NRC·CNRC

NRC.CANADA.CA

Measurement and impacts of the mass fraction of volatile coatings on soot

Joel C. Corbin[1], Timothy A. Sipkens[1], Arash Naseri[2], and Jason Olfert[2]

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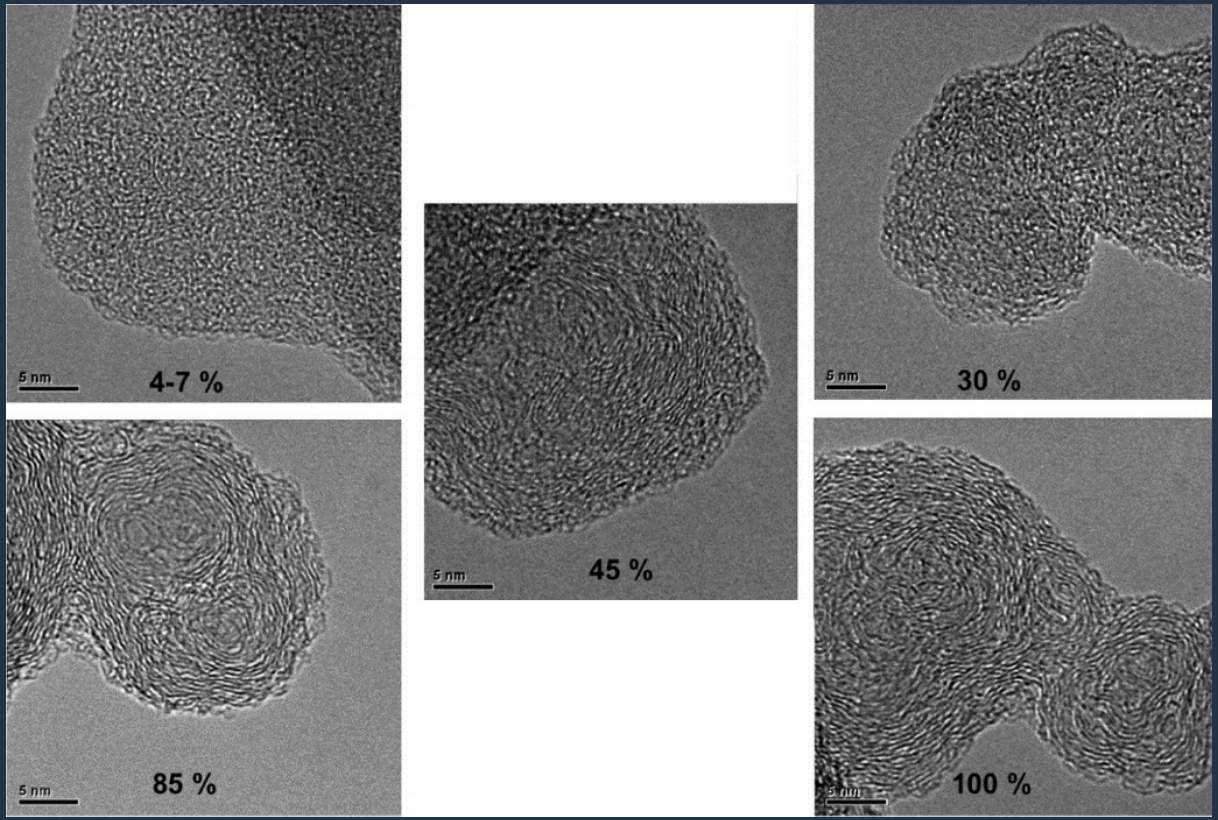
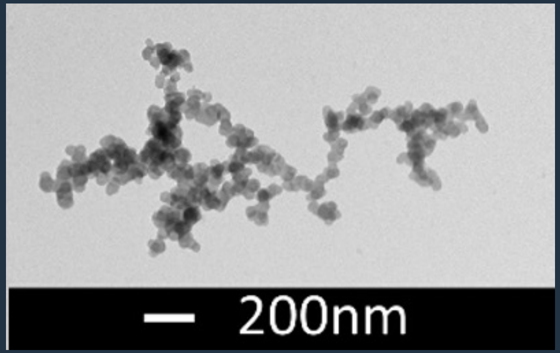
ETH NPC, June 2024

