Obtaining the mixing state of black carbon using the CPMA-SP2 method; from concept to the field

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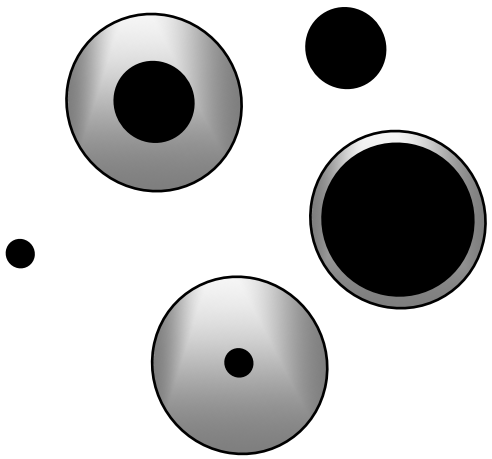
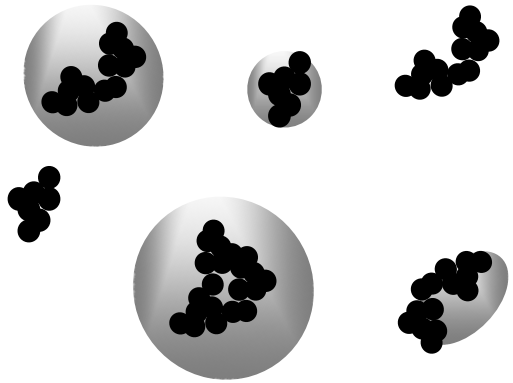
Black Carbon Mixing State

- Even freshly emitted black carbon (BC) is likely to have a coating of semi-volatile, non-BC material
- The “mixing state”, describes what fraction of the aerosol comprises non-BC material
- Typical treatment of the situation is to use a core/shell model

CORE/SHELL MODEL



REALITY?



Current equipment – new method

Centrifugal Particle Mass Analyzer (CPMA)

Principle: Mass:charge selection

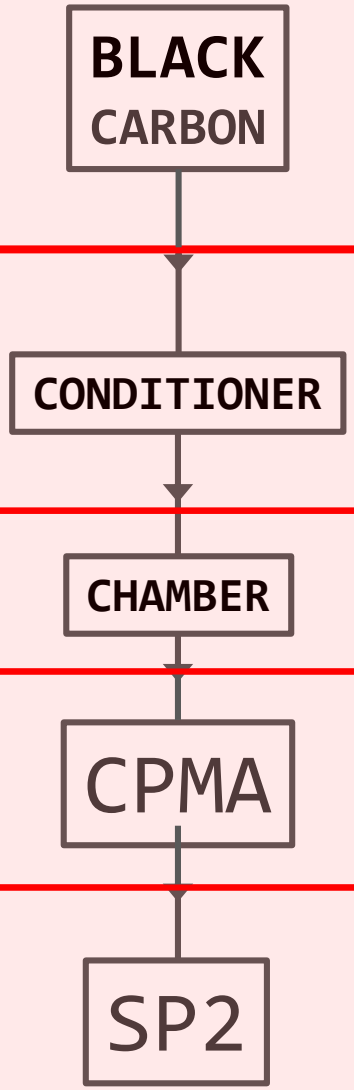
Data product: Total bulk particle mass (M_P)

Single Particle Soot Photometer (SP2)

Principle: Laser-induced incandescence (LII)

Data product: Single particle Black Carbon mass (M_{BC})

The coupled CPMA-SP2



- Inverted methane burner
- Polydisperse BC aerosol
- Very little non-BC material

- Dilution stage
- Dryer
- Thermal denuder x2
- Activated Carbon

- Teflon bag
- Photo-oxidation with p-xylene

- Step-scanned from 0.3 fg to 30 fg
- Total particle mass
- Monodisperse* aerosol

- Single-particle BC mass

*multiply charged

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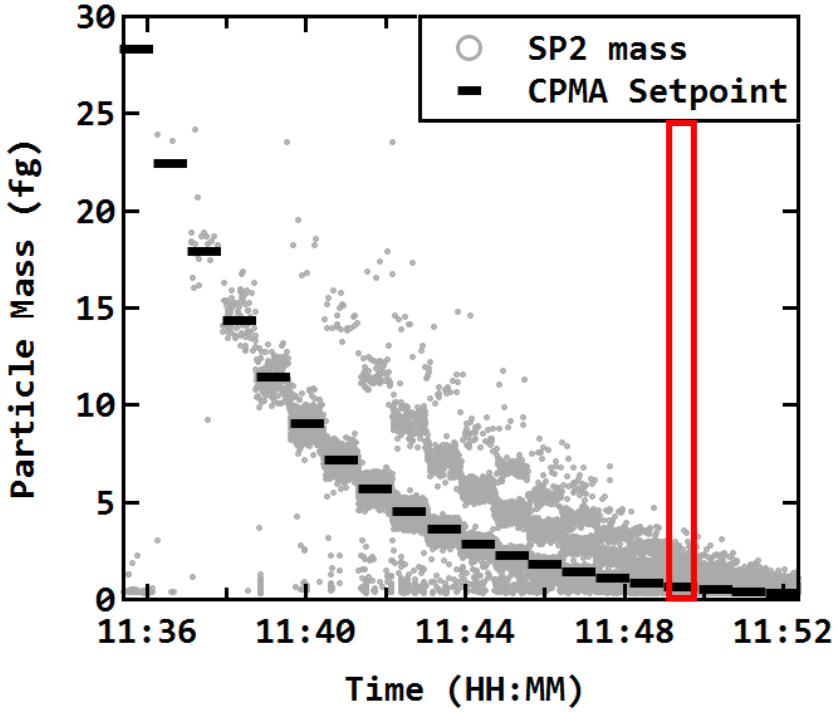
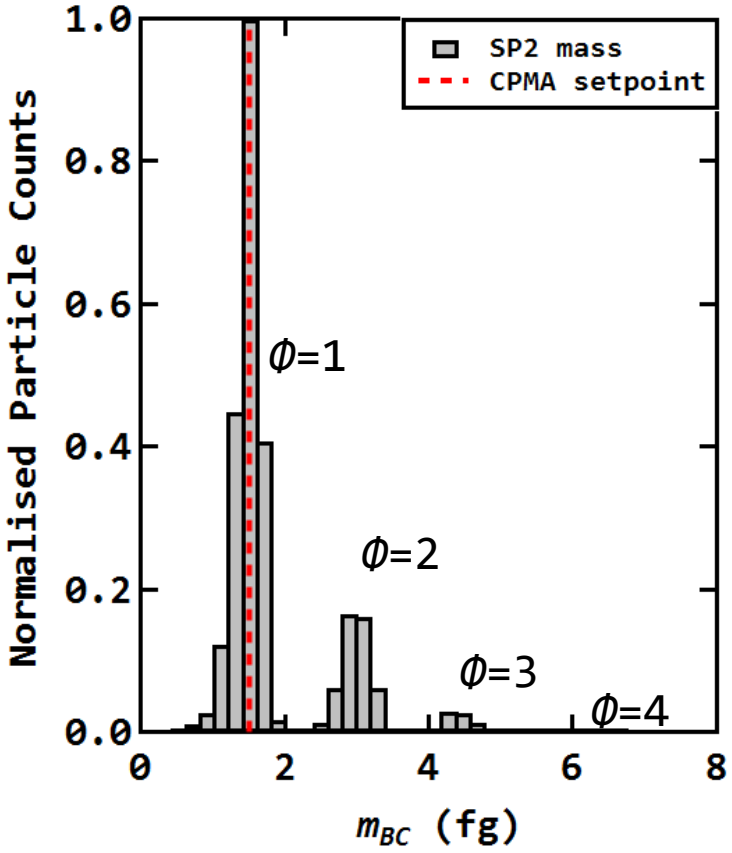
Uncoated Black Carbon

