



Wir schaffen Wissen – heute für morgen

**Paul Scherrer Institute
Laboratory of Atmospheric Chemistry**

Martin Gysel

**Refractory black carbon mass and mixing state
measurements using the Single Particle Soot Photometer
(SP2)**

- **Laser-induced incandescence:**
 - ➔ «time-resolved LII» and «single particle LII» methods

- **The Single Particle Soot Photometer (SP2)**
 - Measurement of thermal radiation emitted at the boiling point
 - ➔ empirical calibration for refractory black carbon (rBC) mass needed
 - ➔ rBC mass measurement is independent of BC mixing state
 - Measured BC properties and dynamic range
 - Optical sizing
 - **BC mixing state and particle morphology information**
 - **Potential interference from metal, volcanic ash or dust particles**
 - ➔ they can be identified

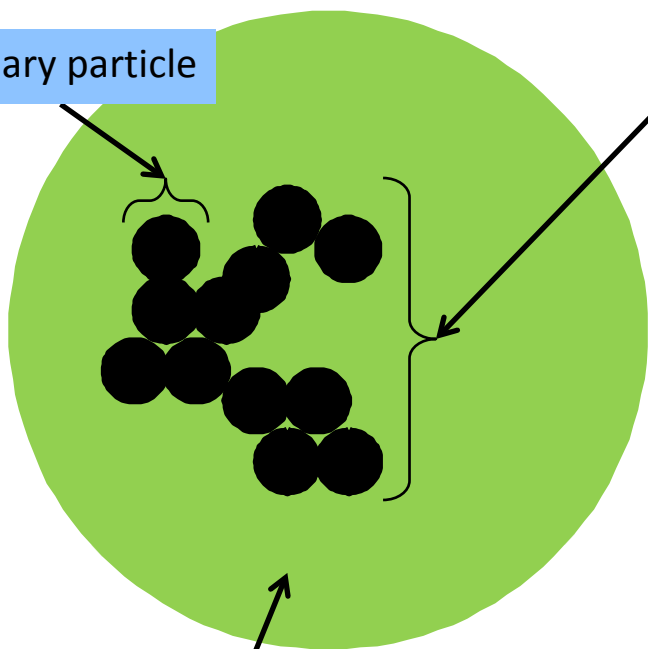
- **Comparison with thermal-optical and light-absorption methods**
 - ➔ rBC is not so different from EC, eBC (COSMOS), ...

soot particle

(in the context of the SP2: «BC-containing particle»)

«BC core» = aggregate of primary particles, composed of black carbon (elemental carbon, ...)

primary particle



«coating»

(organic carbon, inorganic salts)

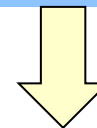
- almost «pure carbon» (>90% C)
- graphitic microstructure with some disorder
- fractal-like aggregate of primary spheres
- insoluble in any solvent
- strongly light-absorbing («black»)
- extremely refractory ($T_{\text{sublim}} \approx 4000 \text{ }^\circ\text{C}$)

see e.g. Petzold et al. (2013) for terminology

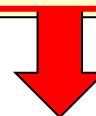
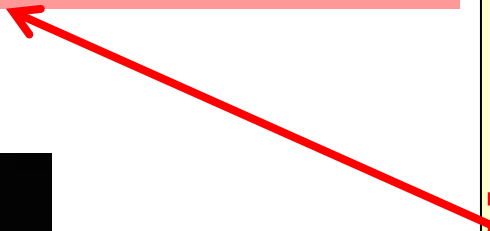
Laser-induced incandescence is NOT a light-absorption based method!

Some light-absorption by the investigated material is required to heat it in the laser beam. However, the light-absorption cross section of the material has no direct influence on the measured thermal radiation signal.

«BC core» = aggregate of primary particles, composed of black carbon (elemental carbon, ...)



- almost «pure carbon» (>90% C)
- graphitic microstructure with some disorder
- fractal-like aggregate of primary spheres
- insoluble in any solvent
- strongly light-absorbing («black»)
- extremely refractory ($T_{\text{sublim}} \approx 4000 \text{ }^\circ\text{C}$)



Laser-induced incandescence (LII): measurement of the thermal radiation emitted by the «BC core» at sublimation point
 → indirect measure of the mass of refractory black carbon (rBC mass)

«Time-resolved LII» (e.g. Schulz et al., 2006):

➤ *Principle:*

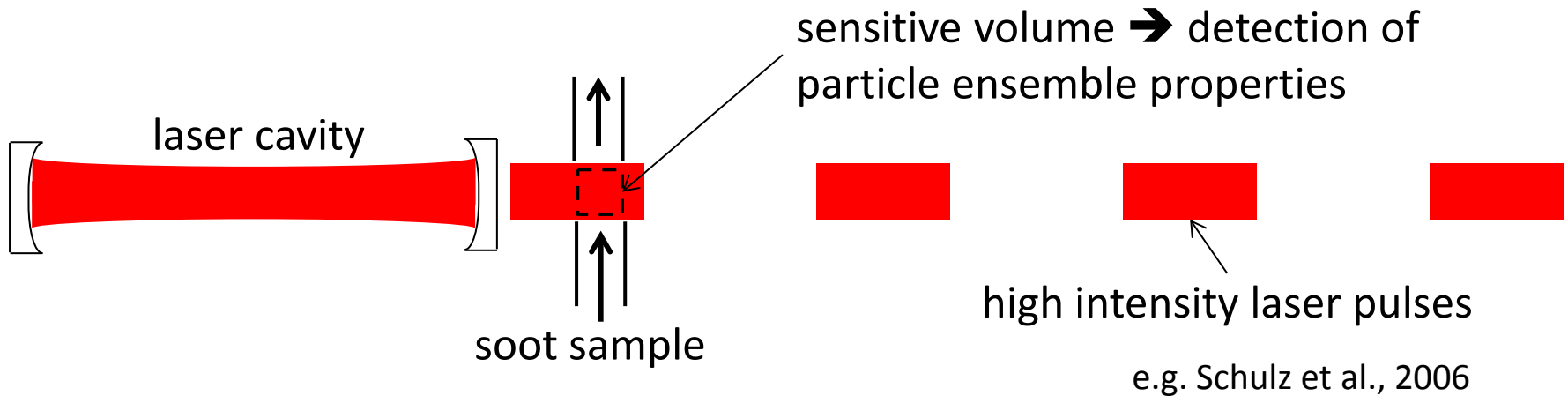
- **Pulsed laser used to heat the particles**
- Detection of the thermal radiation from all particles in the sensitive volume
➔ **properties of the whole particle ensemble, mainly BC mass concentration**
- **No empirical calibration with BC reference material needed (?)** (Snelling et al., 2005)

➤ *Application:*

- **Most commonly used for detection of BC in combustion exhaust** in laboratory applications
- More recently also used for field measurements of BC in atmospheric aerosols

➤ *Some field deployable instruments:*

- **LII 300 from ARTIUM Technologies Inc.** (<http://www.artium.com/>):
Dynamic range for BC is around $<0.2 \mu\text{g}/\text{m}^3 - 20 \text{g}/\text{m}^3$ ➔ suitable for combustion exhaust, while **not quite sensitive enough for clean atmospheric environments**
- **NRC's LII instrument** (Smallwood, PhD thesis, 2008; Chan et al., 2008):
Lower detection limit: $0.015 \mu\text{g}/\text{m}^3$ ➔ **suitable for atmospheric applications.**



Time-resolved measurement of the thermal radiation emitted after the laser pulse:

- Detection at two different wavelength bands → **particle temperature**
- Decay curve of thermal emission → **effective primary particle size**
- Temperature + size + thermal emission → **BC mass concentration** can be calculated from first principles (i.e. **no empirical calibration needed**)
- Extremely high laser fluence
→ **no lower detection limit in terms of BC mass per particle** (for relevant sizes)
- Detection of thermal radiation emitted by all particles in the sensitive volume
→ **suitable for high BC mass concentrations**
→ **no single particle data**

«Single particle LI» (e.g. Schwarz et al., 2006):

➤ *Principle:*

- Continuous-wave intra-cavity laser used to heat the particles
- Detection of peak thermal radiation emitted by individual particles at sublimation point
 - ➔ **single particle properties**
- Jet nozzle used to direct particle beam through the laser
 - ➔ **100% detection efficiency** (within given BC particle size limits)
- **Empirical calibration needed**