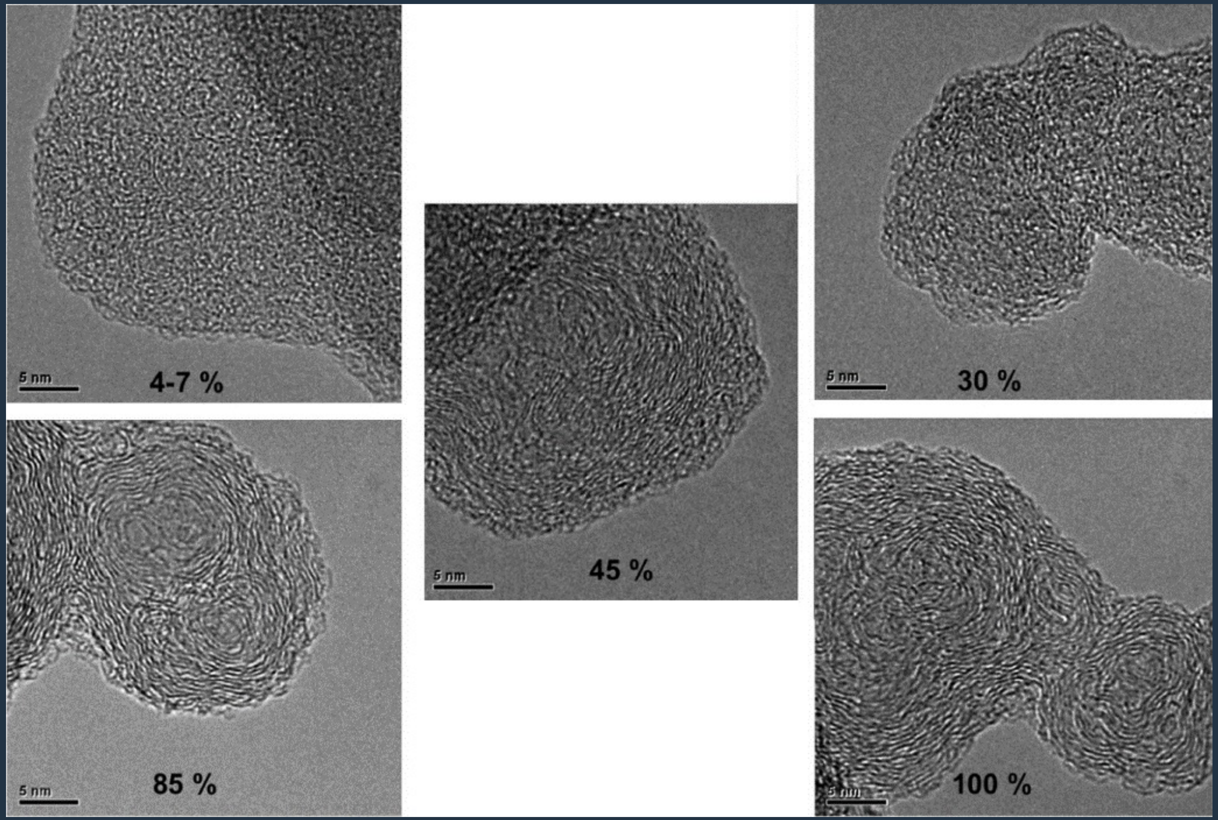
Atmospheric soot

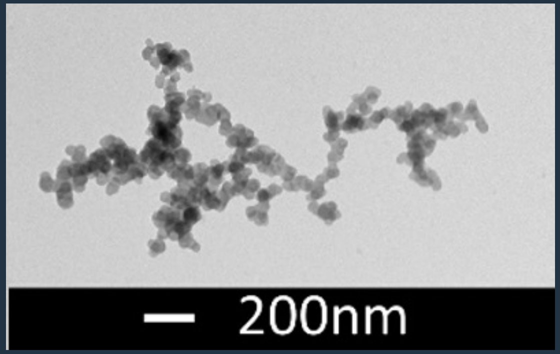


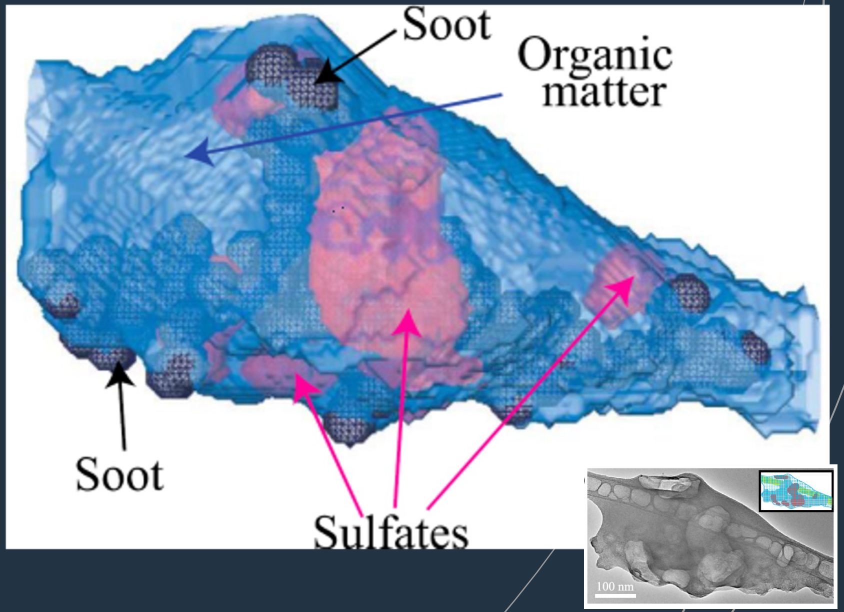


Range of soots from Vander Wal et al. (2004)
Mixed soot from Adachi and Buseck, J Geophys Res 2010

Atmospheric soot… often mixed or "coated"