- 30 fg to 0.3 fg
- Multiply charged particles easily identified ($\phi = n$)
- Analogous to calibration of SP2





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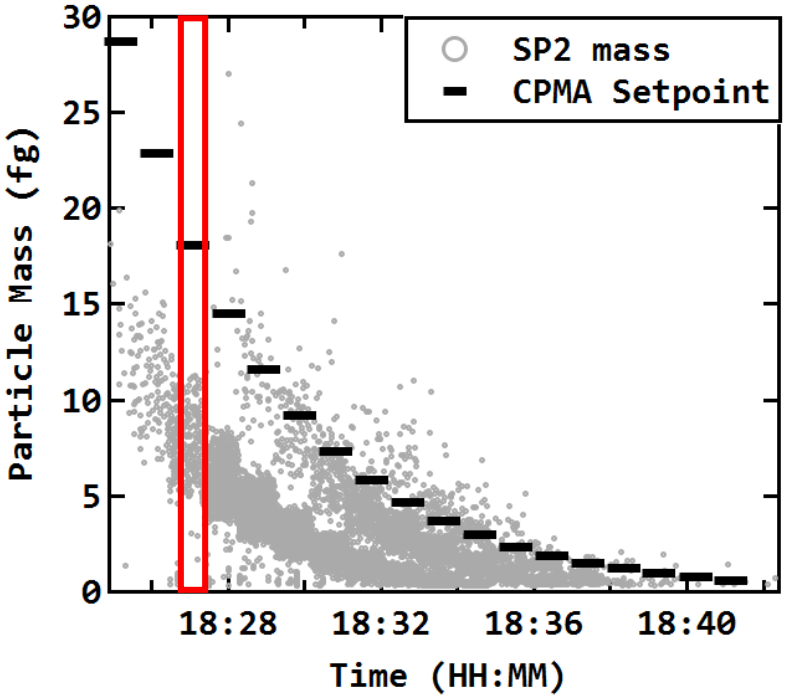
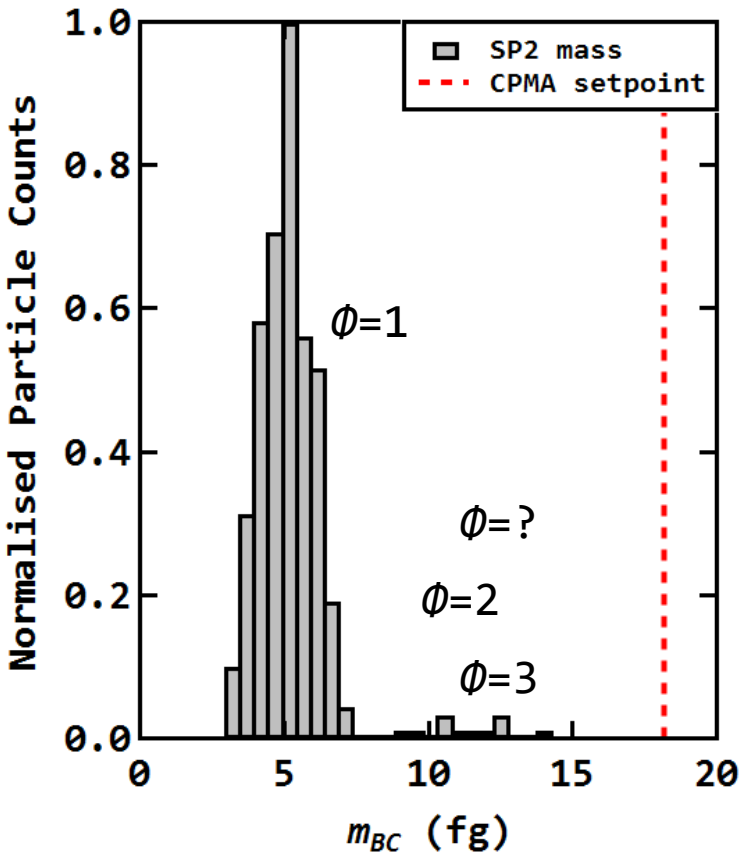
Coated Black Carbon

