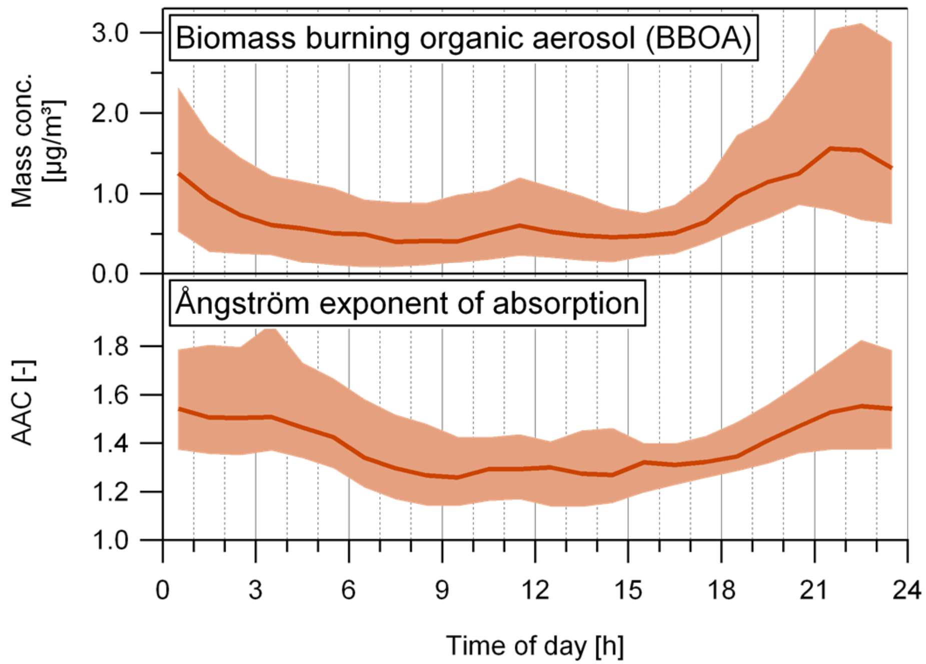
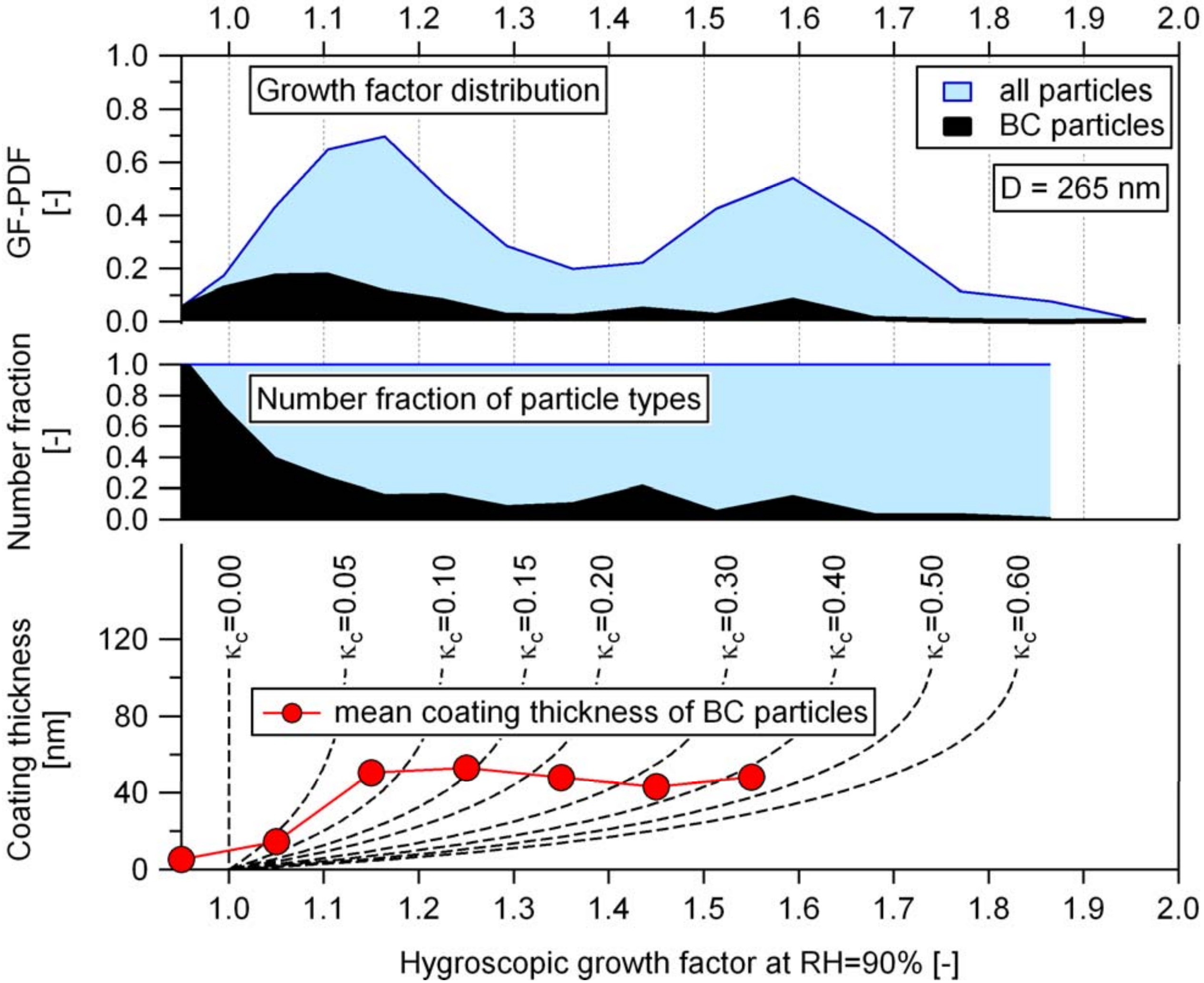
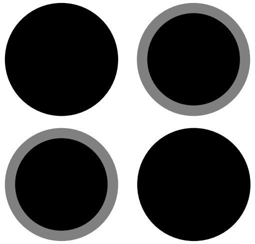