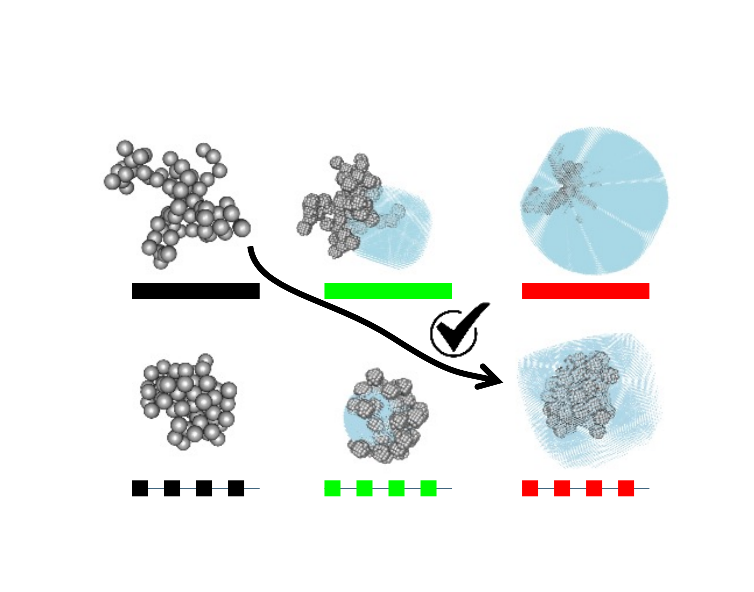


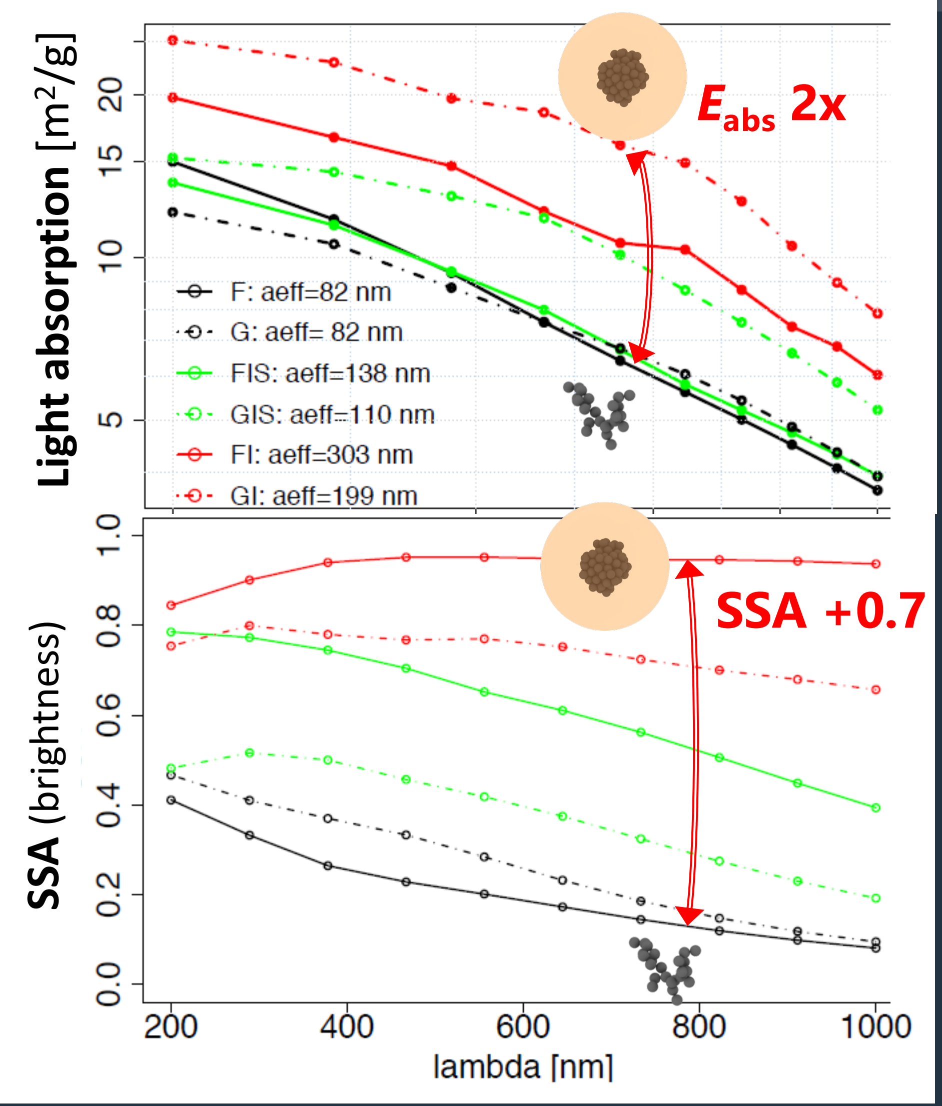
- ➢ Mixing occurs over 2-4 hours in daylight

Range of soots from Vander Wal et al. (2004)
Mixed soot from Adachi and Buseck, J Geophys Res 2010

Soot morphology is crucial to understanding its light absorption

Soot climate warming is comparable to that of CO_2 [1]