- 60 fg to 0.6 fg
- Multiply charged particles difficult to identify
  - Distribution recovered with deconvolution
  - Fredholm integral equations





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BC mixing state

- Previous studies typically derive coating thickness
- However, as BC is highly fractal, semi-volatile “coating” is likely to fill voids and ”process” BC
- For the first time, the mass of non-BC material can be directly and accurately measured:

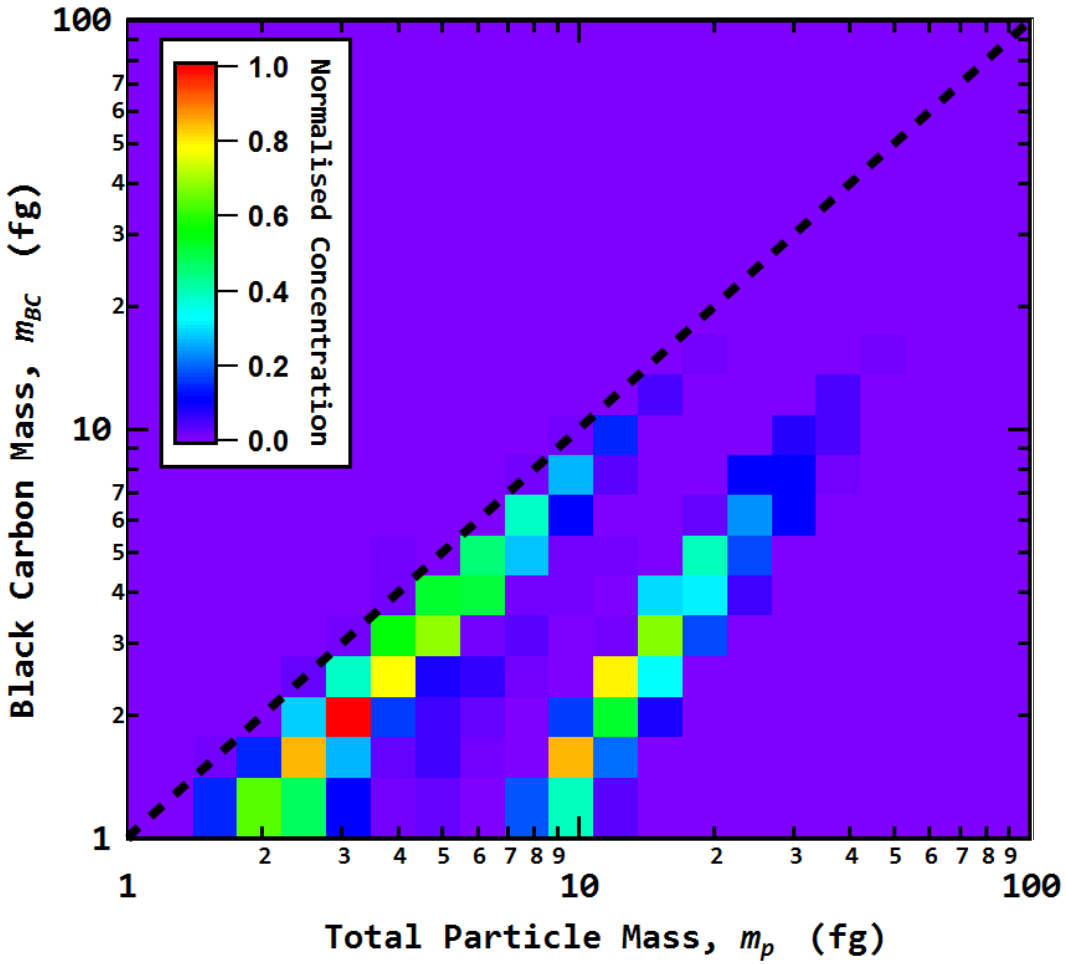
$$M_{COATING} = M_{CPMA} - M_{SP2} \quad \boxed{= M_P - M_{BC}}$$

- Double integration results in both the total mass and BC-mass concentrations, as a two-variable number distribution

e.g.:

$$\frac{\mathrm{d}M}{\mathrm{d}\log m_{rBC}} = \int_0^{\infty} \frac{\partial^2 N}{\partial \log m_p \, \partial \log m_{rBC}} m_p \, \partial \log m_p$$