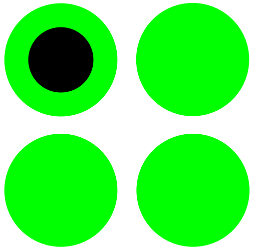

Growth factor distribution
all particles
BC particles
D = 265 nm
GF-PDF [-]
Number fraction of particle types
Number fraction [-]
κ_c=0.00
κ_c=0.05
κ_c=0.10
κ_c=0.15
κ_c=0.20
κ_c=0.30
κ_c=0.40
κ_c=0.50
κ_c=0.60
mean coating thickness of BC particles
Coating thickness [nm]
Hygroscopic growth factor at RH=90% [-]

Conclusions for BC in Paris (winter season)



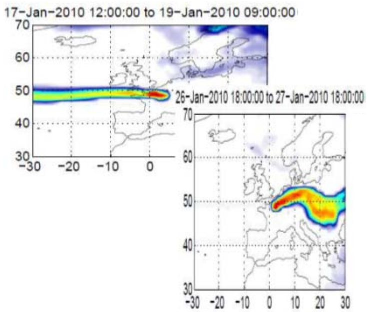
Traffic BC:

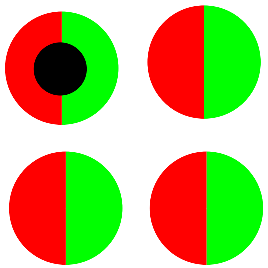
- uncoated
- non-hygroscopic
- major BC source in Paris



Biomass burning BC:

- medium organic coating
- slightly hygroscopic
- minor BC source in Paris





Aged BC:

- medium to thick organic/inorganic coating
- strongly hygroscopic
- minor contribution to BC in Paris

Importance of BC mixing state