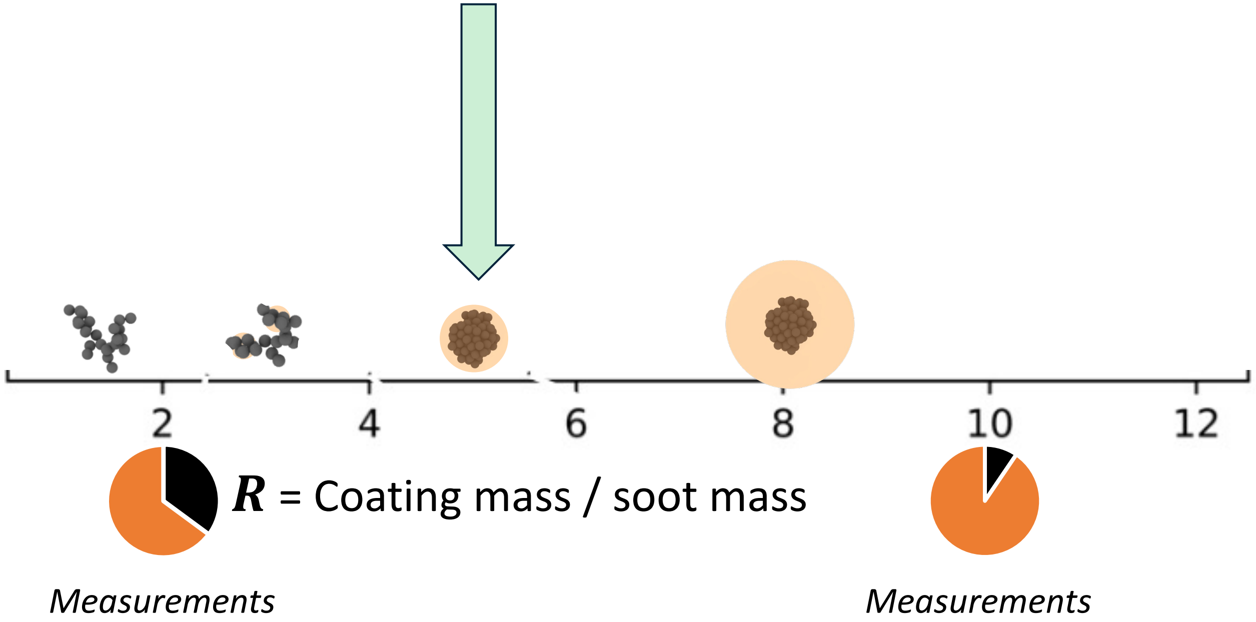




[1] Ramanathan & Carmichael 2008; *[2; figures]* Scarnato et al., 2013