Two-Variable Number Distribution



- Uncoated, bare BC

  $M_p = M_{BC}$

- BC coated with p-xylene oxidation products over a number of hours

  $M_p > M_{BC}$

- Fresh BC injected into chamber, co-existing with coated BC

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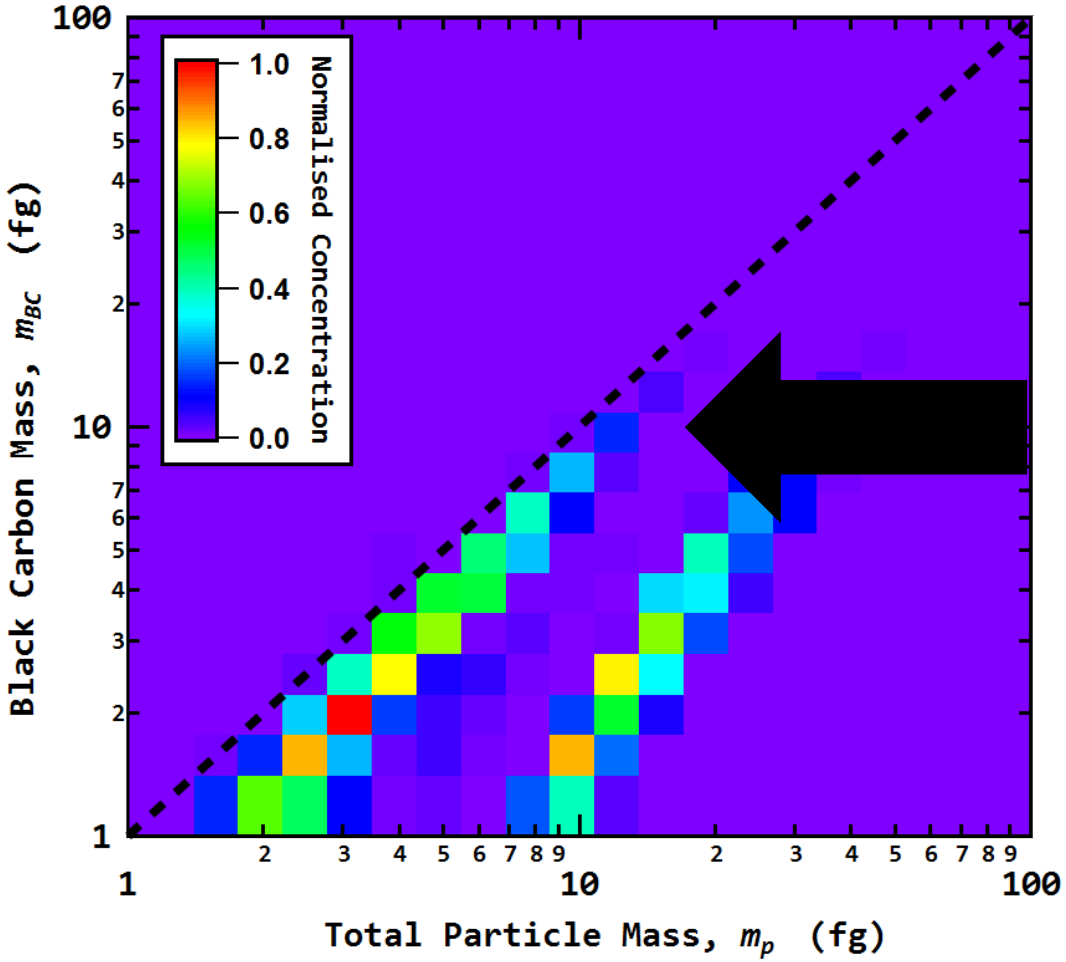
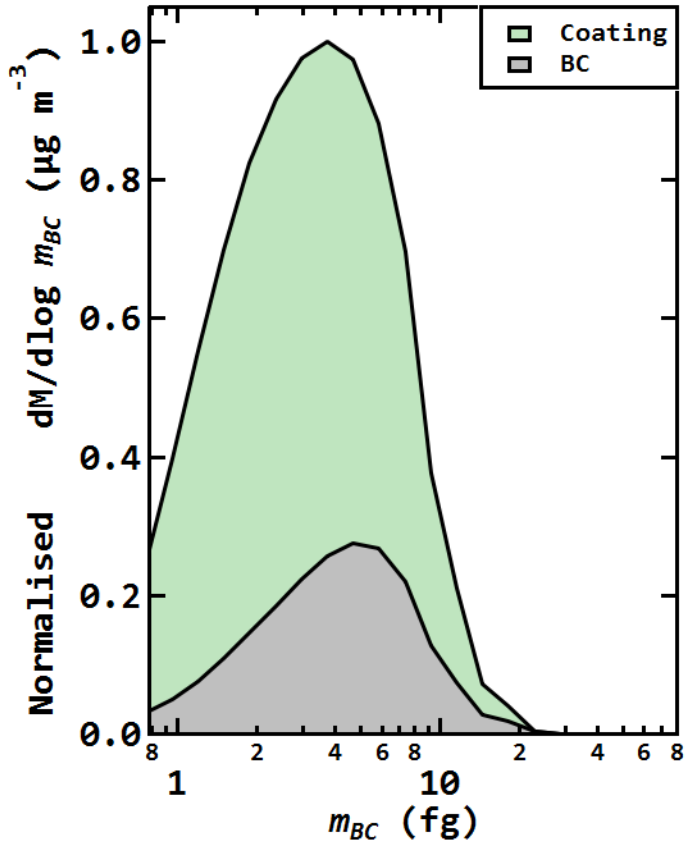
BC mass distributions



