Strengths and Limitations of the Single Particle Soot Photometer (SP2)

Black Carbon (BC) in Paris

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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.](image-url)
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.

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.
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.

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References


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

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Single Particle Soot Photometer (SP2)

Nd:YAG laser
\[ \sim 3 \text{ MW/cm}^2 \]
[\lambda = 1064 \text{ nm}]

PMT

APD

detection of incandescent light \( \Rightarrow \) BC mass

detection of scattered light \( \Rightarrow \) optical sizing

SP2 specifications

Strengths of the SP2:
- Quantitative detection of BC in single particles
- 100% detection efficiency* (*above the lower detection limit)
- 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 ($D_{BC} \approx 70-100$ 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

Manchester, UK

Growth factor distribution:
- all particles (CPC)

Adapted from: McMeeking et al., ACP, 2011

Hygroscopic growth factor at RH=90% [-]

GF-PDF [-]

0.0 1.0 2.0 3.0 4.0 5.0 6.0

0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2

fresh emissions aged background aerosol
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.

Adapted from: McMeeking et al., ACP, 2011
Aerosol measurements in Paris (MEGAPOLI project)

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

westerly

continental
Distinct peaks in diurnal cycles of BC are from traffic emissions.
• 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.
Hygroscopic properties of the aerosol

- Background aerosol is strongly hygroscopic
- Traffic emissions are non-hygroscopic
- Biomass burning emissions are slightly hygroscopic

GF-PDF [-]

Growth factor probability density function

Hygroscopic Growth factor, GF [-] (RH = 90%)

D₀ = 265 nm
Hygroscopicity of BC particles

Growth factor distribution

Paris

D = 265 nm

Hygroscopic growth factor at RH=90% [-]

HTDMA
CPC
SP2

Paris in winter
≠
Manchester in summer

Adapted from: McMeeking et al., 2011

Manchester, UK

Hygroscopic growth factor at RH=90% [-]

all particles
BC particles

Adapted from: McMeeking et al., 2011
Hygroscopicity of BC particles

![Graph showing growth factor distribution and number fraction of particle types at RH=90% for all particles and 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

**Legend:**
- HTDMA
- CPC
- SP2

**Graph:**
- Growth factor distribution:
  - All particles
  - BC particles
  - D = 265 nm
- Number fraction of particle types:
  - Hygroscopic growth factor at RH=90% [-]
Coating of BC particles

Growth factor distribution:
- all particles
- BC particles

D = 265 nm

Number fraction of particle types:

mean coating thickness of BC particles:

Hygroscopic growth factor at RH = 90% [-]

- 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 Swiss National Science Foundation

And last but not least:

- Thank you for your attention!
SP2 signals of a coated BC particle

- Particle heats up
- BC core evaporates
- BC reaches boiling point

Flight path of the particle:
- Optical sizing from elastically scattered light
- BC mass from peak of thermal radiation (laser-induced incandescence)

Laser intensity profile
SP2 calibration for BC mass

SP2 is about 35% more sensitive to Aquadag and fullerene soot

⇒ What about the sensitivity to atmospheric BC?
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)
Lower detection limit: ~0.3-1.0 fg BC ($D_{BC} \sim \text{70-100 nm}$) (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

Good agreement between all SP2’s \(\Rightarrow\) precise and reproducible method

Laborde et al., AMTD, 2012
Reproducibility of optical sizing

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

Laborde et al., AMTD, 2012
Ångström exponent of absorption is consistent with traffic influence during daytime and wood burning influence during nighttime.
Particle number concentration

Number concentration [#/cm³]

SP2:
- all detected
- BC containing (D_{core} > 80 nm)
- purely scattering

SMPS:
- CN_{>140nm} (SP2 size range)
- CN_{>20nm} (all particles)

Date [DD/MM]
Calculation of BC mass from organic aerosol components

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

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

\[ \Rightarrow \] 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

Growth factor distribution

Number fraction of particle types

Coating thickness [nm]

Hygroscopic growth factor at RH=90% [-]
Coating thickness: traffic < biomass burning < aged
Successful hygroscopicity-CCN closure:

⇒ $\kappa$-Köhler theory describes the CCN activation behaviour well across the whole investigated 3-dimensional parameter space $D_{\text{dry}}$-SS-GF!
SP2 specifications

Strengths of the SP2:

• Quantitative detection of BC in single particles
• 100% detection efficiency* (*above the lower detection limit)
• BC mass measurement is independent of particle mixing state.
• Optical sizing provides semi-quantitative information on the mixing state of individual BC particles.

⇒ extremely sensitive

Limitations of the SP2:

• Lower detection limit: ~0.3-1.0 fg BC per particle \(D_{BC} \approx 70-100 \text{ nm}\)
• Coincidence problems can already occur at atmospheric particle number concentrations (polluted locations).
• Not really a “plug and play” instrument
Single Particle Soot Photometer (SP2)

Incandescence: ~630-800 nm

High reflectivity mirror

Incandescence: ~350-800 nm

Nd:YAG crystal lasing at 1064nm

Pump Diode

Optical filters

Scattered light - high gain

Avalanche photodetectors

Scattered light - low gain

Figure: Gao et al., Aerosol Sci. Technol., 2007.
Experimental setup

Air conditioned trailer

HTDMA

CPC

SP2

HR-ToF-AMS

SMPS

Aethalometer

Other instruments

PM$_{10}$ sampling inlet
Experimental setup

Air conditioned trailer

HTDMA → CPC → SP2

HR-ToF-AMS

SMPS → Aethalometer → Other instruments

PM$_{10}$ sampling inlet
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

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

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.
Calculation of BC mass from organic aerosol components

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Diurnal cycles

- BC mass concentration
- Number fraction of BC* particles ($n_{BC}/n_{CN}$)
  - *only BC cores >80 nm
- Hydrocarbon-like organic aerosol (HOA)
- Number fraction of non-hygroscopic* particles
  - *GF<1.05

Biomass burning organic aerosol (BBOA)

Ångström exponent of absorption

Time of day [h]
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