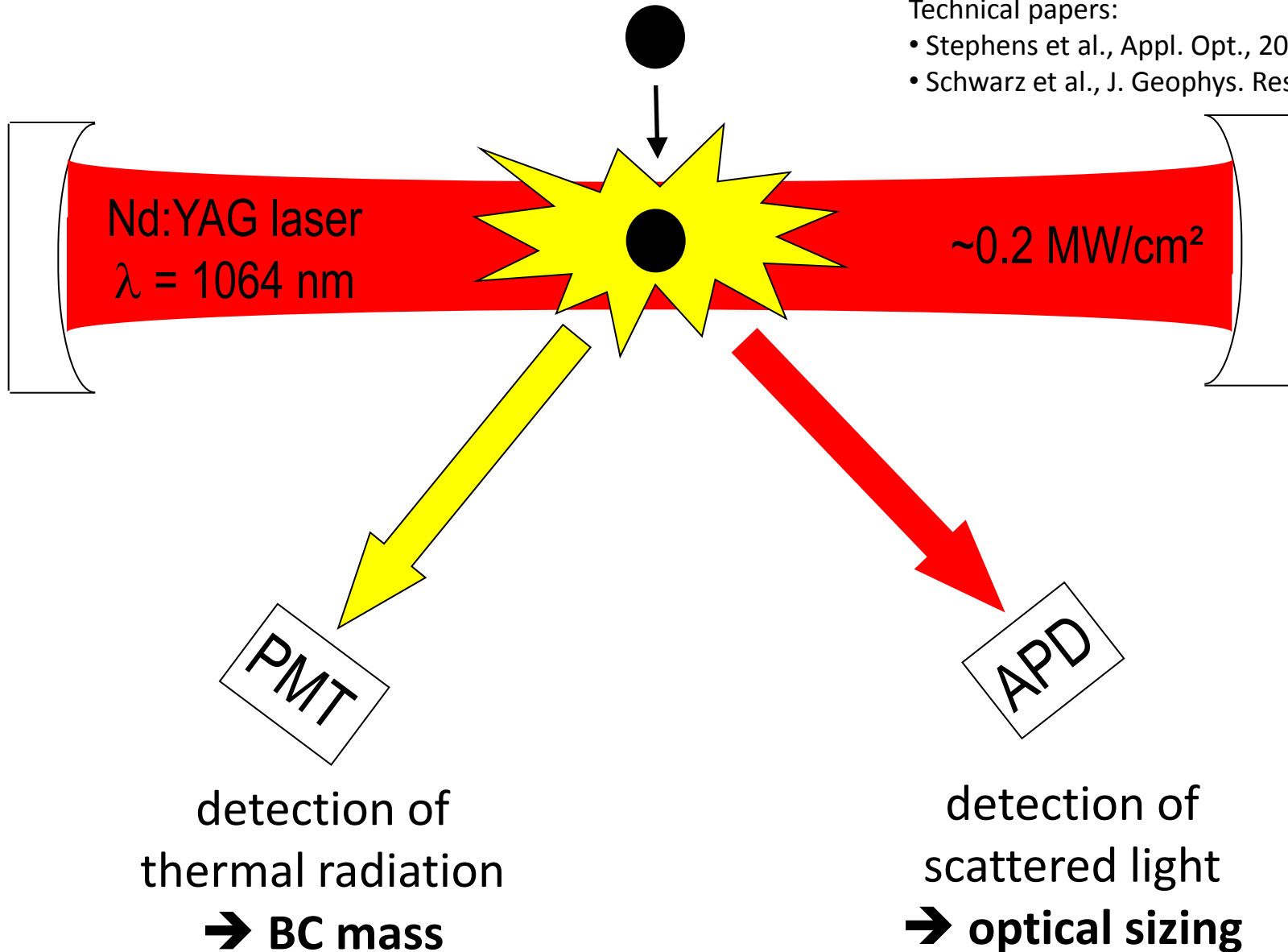
➤ *Application:*

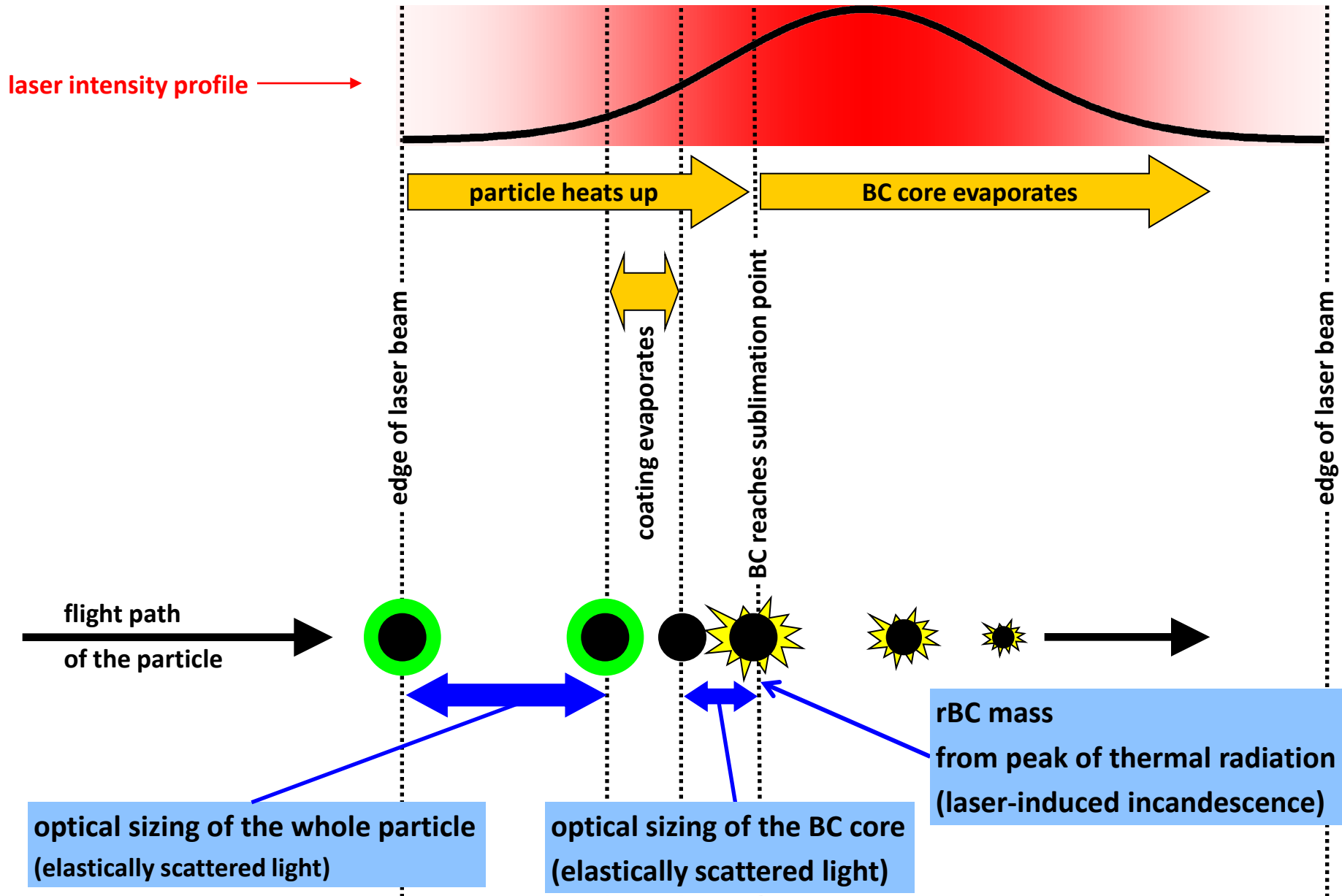
- **Extremely sensitive**, as every single particle is detected
- **Limited to atmospheric BC mass concentrations** due to coincidence errors at high particle number concentrations.
- Also applied for detection of BC in ice core, snow and rain samples (e.g. McConnell et al., 2007; Schwarz et al., 2012; Ohata et al., 2011; Wendl et al., 2014)
- **Provides additional information on BC mixing state**

➤ *The only commercially available instrument* (to my knowledge):

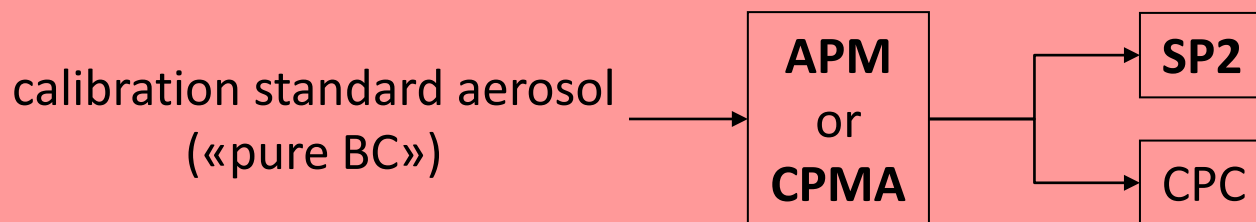
- Single Particle Soot Photometer (SP2) from Droplet Measurement Technology (DMT) (Stephens et al., 2003; Schwarz et al., 2006)

Technical papers:
 • Stephens et al., Appl. Opt., 2003.
 • Schwarz et al., J. Geophys. Res., 2006.



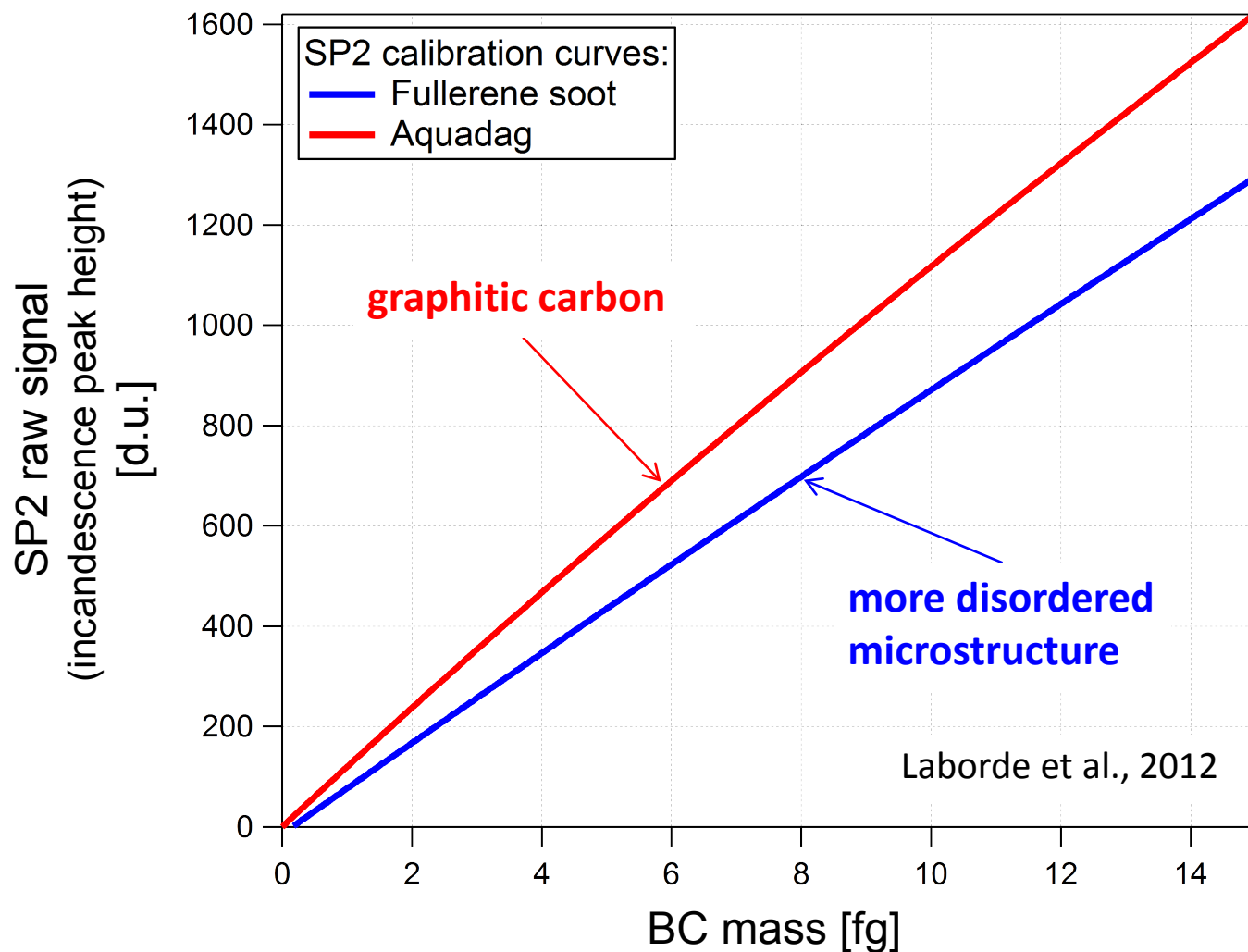


- **Particle Mass Analyser, APM or CPMA, is used as a mass reference** (they select particles directly by their mass)
- **«Pure BC» is used as calibration material:**
 - Thermo-denuded diesel, wood combustion or ambient soot
 - Fullerene soot or Aquadag (commercially available BC)



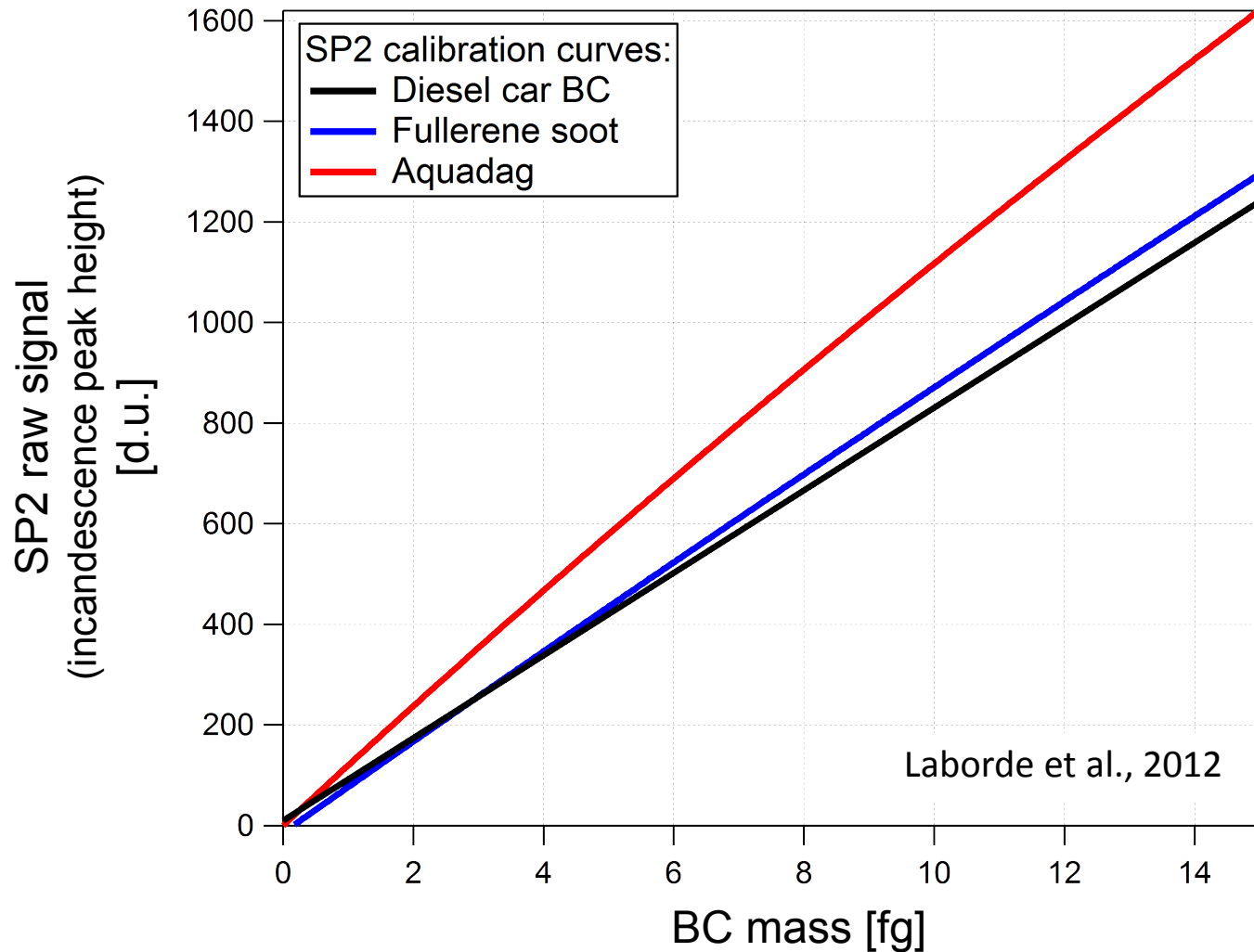
Alternative approach:

- **Use a Differential Mobility Analyser (DMA)** for size-selecting fullerene soot or Aquadag
- **Use effective density data from literature** to calculate mass from mobility diameter (Moteki and Kondo, 2010; Gysel et al., 2010)
 - ➔ **~10% additional calibration uncertainty**



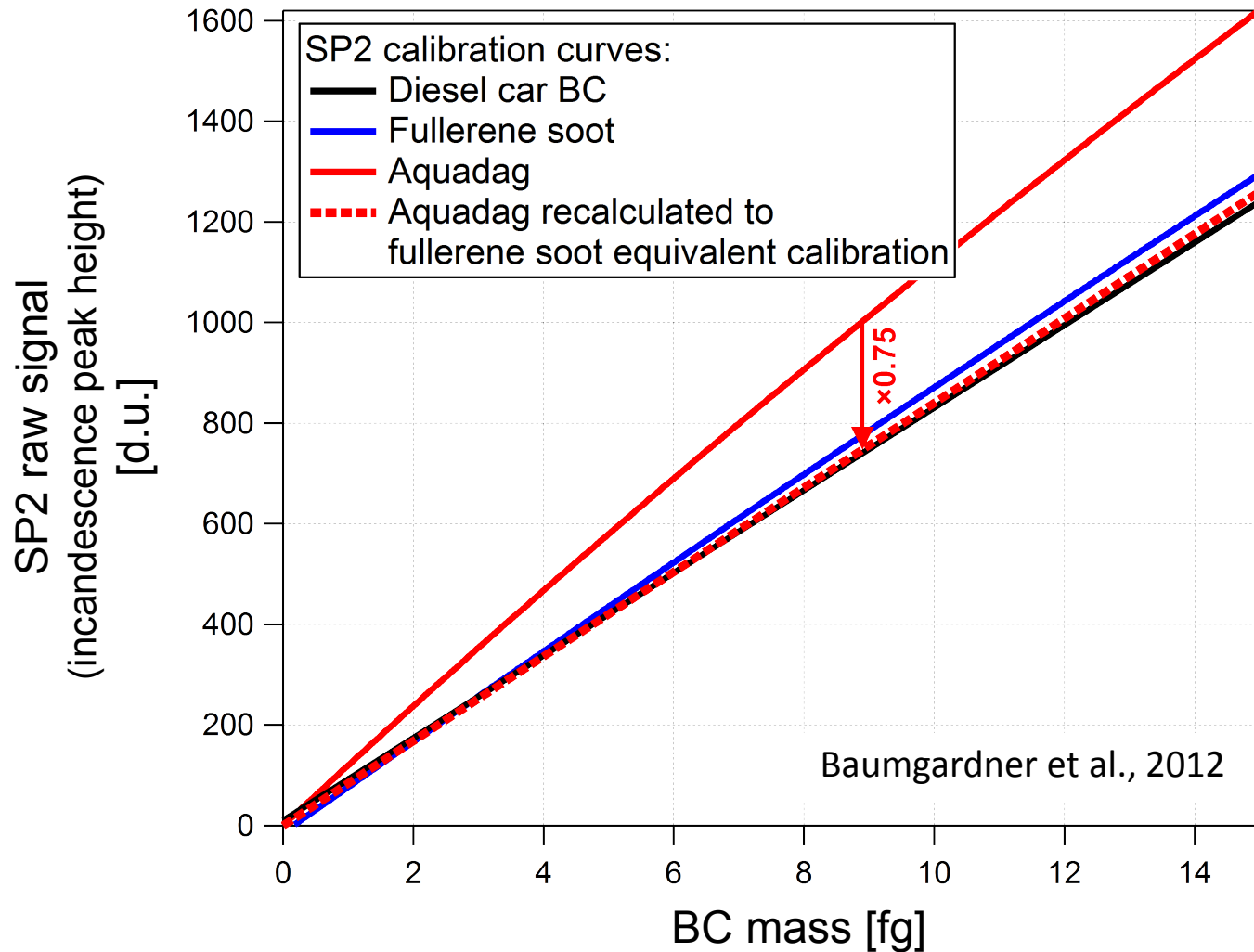
➔ **Bad news: SP2 calibration curves for different BC types can differ by at least 30-40%**

➔ **Good news: the rBC mass measurement by the SP2 is not influenced by BC mixing state!**
(e.g. Moteki and Kondo, 2007; Slowik et al., 2007)

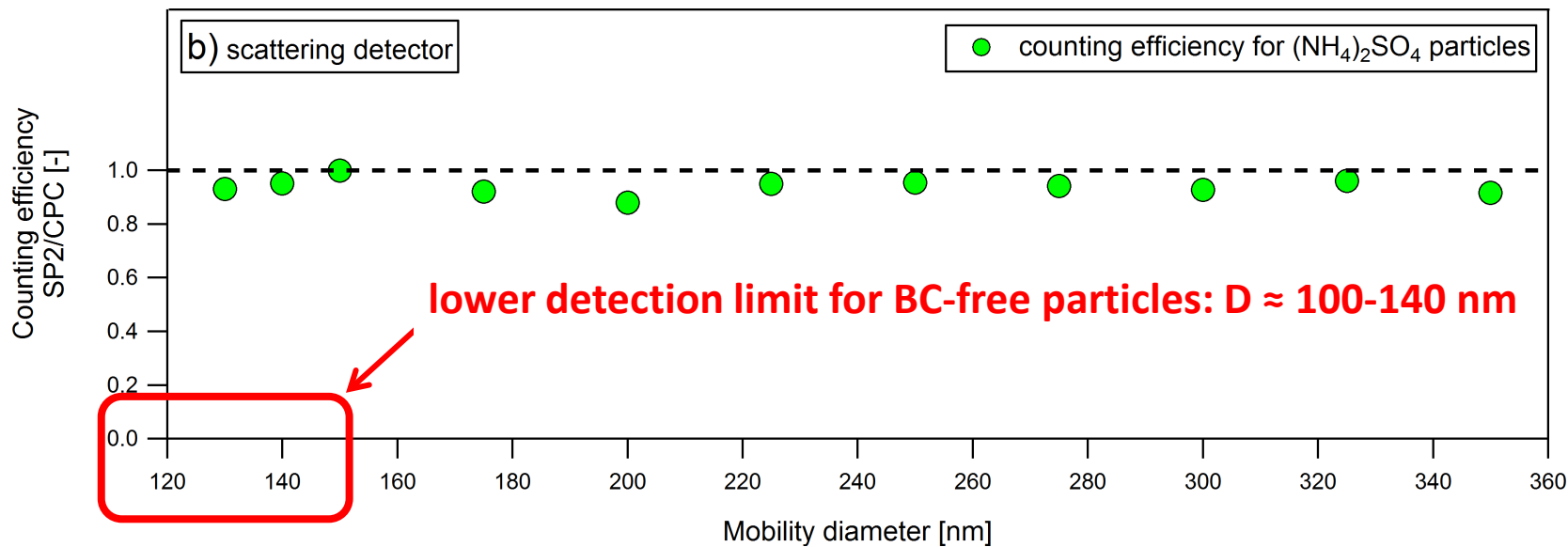


- ➔ Calibration curve for diesel car BC agrees well with that of fullerene soot
- ➔ Diesel car BC calibration is also representative of SP2 sensitivity to BC from wood combustion and BC in ambient aerosol (Moteki and Kondo, 2010; Laborde et al., 2012)

Calibration standard for the SP2 and associated uncertainty

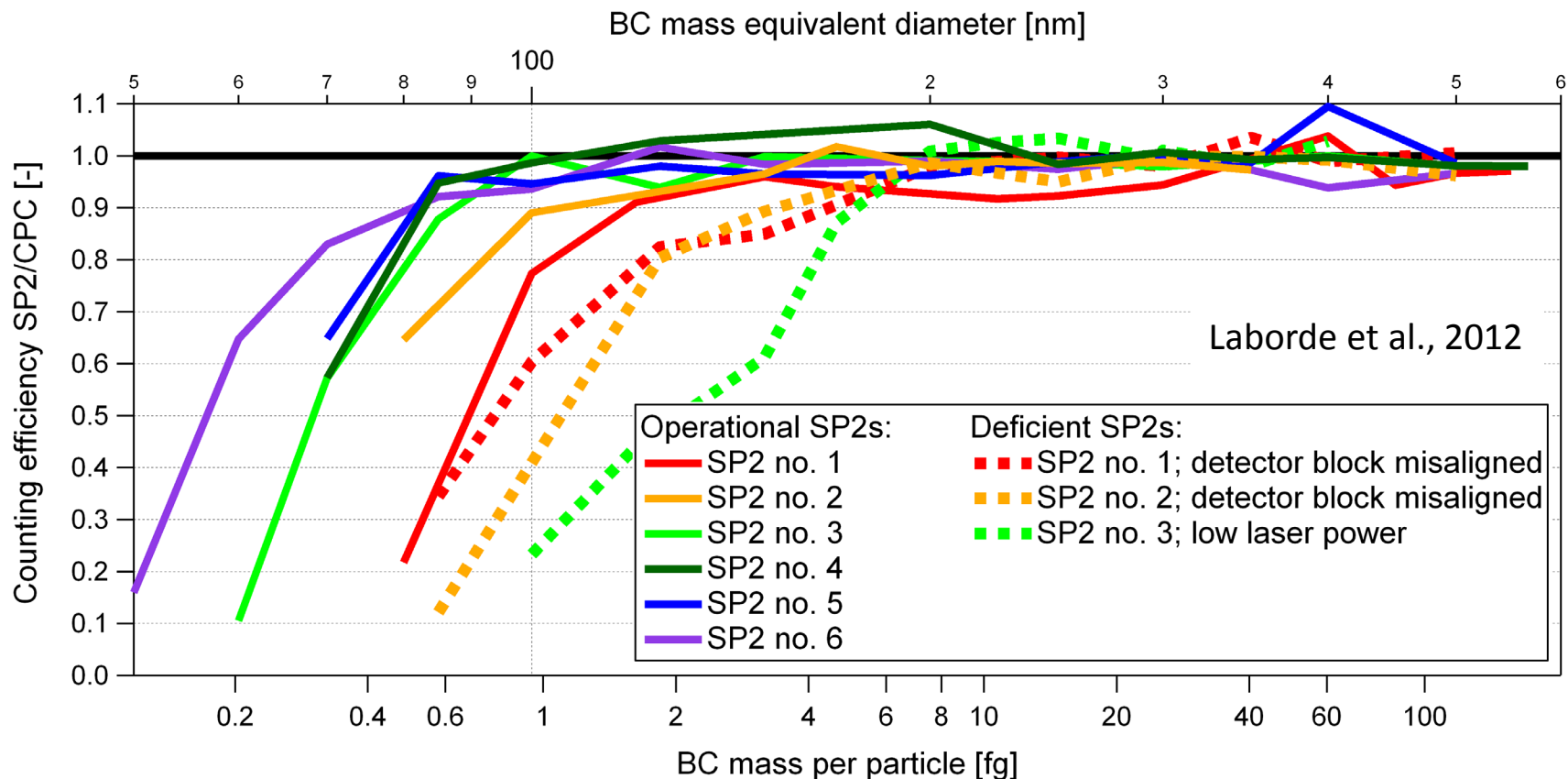


- ➔ **Calibration standard: fullerene soot (batch FS12S011) or Aquadag (needs recalculation)**
- ➔ **Absolute BC mass calibration uncertainty for atmospheric aerosols: $\sim \pm 20\text{-}30\%$**
(can occasionally be larger or smaller for certain soot aerosol types)



➔ 100% counting efficiency (above lower detection limit; “no” upper limit for counting)

Lower detection limit of the SP2 for BC-containing particles



- **Lower detection limit for BC: $m_{rBC} \approx 0.3-1.0$ fg BC / $D_{BC} \approx 70-100$ nm** (“no” upper limit) (see Schwarz et al., 2010; Laborde et al., 2012).