Coating mass on black carbon particles



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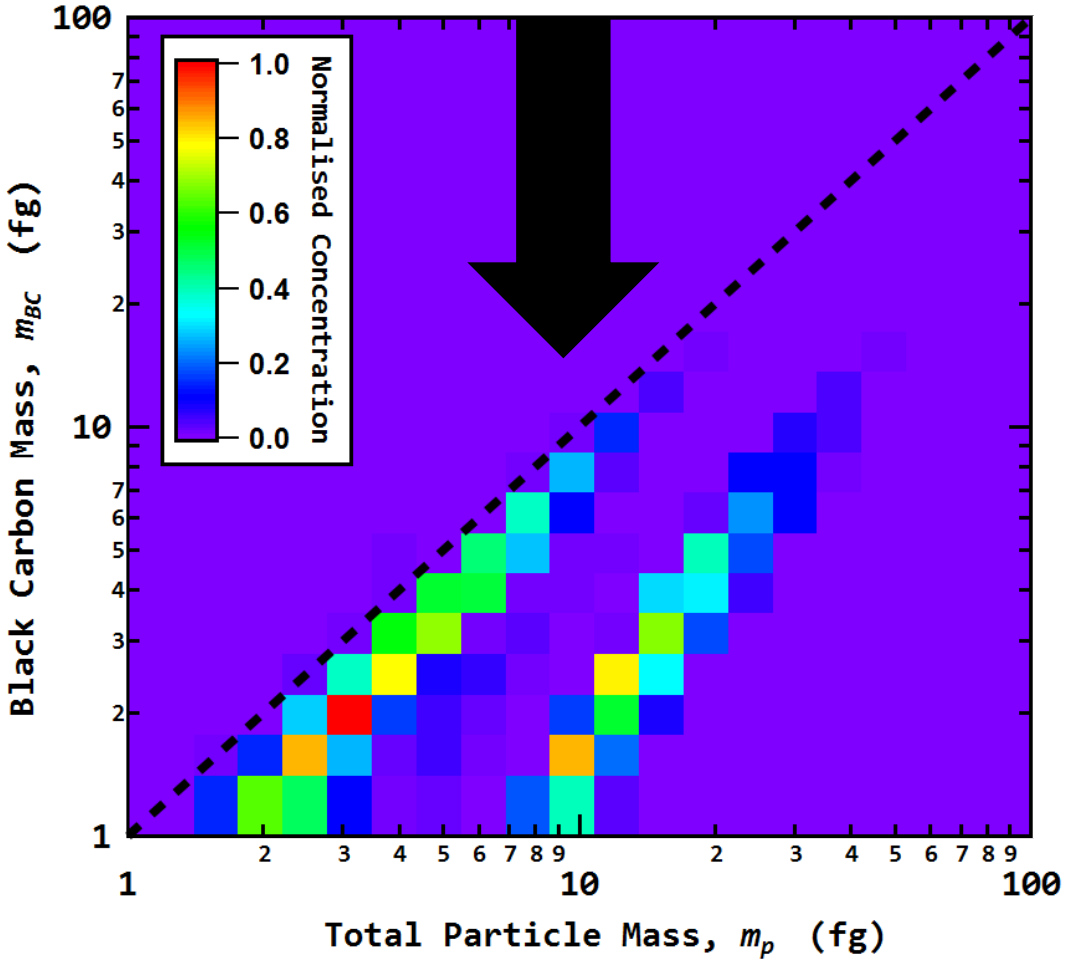
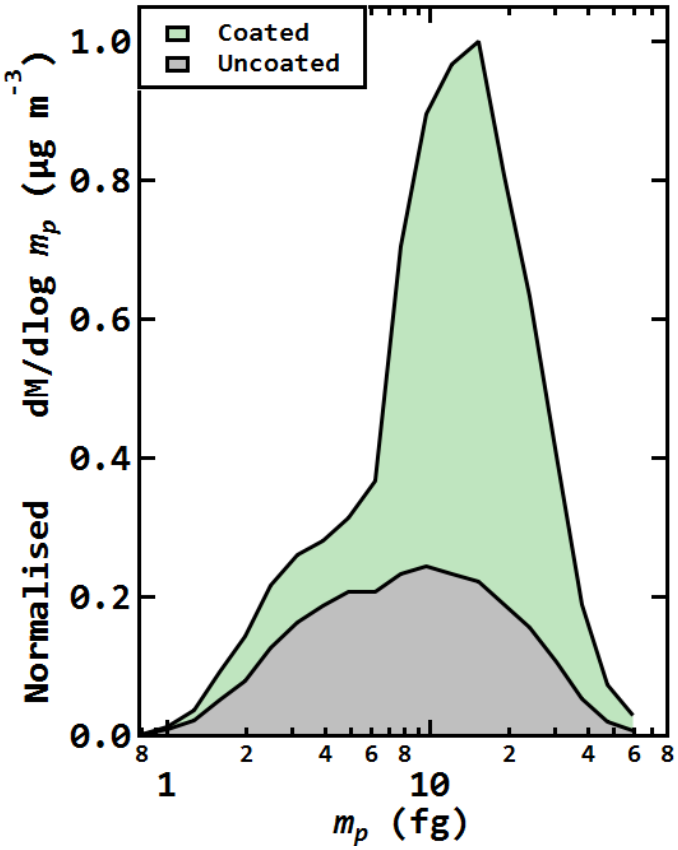
Total mass distributions



Two populations of particles co-exist



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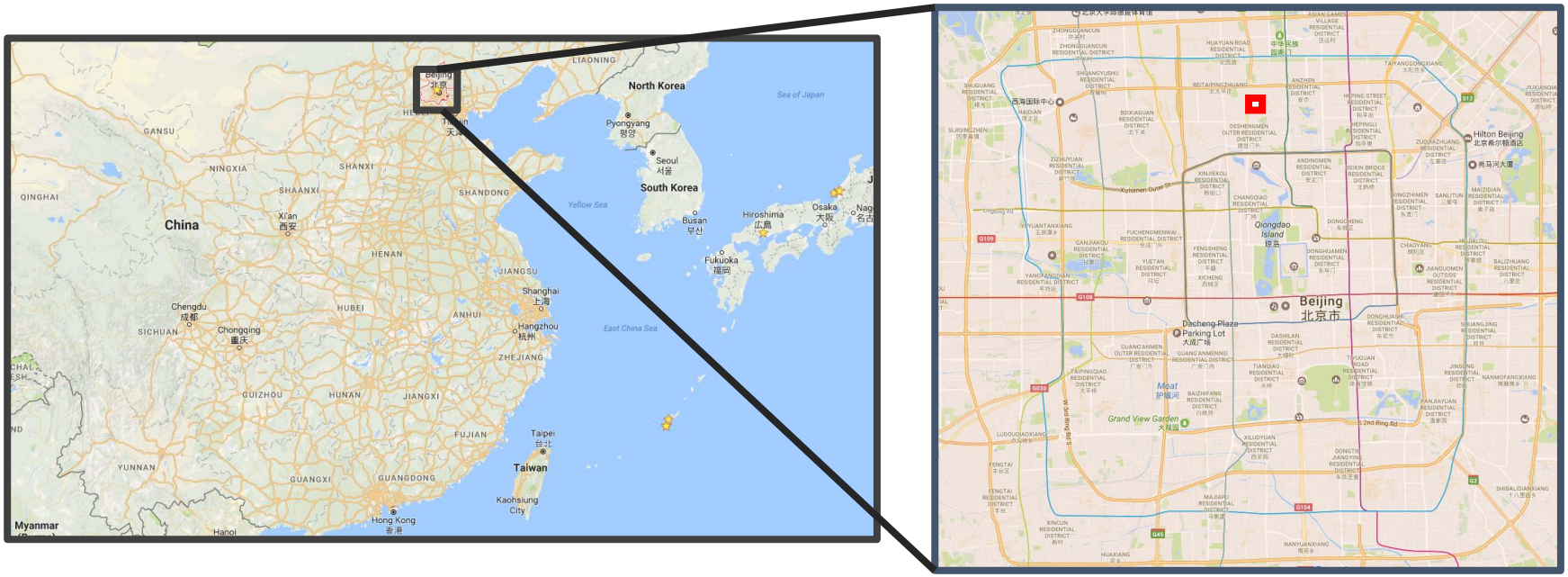
Ambient BC mixing state in China