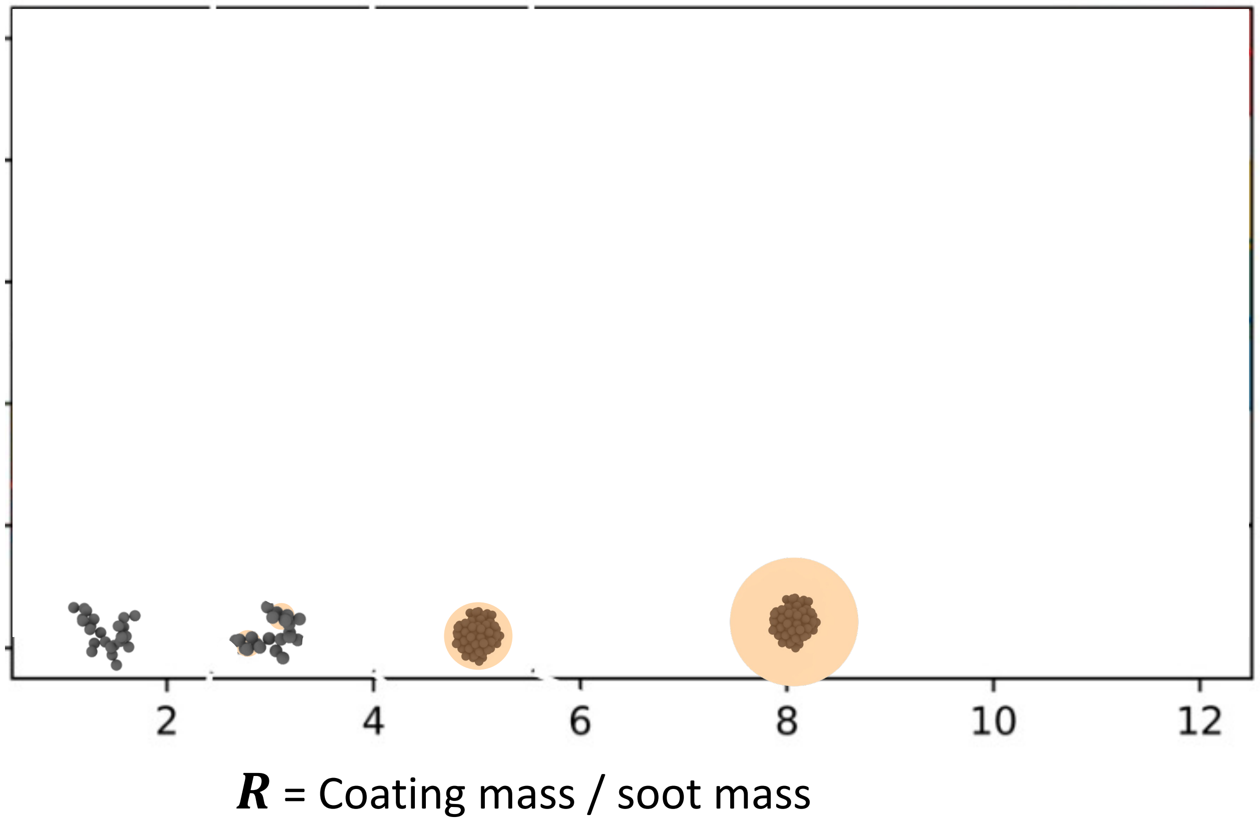
Quantifying soot coatings using R

Spherical at R > 5
(Sipkens and Corbin, Carbon 2024)