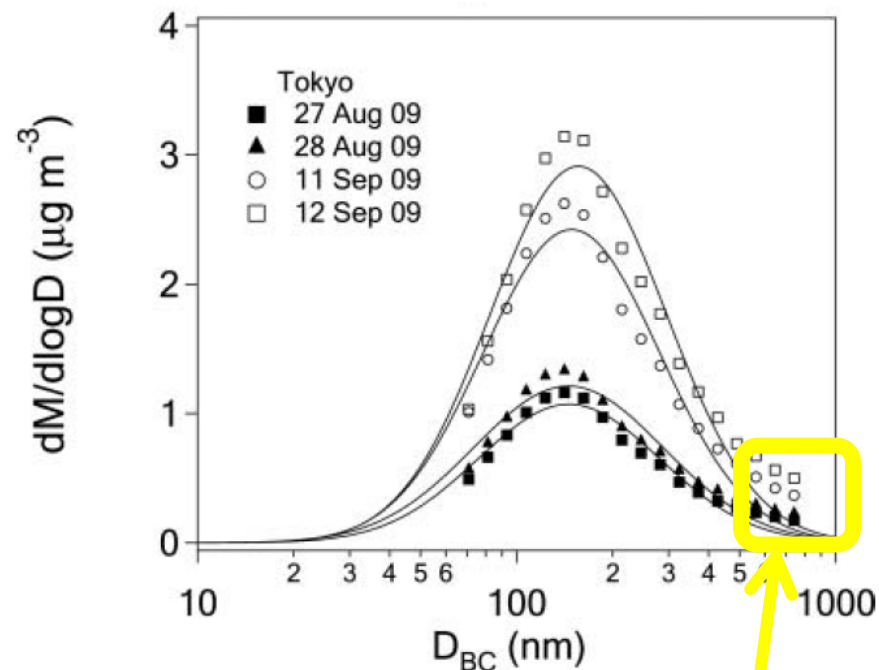
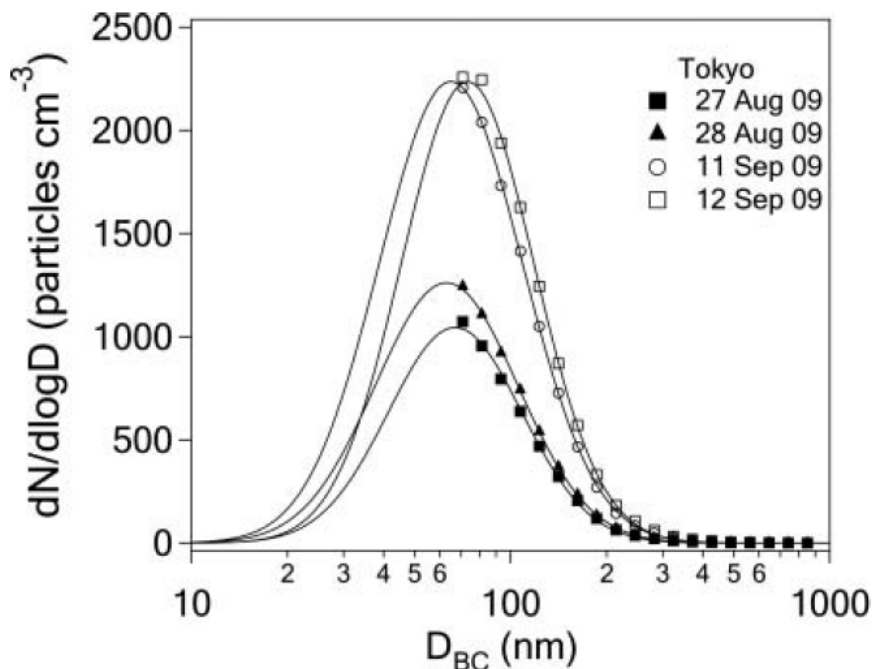
- **Careful preparation of SP2 is critical for detection of particles with small BC mass!**

- The above detection limit applies for sufficiently compact particles. **PALAS soot is not detected by the SP2 even at 2 fg BC per particle** due to its extremely low effective density! (Gysel et al., 2012).

Number

Example from Kondo et al., 2011

Mass



BC number size distribution:

- Mode diameter is near the lower detection limit of the SP2
 → more than ~50% of the particles are typically below the detection limit

BC mass size distribution:

- Mode diameter is typically around $D_{BC} \approx 150$ nm (between 100 nm and 200 nm)
 → dominant fraction of submicron BC mass falls within the detection limits of the SP2
 (this may not be true for fresh exhaust from efficient combustion sources)

Note: the upper detection limit is typically at $D_{BC} \approx 500 - 800$ nm, or even larger (depends on settings)

- «No» lower concentration detection limit (in the absence of leaks)
- Coincidence imposes upper concentration detection limit

Optical sizing:

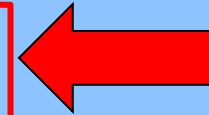
- Coincidence occurs at particle number concentrations above $\sim 1'000\text{-}3'000\text{ cm}^{-3}$ (with $D_{\text{opt}} > \sim 120\text{ nm}$) (this can be influenced within certain limits via instrument settings)

BC number concentration:

- Coincidence can be avoided up to at least $\sim 10'000\text{ cm}^{-3}$, when skipping the optical sizing
- When optical sizing is done, then the limit for optical sizing becomes relevant

BC mass concentration:

- Above coincidence limits translate to BC mass concentrations of $\sim 1\text{-}10\text{ }\mu\text{g m}^{-3}$
 ➔ **coincidence can become an issue in polluted environments**
- However, the bias due to coincidence is smaller for “BC mass” than for «BC number», as mostly small BC particles with negligible mass are lost



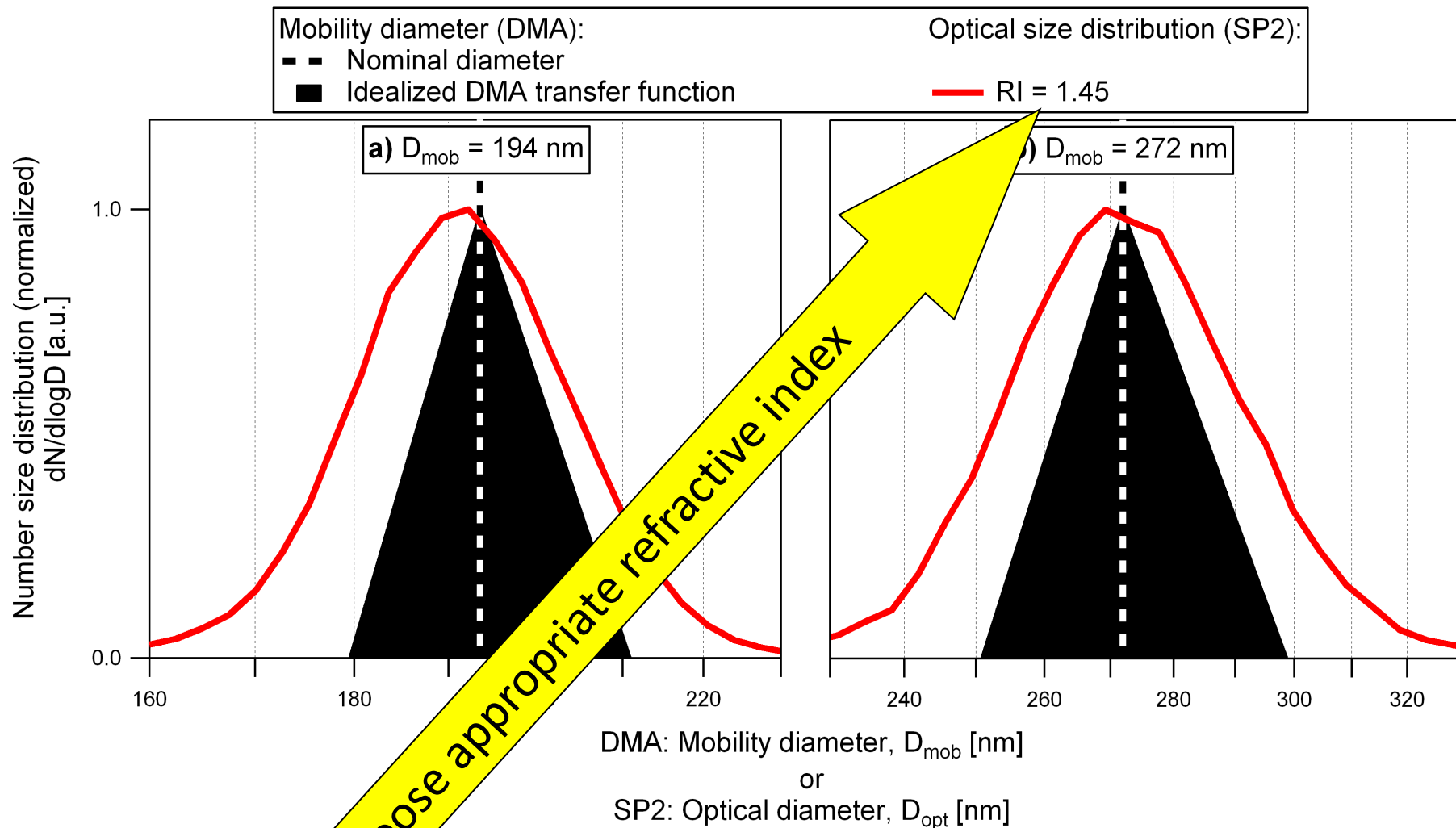
BC mixing state information:

- Coincidence is a critical issue for reliable mixing state measurements
 ➔ number concentration of particles above lower size detection limits of the SP2 must be kept below around $\sim 1'000\text{-}3'000\text{ cm}^{-3}$

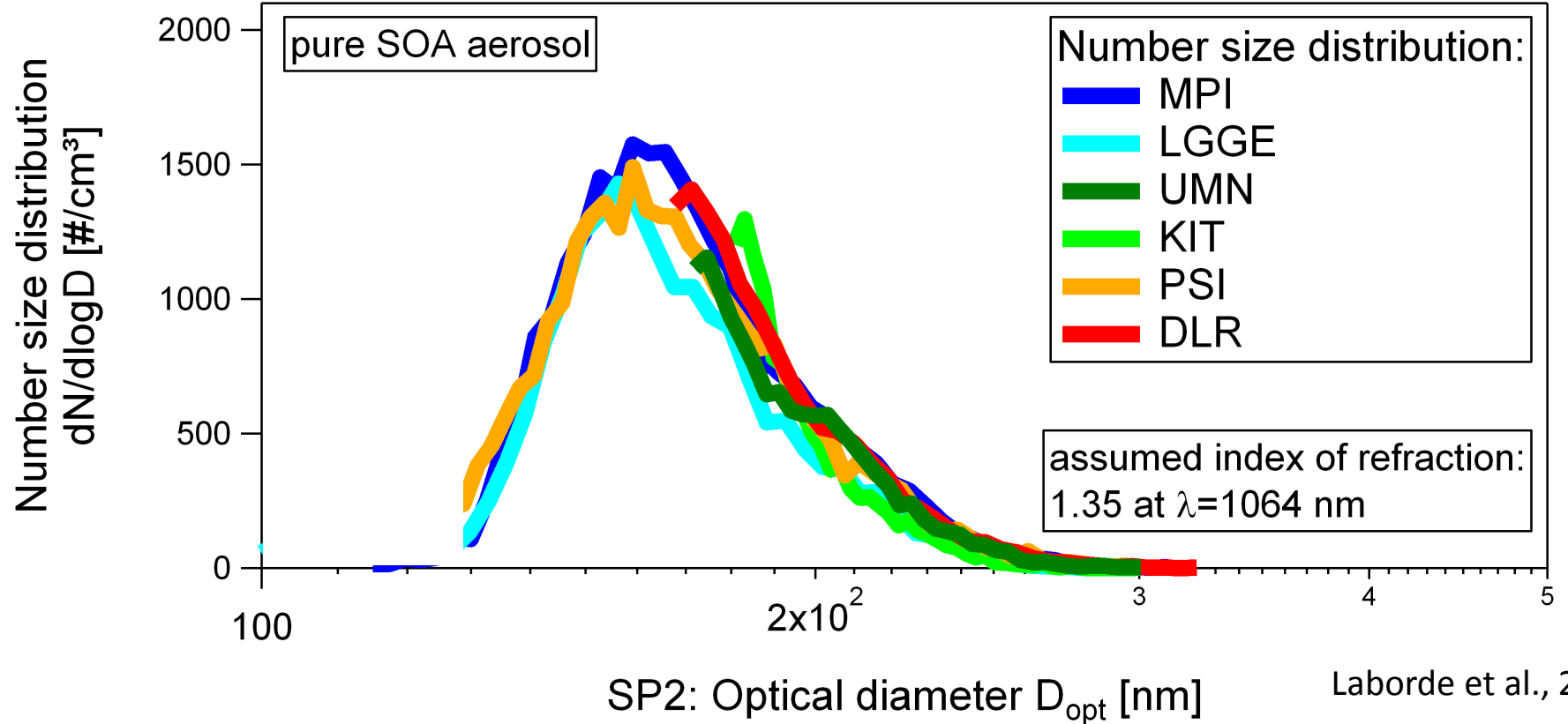
Note: these numbers are all just a very crude guess!