The CPMA-SP2 system was deployed in central Beijing during November 2016 as part of a field campaign at the Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing



The CPMA-SP2 system was operated in a fully automated fashion using Labview code running on the SP2 computer

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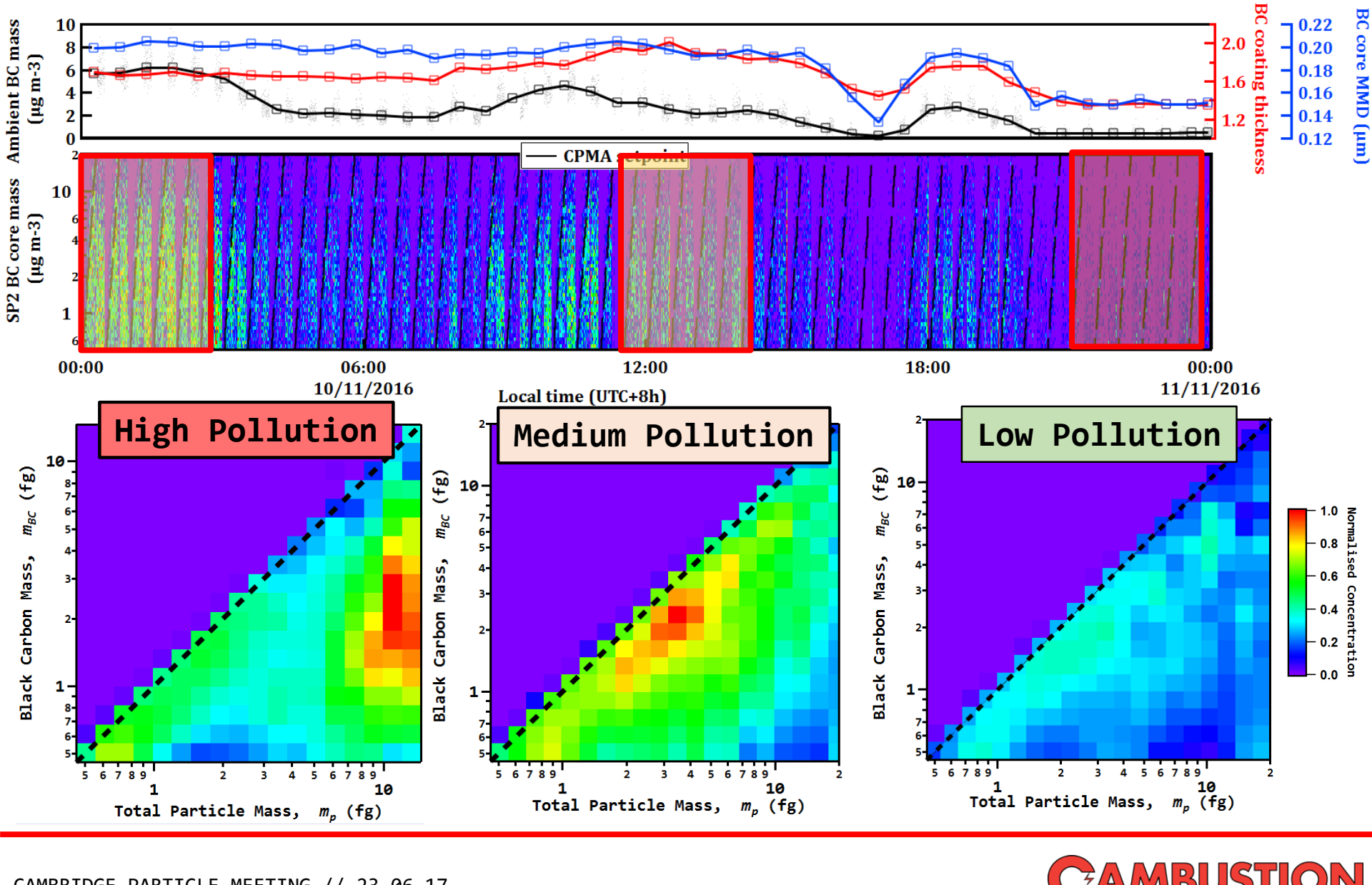
Thursday
14:00
Friday
08:00