Sipkens and Corbin, 2024

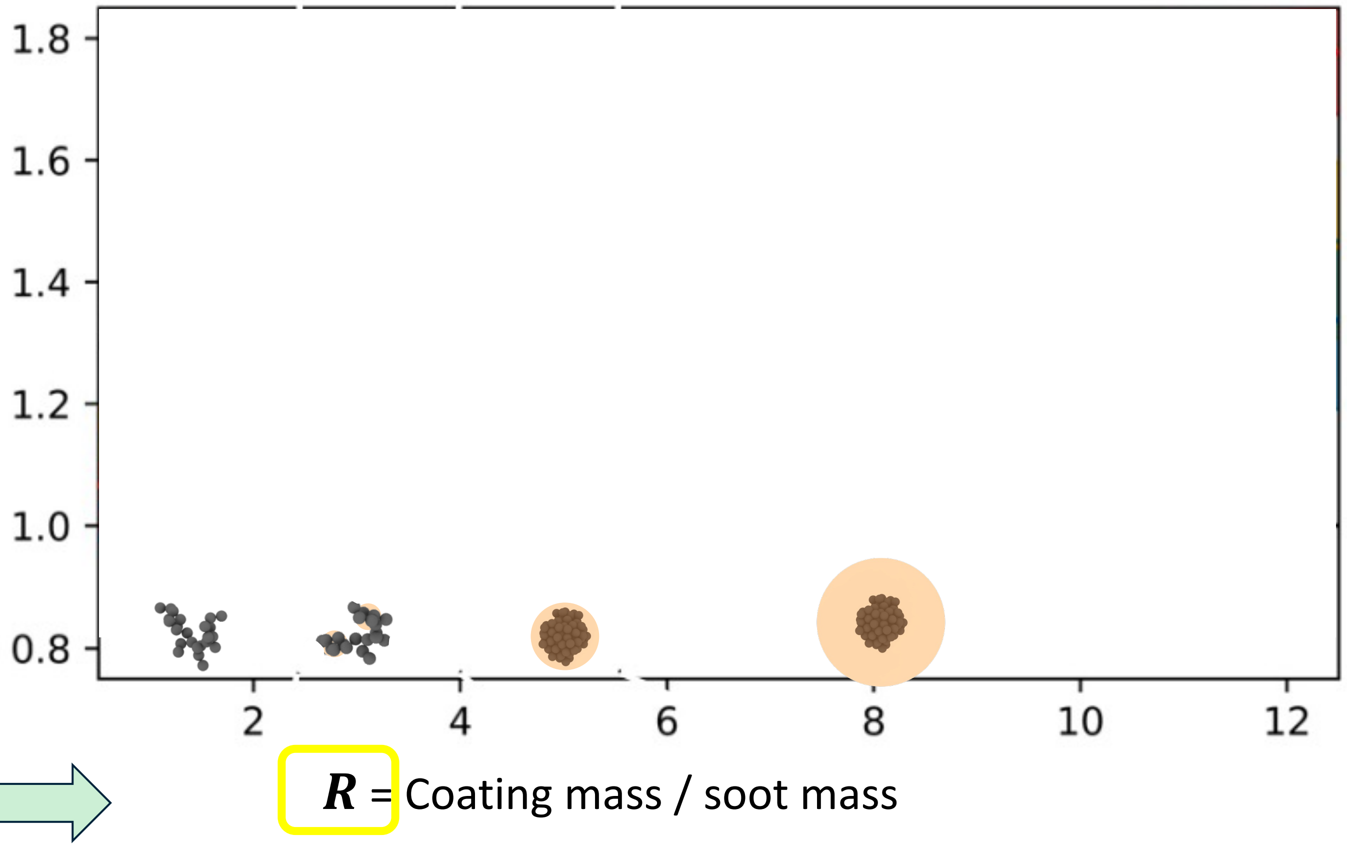
Quantifying the effects of soot coating using E_{abs}