- **The elastically scattered laser light is used for optical sizing**
- **Absolute calibration** of measured (partial) scattering cross section is done **with certified PSL spheres** (only 1 size needed)
- **Mie theory for homogenous spheres** is used to infer optical diameters from measured scattering cross sections
 - ➔ **optical diameters are only meaningful when using appropriate index of refraction**
- Measurement of size-selected ambient aerosol can be used to determine the appropriate index of refraction

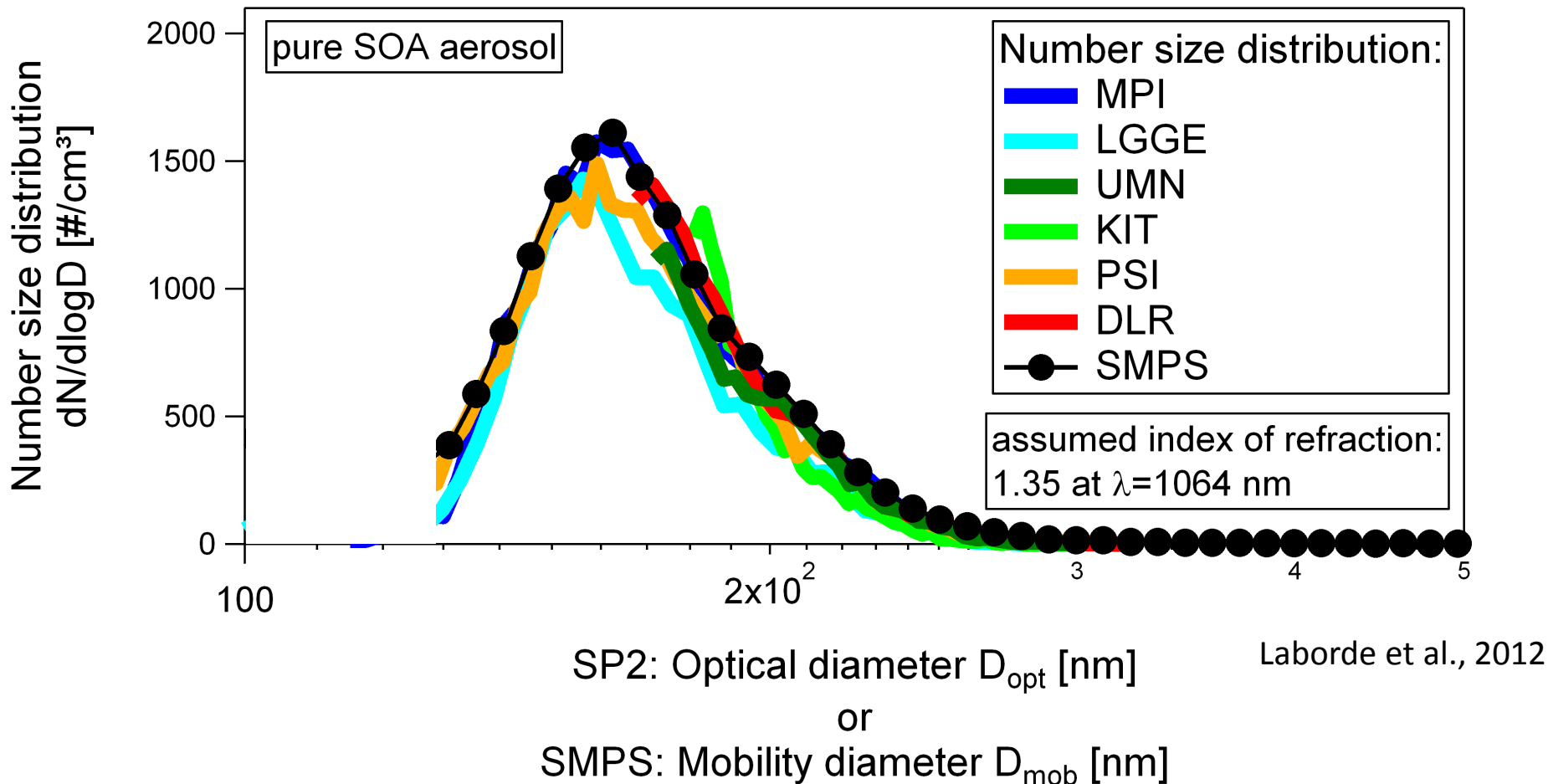
Optical sizing of BC-free particles: Comparison of SP2 with DMA (mobility diameter)



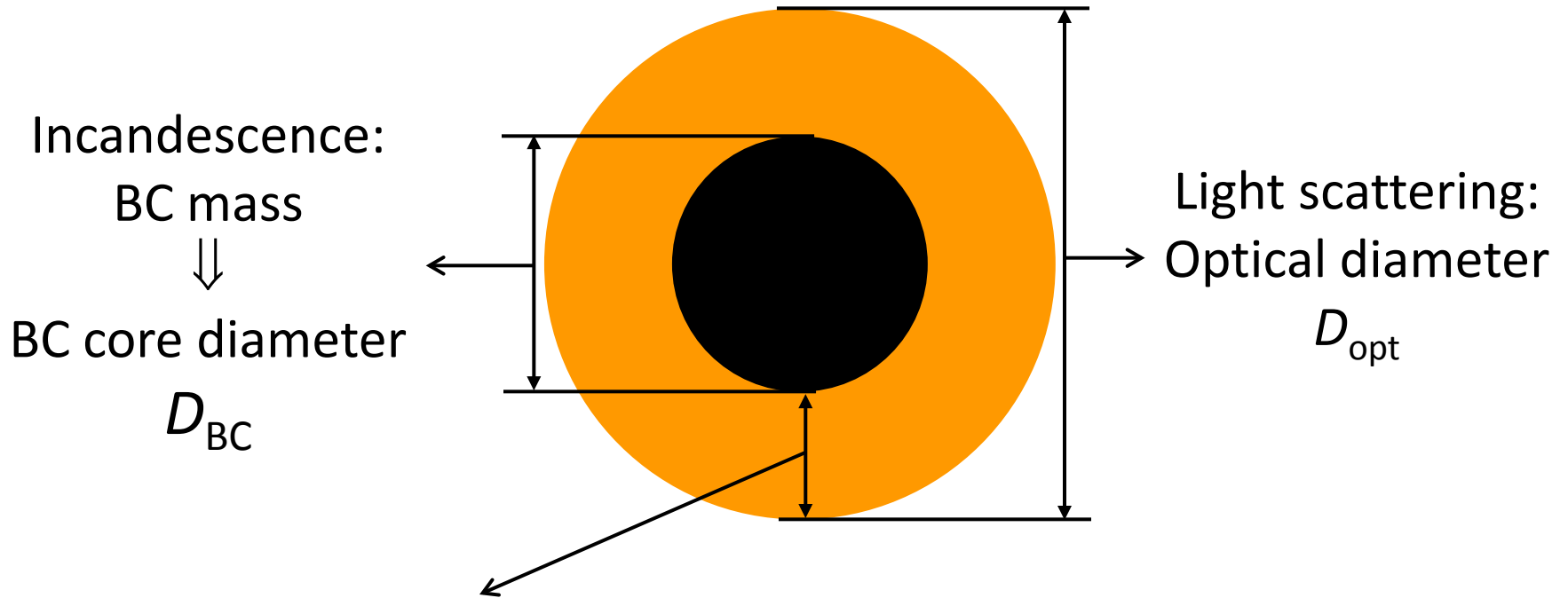
Example from Paris: Optical sizing by the SP2 agrees well with selected mobility diameter
 (in this case with assuming a refractive index of ~ 1.45 @ 1064 nm)



➔ SP2 instruments agree well with each other



➔ Good agreement between SP2 and SMPS (when using appropriate index of refraction)



Coating thickness

$$\Delta_{coat} = 0.5 (D_{opt} - D_{BC})$$

Methodology:

- Gao et al., Aerosol Sci. Technol., 2007
- Schwarz et al., Geophys. Res. Lett., 2008
- Moteki and Kondo. J. Aerosol Sci., 2008
- Laborde et al., Atmos. Meas. Tech., 2012

Spherical concentric core-shell morphology is assumed for inferring the coating thickness