Ambient BC mixing state in China



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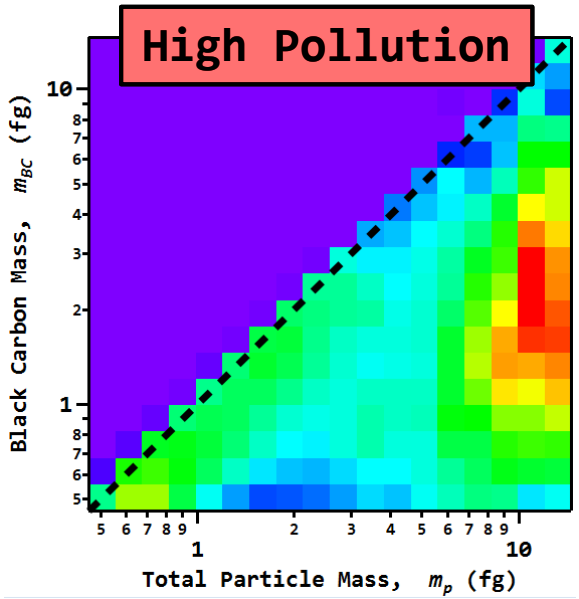
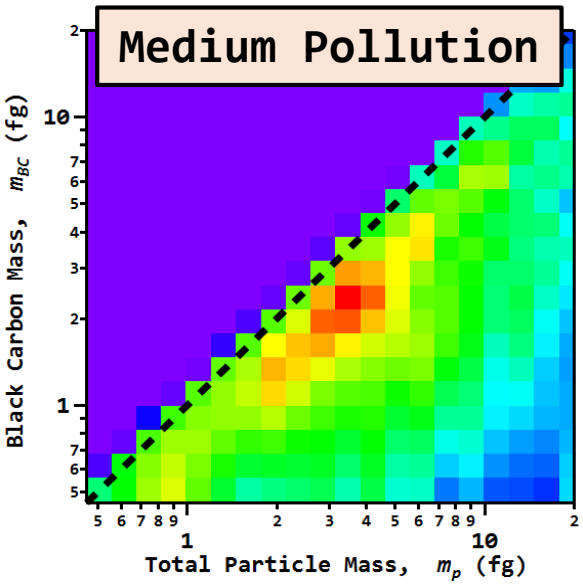
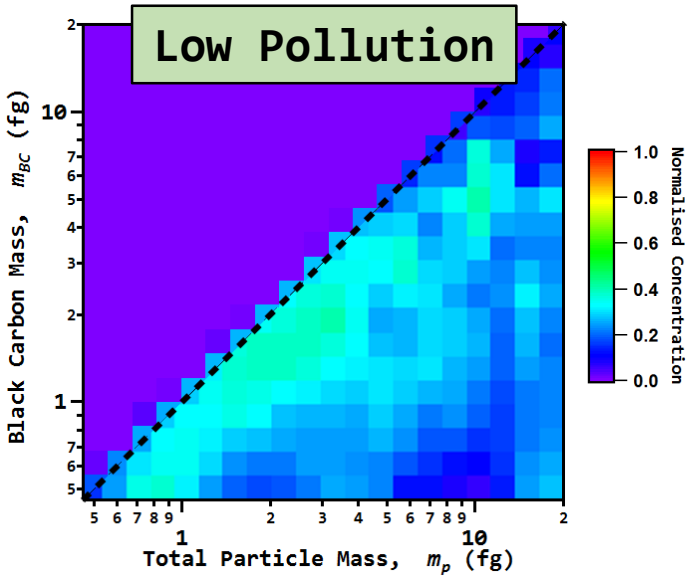
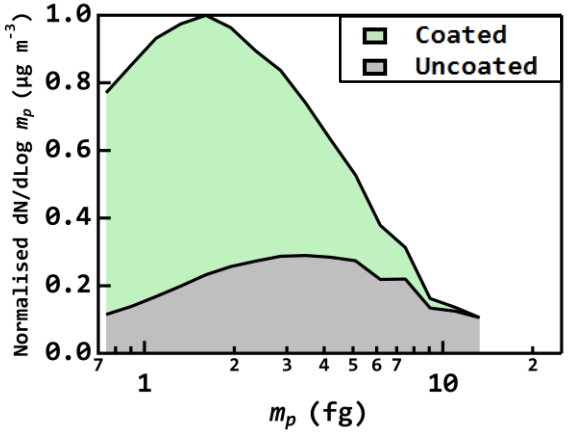
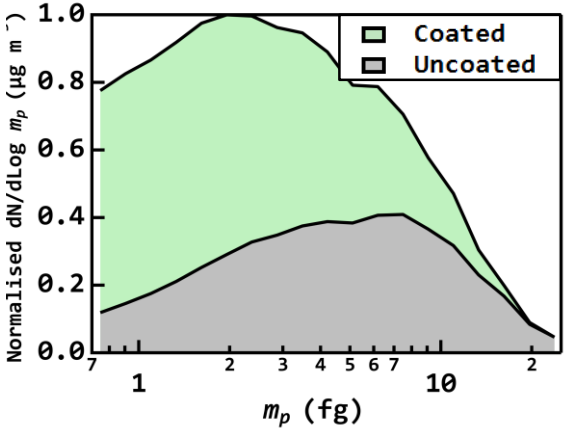
Ambient BC mixing state in China

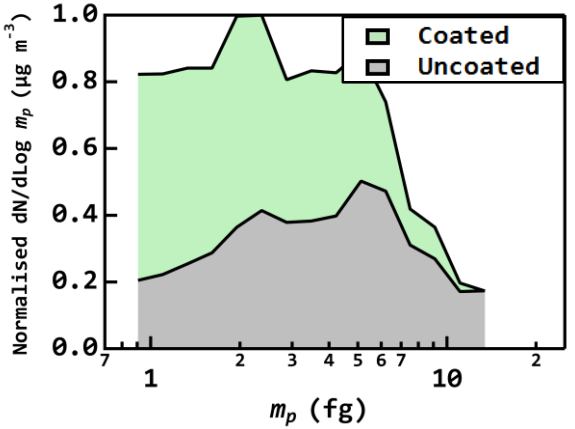












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Summary

1. Coating mass information can be obtained over a much wider range of particle mass compared to SP2 only methods (restricted in the SP2 by the sensitivity to light scattered by rBC)

2. Coating mass is measured directly; no assumptions for coating density or refractive index are needed. Distributions of coated and uncoated particles observed simultaneously.

3. Method does not make assumptions regarding morphology

   (e.g. core/shell model)

4. Powerful, high resolution information can also be linked to BC sources, emissions, lifetime, and optical properties of BC under complex environments

Questions?

Thanks to:

University of Alberta

University of Manchester

IAP China

Nanjing University

& Cambridge Particle Meeting!