Fierce et al., Nature Comm 2016; PNAS 2020

Quantifying the effects of soot coating using E_{abs}

$$E_{abs} = \frac{\text{coated absn}_\lambda}{\text{initial absn}_\lambda}$$



$$R = \frac{\text{measure coating mass}}{\text{measure soot mass}}$$

Fierce et al., Nature Comm 2016; PNAS 2020

Quantifying the effects of soot coating using E_{abs}

$$E_{abs} = \frac{\text{coated absn}_\lambda}{\text{initial absn}_\lambda}$$

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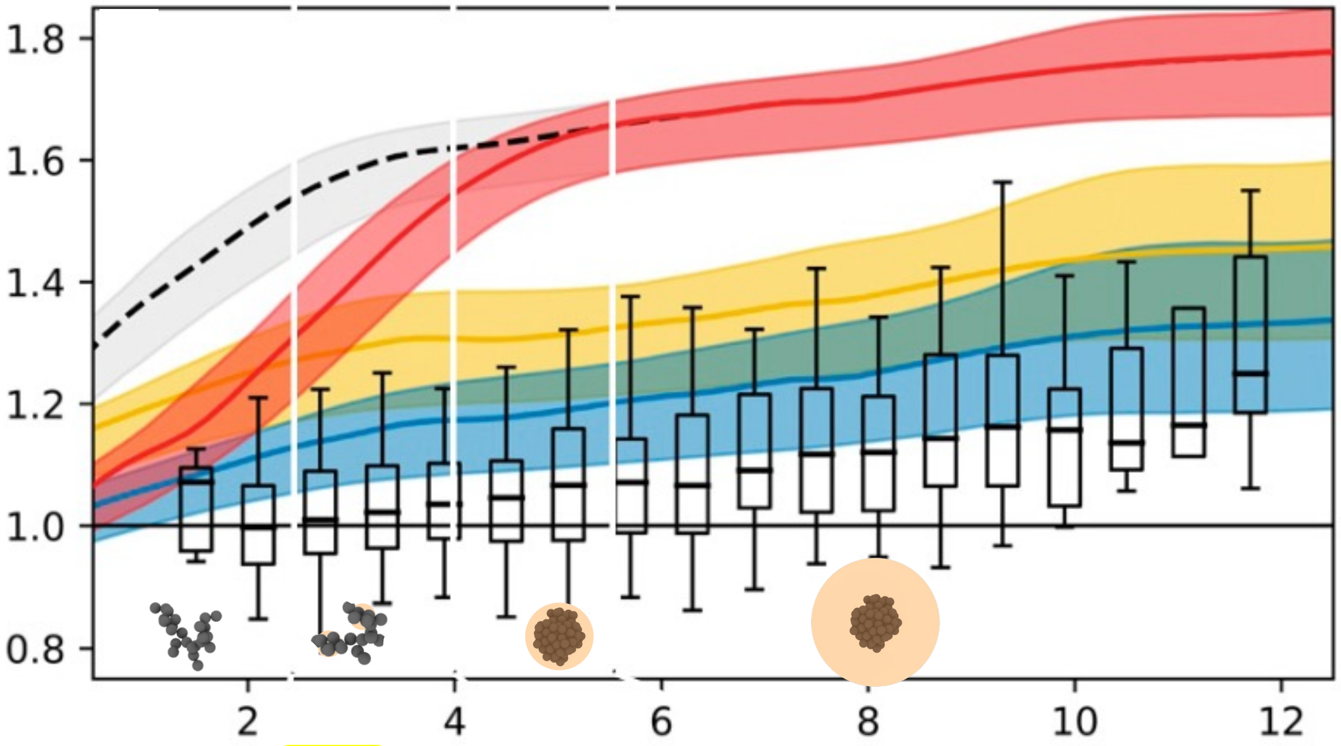
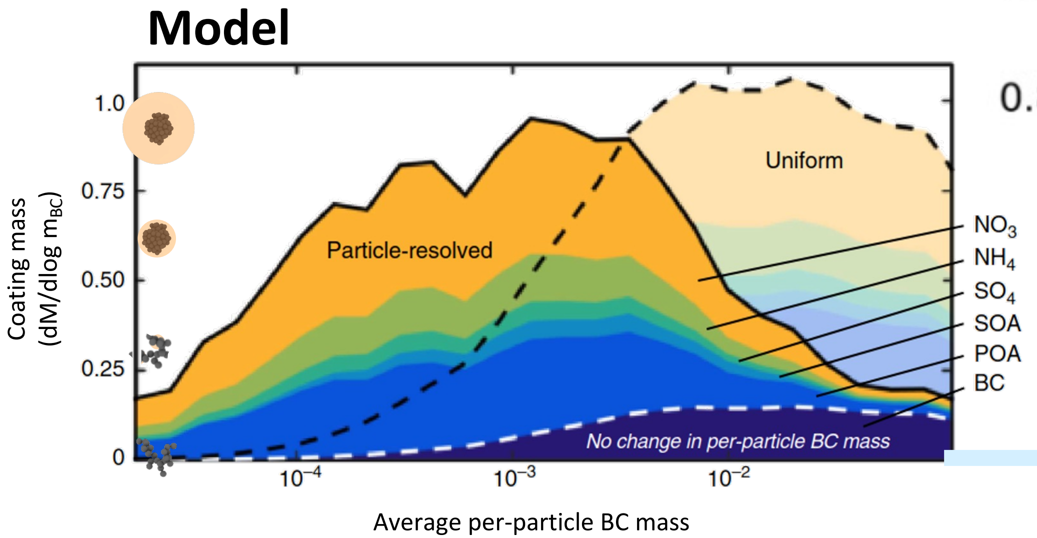