laser intensity profile →

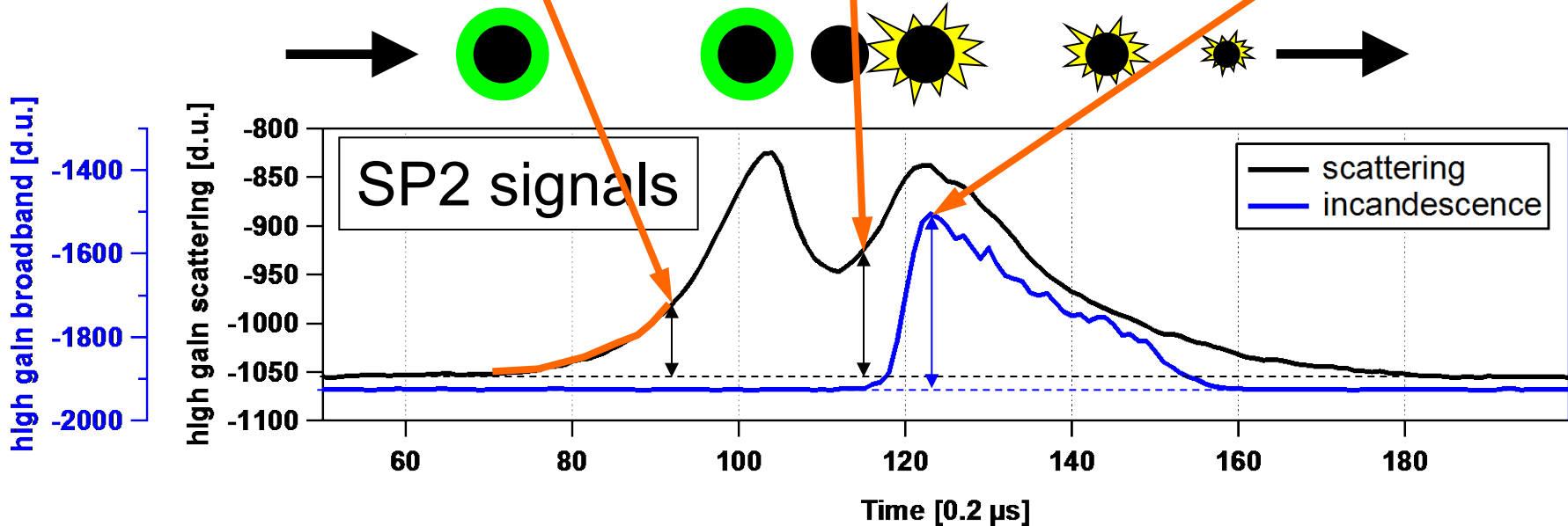


optical sizing of the bare BC core

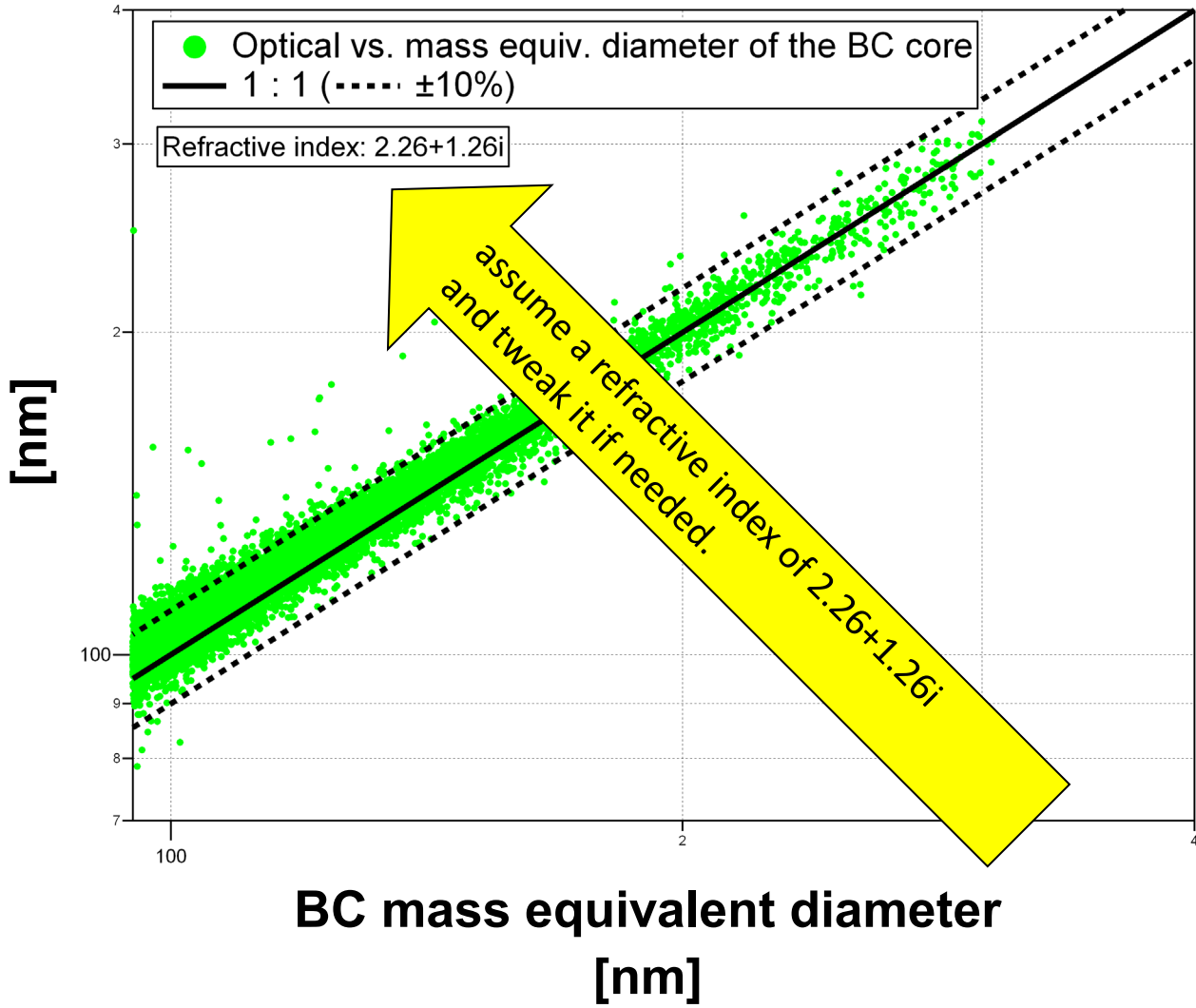
cross-check between mass and optical size of the bare BC core

optical sizing of total particle (LEO-fit)

BC mass measurement

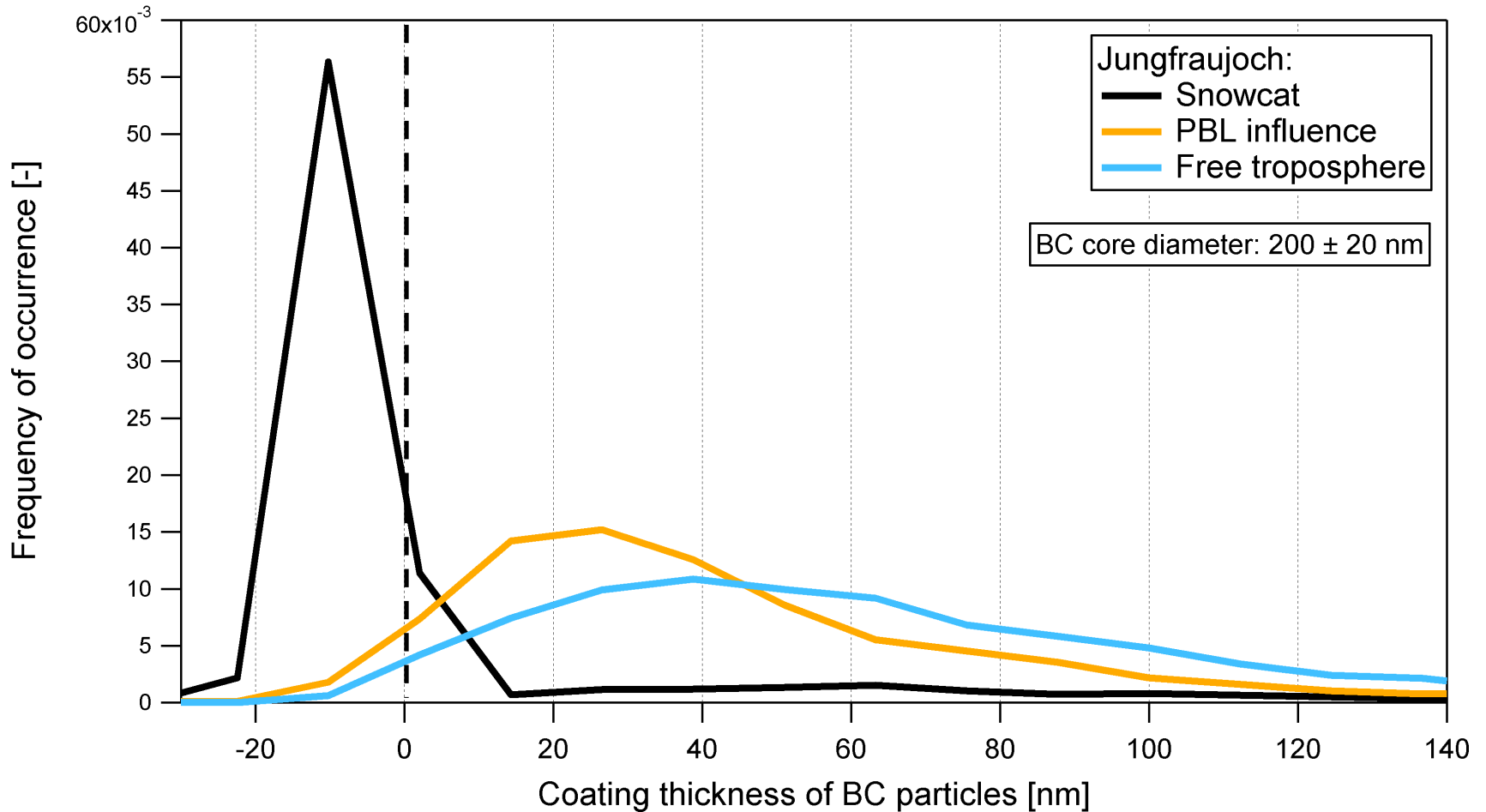


Optical diameter of the bare BC core
[nm]



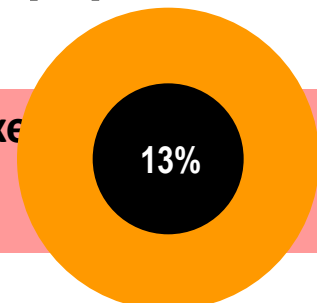
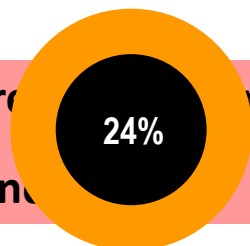
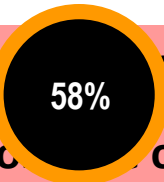
Excellent agreement between mass equivalent and optical diameter of the bare BC core
➔ this ensures correct coating thickness measurement for uncoated BC particles.

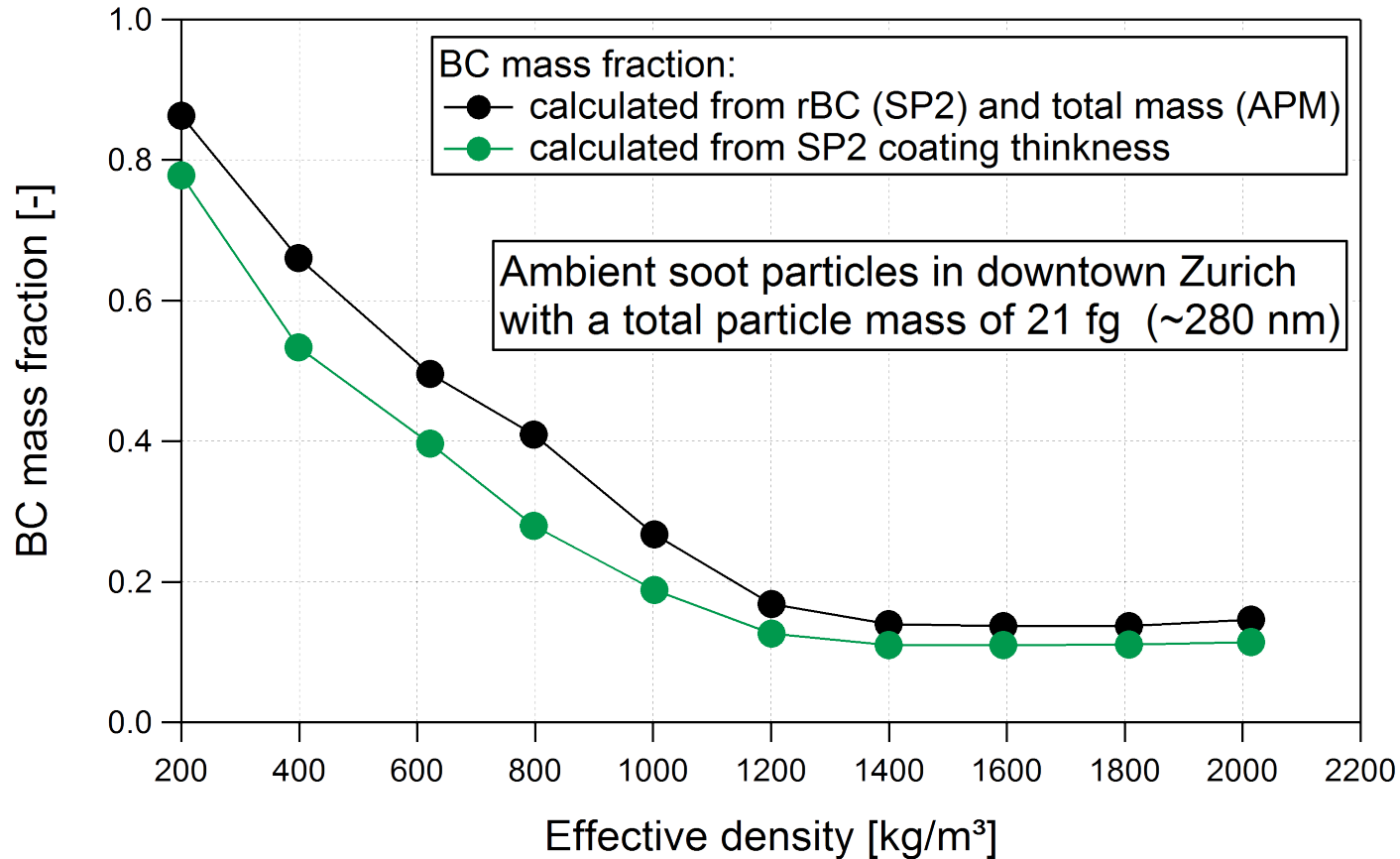
Histogram of BC coating thickness for different aerosols at the Jungfraujoch



→ Aged soot particles at the Jungfraujoch are mostly coated with soluble coatings.