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Further work…

Investigate the non-BC particle population (scattering channel, total CPC, etc)

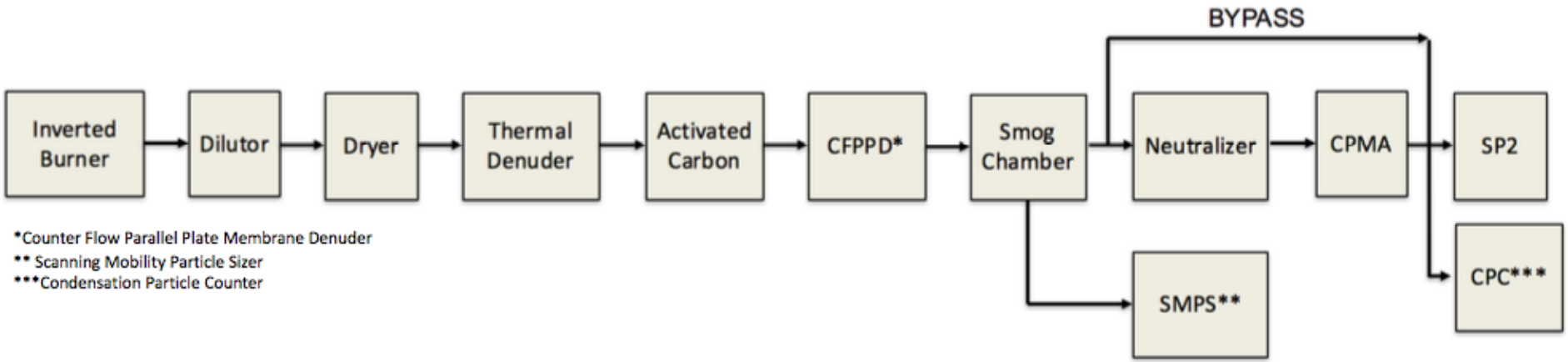
Automated software tools

- operation
- analysis

Variety of soot-sources

Primary-particle exploration (e.g. changing burner conditions)

Conditioner



Experimental setup where bare, uncoated BC particles were injected into a smog chamber.

Coating was grown over time and sampled using a CPMA-SP2 system.

A bypass scan where the SP2 sampled the chamber directly was conducted in order to correct for CPMA losses

Theory [i]

The recovery of mass distributions at the i th CPMA setpoint (R_i) requires solution of a set of Fredholm integral equations (Collins, Flagan, Seinfeld 2002):

$$R_i = \int_0^\infty \int_0^\infty \frac{\partial^2 N}{\partial \log m_\mathrm{p} \partial \log m_\mathrm{rBC}} \log m_\mathrm{p} \log m_\mathrm{rBC} \Psi(i, m_\mathrm{p}) \partial \log m_\mathrm{p} \partial \log m_\mathrm{rBC} \quad i = 1, 2, 3, \ldots, I$$

Where $\frac{\partial^2 N}{\partial \log m_\mathrm{p} \partial \log m_\mathrm{rBC}} \log m_\mathrm{p} \log m_\mathrm{rBC}$ is the unknown two variable number distribution with masses between $\log(m_\mathrm{p})$ and $\log(m_\mathrm{p}) + \partial\log(m_\mathrm{p})$ and between $\log(m_\mathrm{rBC})$ and $\log(m_\mathrm{rBC}) + \partial \log(m_\mathrm{rBC})$, m_p is the total mass of a particle, m_rBC is the mass of rBC in a particle, and $\Omega(i,m_\mathrm{p})$ is the response of the instrument at the i th measurement channel.

The response of the instrument Ψ (i,m_p) is dependent on the charge fraction of the particles, $f(m_\mathrm{p},\phi)$, and the transfer function of the CPMA, $\Omega(m_\mathrm{p},Z)$. Where ϕ is the number of charges and Z is the electrical mobility.

Theory [ii]

A two dimensional number distribution can be resolved by solving the following system of equations, where $\Psi(i,mp)$ is approximated using the trapezoidal rule and modelled as the kernel function $\Gamma_{i,j}$:

$$\frac{\partial^2 N}{\partial \log m_{\mathrm{p}} \partial \log m_{\mathrm{rBC}}} \vec{\mathbf{\Gamma}} = \frac{\mathrm{d}N}{\mathrm{d}\log m_{\mathrm{rBC}}}$$

$$\Gamma_{i,j} = \log\left(\frac{m_{\mathrm{p}(j+1/2)}}{m_{\mathrm{p}(j-1/2)}}\right) \sum_{\Phi=1}^{\Phi_{max}} f(m_{\mathrm{p}}, \Phi)\Omega(Z, m_{\mathrm{p}})$$

Where the kernel function, $\Gamma_{i,j}$, represents the response of the instrument with a trapezoidal rule approximation for the i th instrument response and the j th solution element (Collins, Flagan, Seinfeld; 2002) of the number distribution of m_{rBC}; $\frac{\mathrm{d}N}{\mathrm{d}\log m_{\mathrm{rBC}}}$

An iterative method was used to solve these equations.

Theory [iii]

An advantage of the two number distribution is that useful mass distributions can be recovered by integration along the total mass or rBC mass domains. Additionally, double integration yields the total mass and rBC mass concentrations. The following mass distributions can be recovered:

$$\frac{\mathrm{d}M}{\mathrm{d}\log m_\mathrm{p}}, \frac{\mathrm{d}M_\mathrm{rBC}}{\mathrm{d}\log m_\mathrm{p}}, \frac{\mathrm{d}M}{\mathrm{d}\log m_\mathrm{rBC}}, \frac{\mathrm{d}M_\mathrm{rBC}}{\mathrm{d}\log m_\mathrm{rBC}}$$

For example, to recover the total mass distribution as a function of *m*rBC the following integration can be conducted:

$$\frac{\mathrm{d}M}{\mathrm{d}\log m_\mathrm{rBC}} = \int \frac{\partial^2 N}{\partial \log m_\mathrm{p} \partial \log m_\mathrm{rBC}} m_\mathrm{p} \partial \log m_\mathrm{p}$$

Mass distributions can be plotted as a function of rBC mass or total particle mass. When plotted against rBC mass, we learn the coating distribution. When plotted against total mass, we see two populations (coated and uncoated), simultaneously.