→ Fresh diesel engine emissions often uncoated





➔ Good agreement for BC mass fraction calculated from SP2 coating thickness with that calculated with total particle mass taken from APM.

«BC» mass fraction of CAST soot determined with:

- **SP2** (calculated from measured coating thickness)
- **Sunset analyser** (thermal-optical method; NIOSH 5040)

| Date/time | $\varepsilon_{EC} \approx EC/TC$ Sunset | ε_{BC} SP2 |
|--------------------|--|---------------------------|
| 23 Nov. 2010 10:19 | 0.38 | Not available |
| 23 Nov. 2010 16:50 | 0.36 | 0.3 |
| 24 Nov. 2010 09:01 | 0.39 | 0.35 |

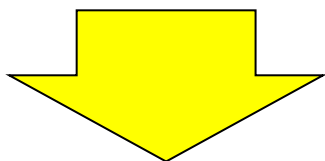
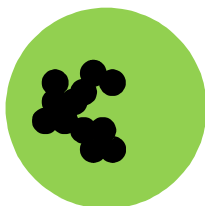
Laborde et al., 2012

➔ Good agreement for “BC” mass fraction determined with SP2 and Sunset analyser

Some BC-containing particles disintegrate into the incandescing BC core and a BC-free chunk when crossing the SP2 laser

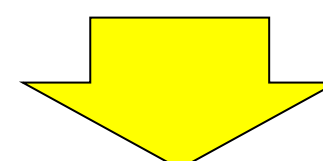
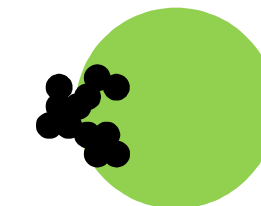
(Sedlacek III et al., 2012; Dahlkötter et al., 2014; Moteki et al., 2014)

BC core fully embedded in the «coating»



No disintegration (except for extreme coatings)
→ **complete (substantial) coating evaporation**

“BC core” attached to the «coating»



BC disintegrates from «coating» in the SP2 laser
→ **almost no evaporation of the coating**

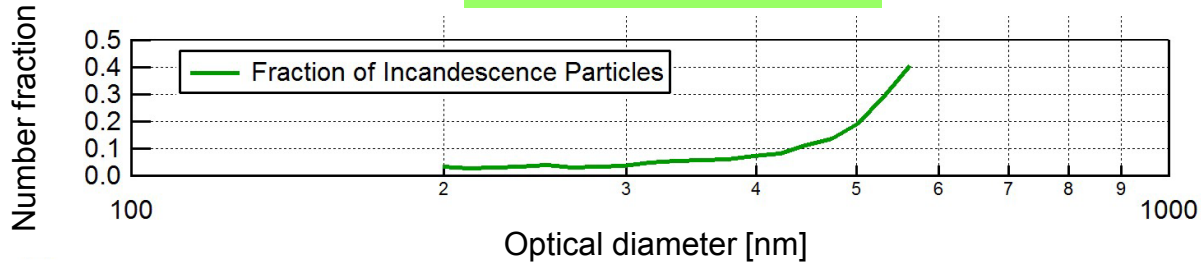
Shown by Moteki et al., 2014

→ The SP2 makes it possible to distinguish between these two morphologies.

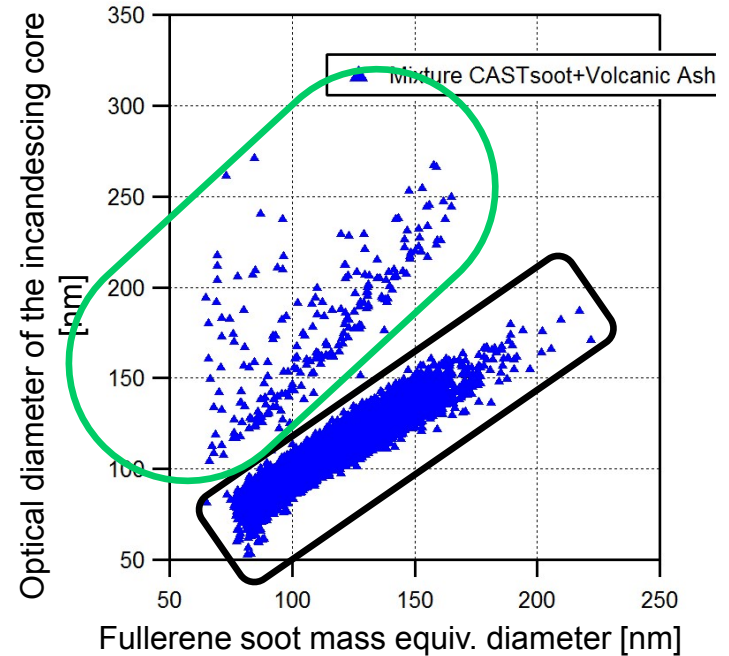
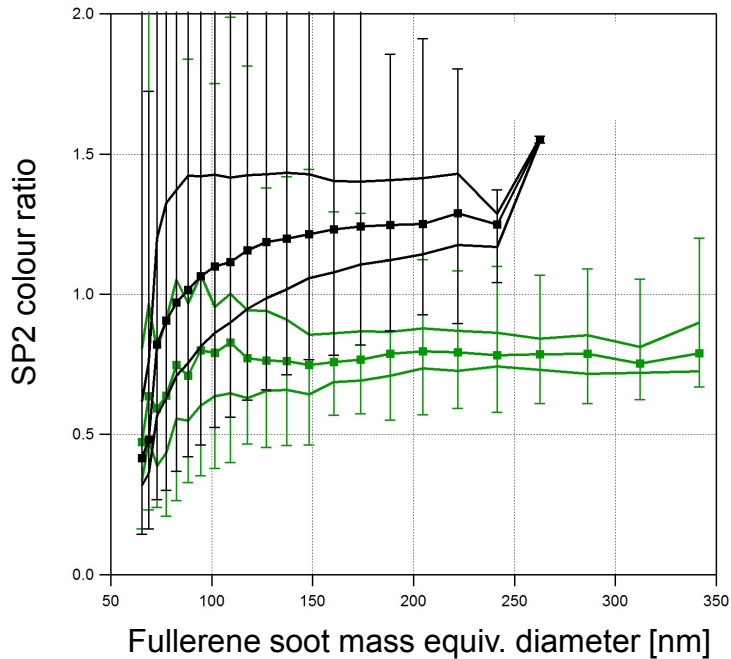
Interference from other incandescing particle types

Highly refractory and moderately light-absorbing materials can also incandesce in the SP2 laser:
 → potential interference from metals, volcanic ash, hematite (in pure form), dust (rarely), ...

Example: volcanic ash

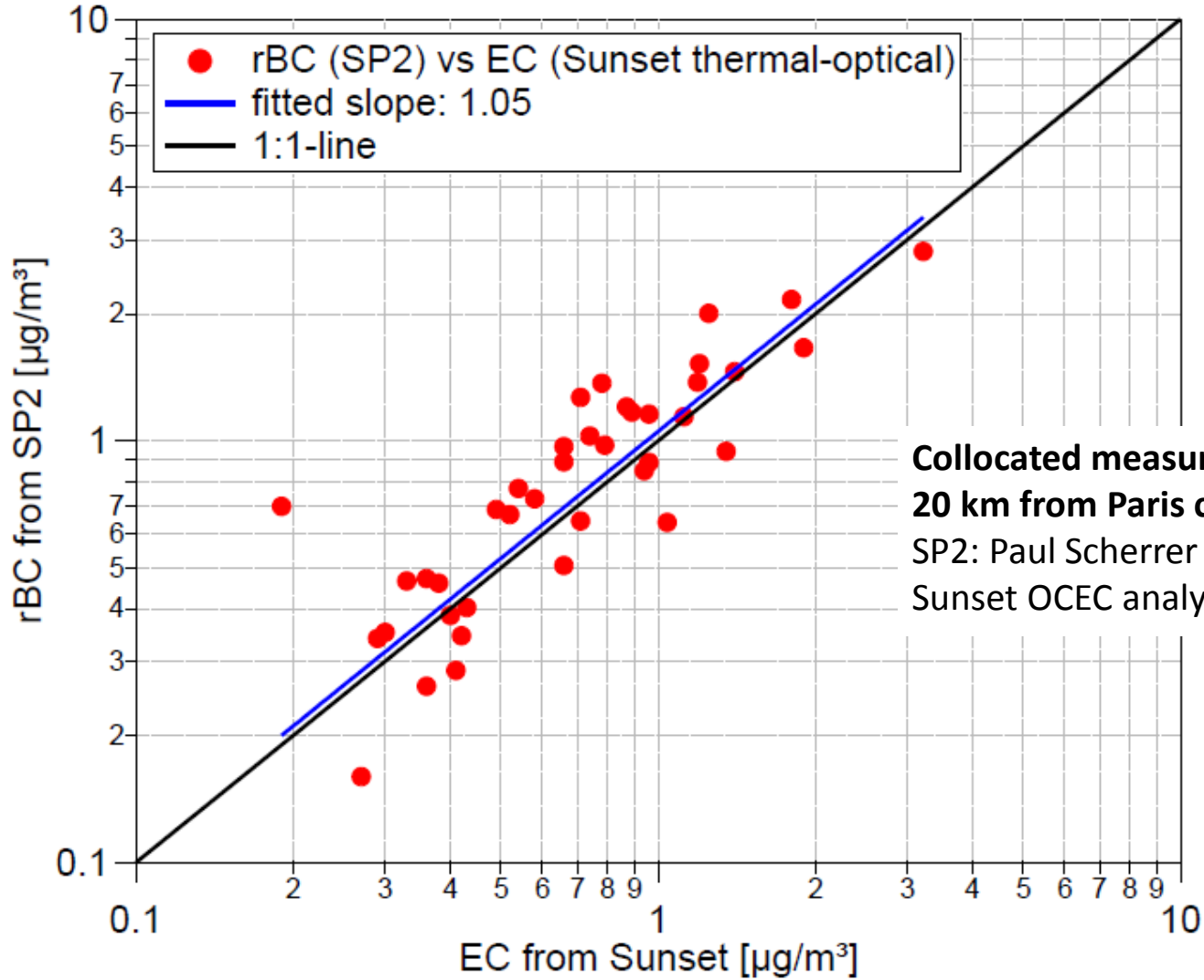


Heimerl et al., in prep.



→ It is possible to distinguish BC particles from other incandescing particles.

Comparison between SP2 rBC and Sunset EC (thermal-optical method)

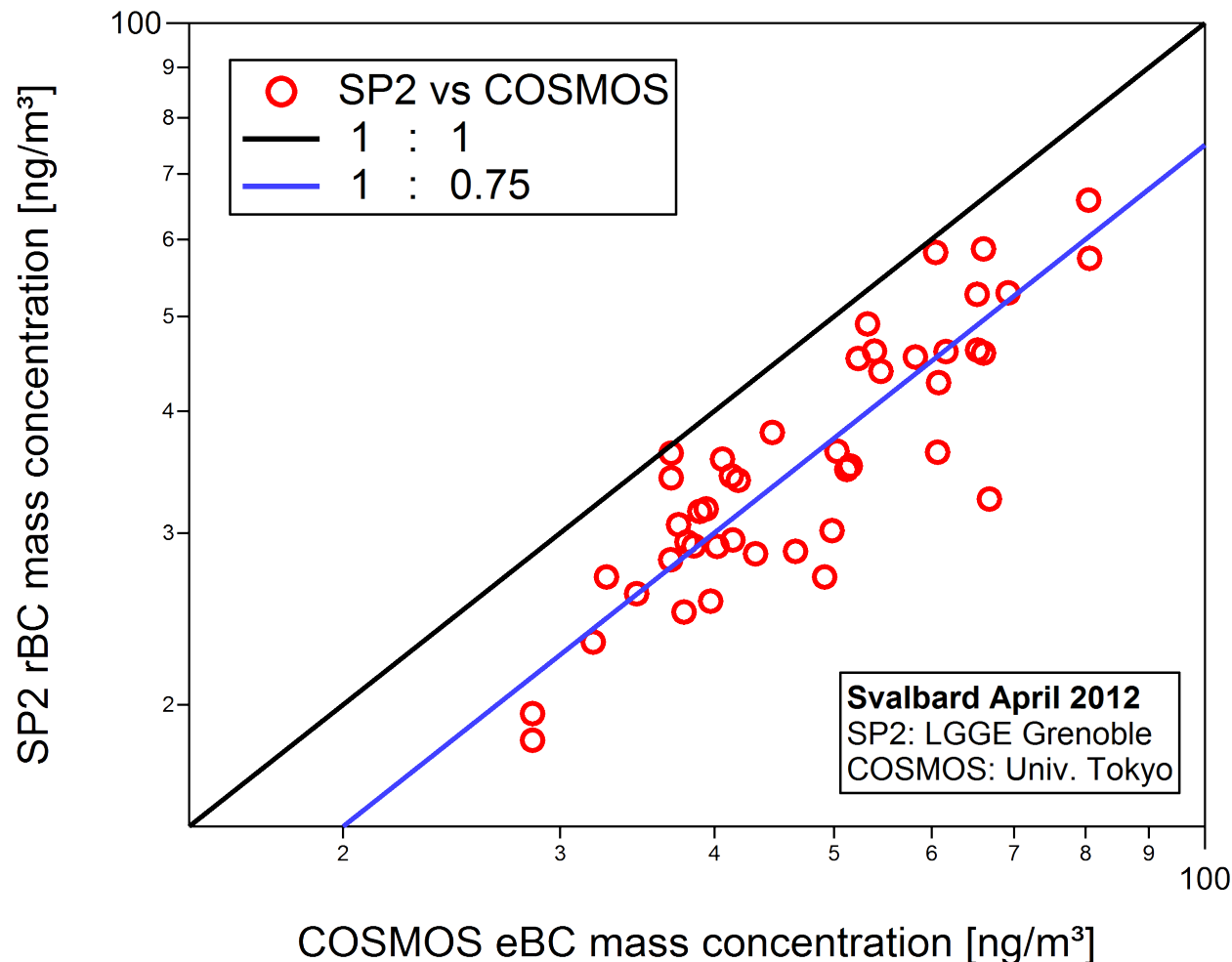


**Collocated measurements at SIRTA site,
20 km from Paris city centre**
SP2: Paul Scherrer Institute
Sunset OCEC analyser: LGGE Grenoble

Laborde et al., 2013

**SP2 and Sunset OCEC analyzer (EUSAAR II protocol) agree within 5% on average
→ this is well within the uncertainty of either method**

Comparison between SP2 and COSMOS (independently calibrated)



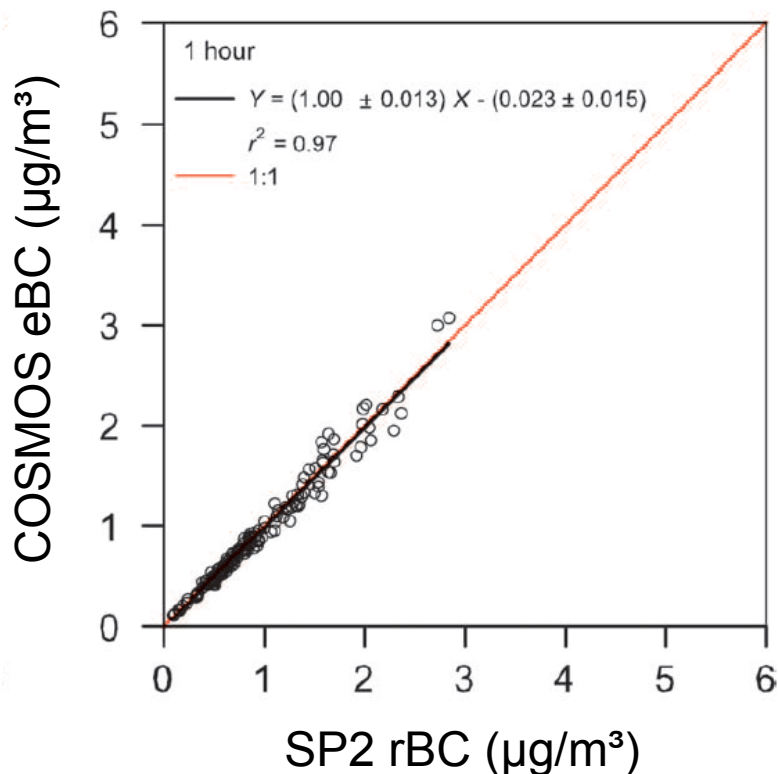
(see Miyazaki et al., 2008,
for COSMOS description)

Zanatta et al., in prep.

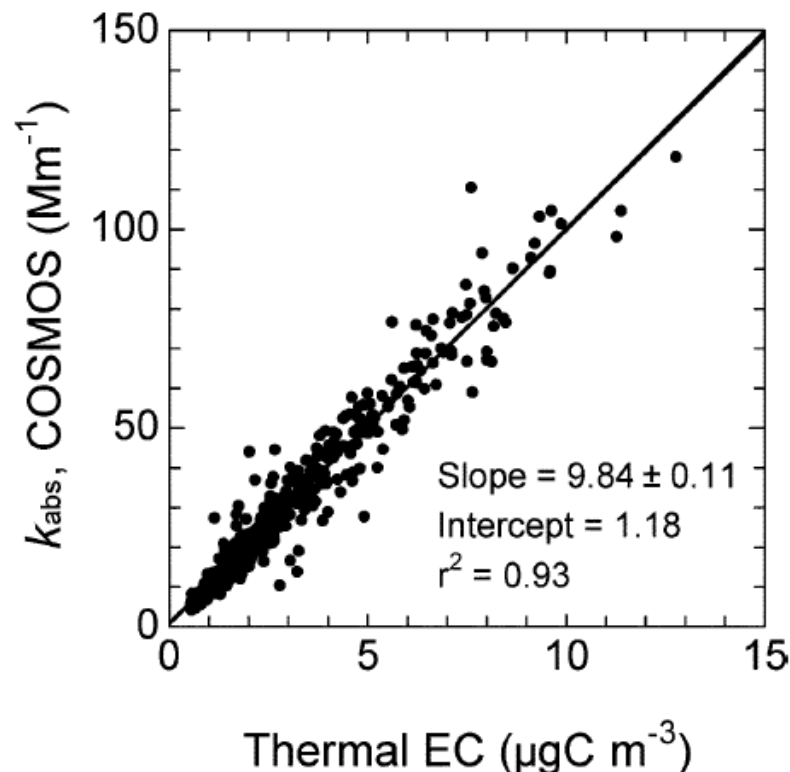
SP2 (rBC) is ~25% lower than COSMOS (eBC)

➔ this is just about within experimental uncertainty, given independent calibration

COSMOS vs SP2
(Kondo et al. 2011)

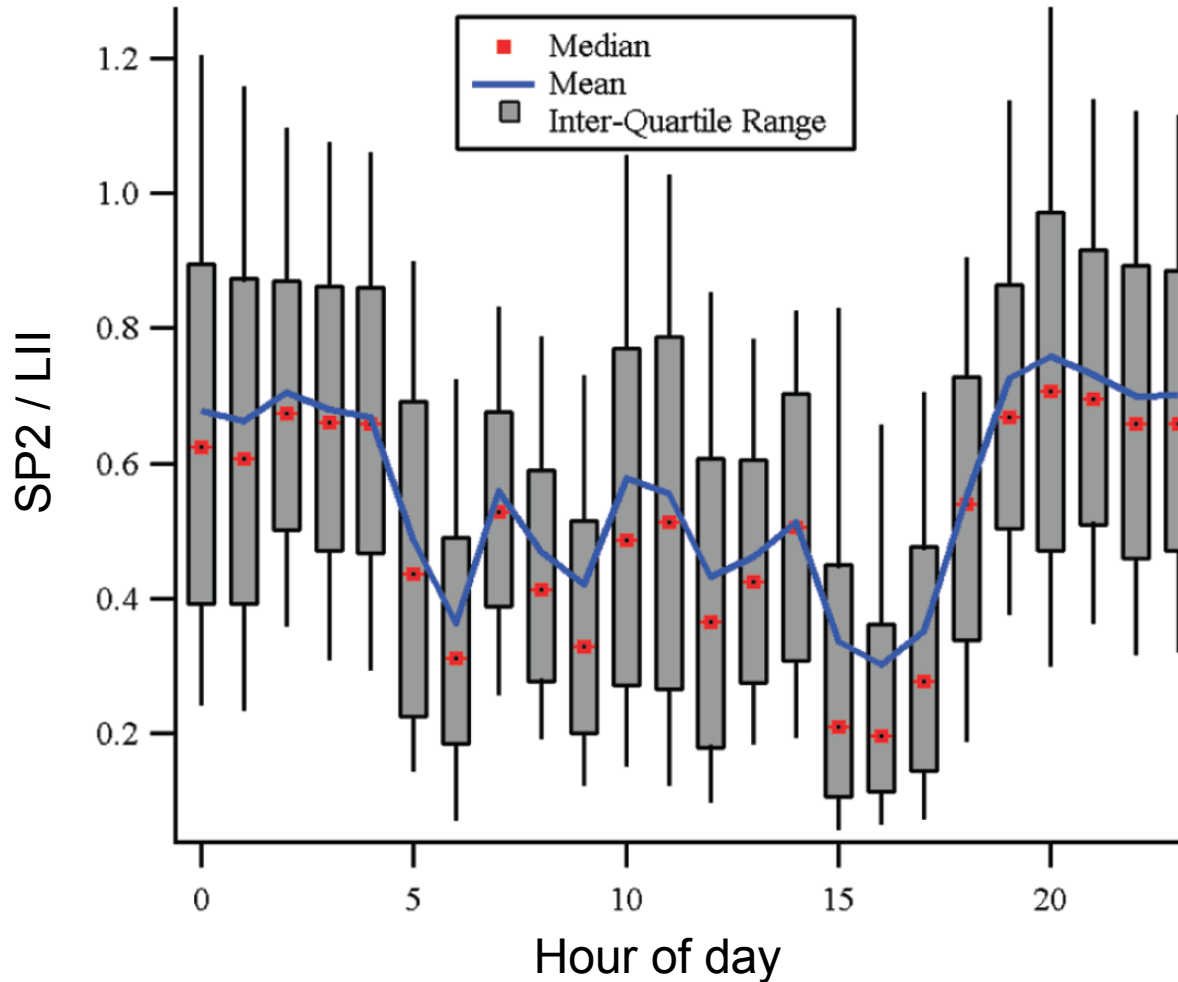


COSMOS vs EC (thermal-optical method)
(Miyazaki et al., 2008)



Consistent results can be achieved between SP2 (rBC), thermal-optical method (EC) and COSMOS (eBC; needs calibration against rBC or EC) (Kondo et al., 2011)

➔ These quantities are more similar than what one might expect!



Liggio et al. 2012

The SP2 measurement is significantly below that of the time-resolved LII instrument!?

- ➔ Part of it may be attributed to small BC cores below SP2 detection limit
- ➔ Did coincidence cause additional problems for the SP2 measurement?
- ➔ Appropriate SP2 calibration?

- **The SP2 is a highly sensitive instrument that provides additional insight into BC mixing state and morphology.**
- **The SP2 is rather for expert use than a simple “plug & play” instrument.**
- **rBC, EC and COSMOS-eBC are more similar than what one might expect.**
(or “systematic differences between these quantities might be as small as differences between multiple users of the same method”).