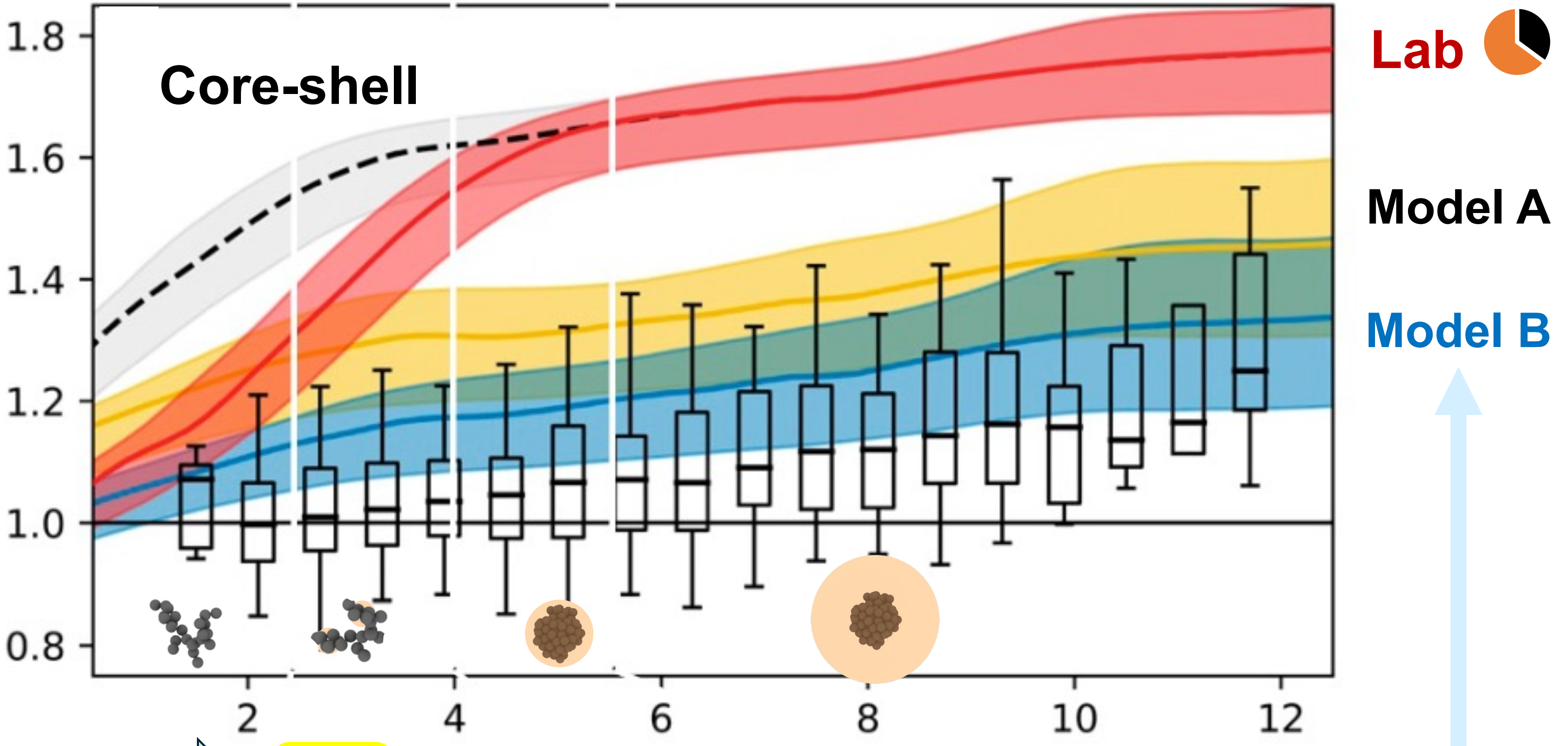
R = Coating mass / soot mass

Fierce et al., Nature Comm 2016; PNAS 2020

Quantifying the effects of soot coating using E_{abs}

$$E_{abs} = \frac{\text{coated absn}_\lambda}{\text{initial absn}_\lambda}$$

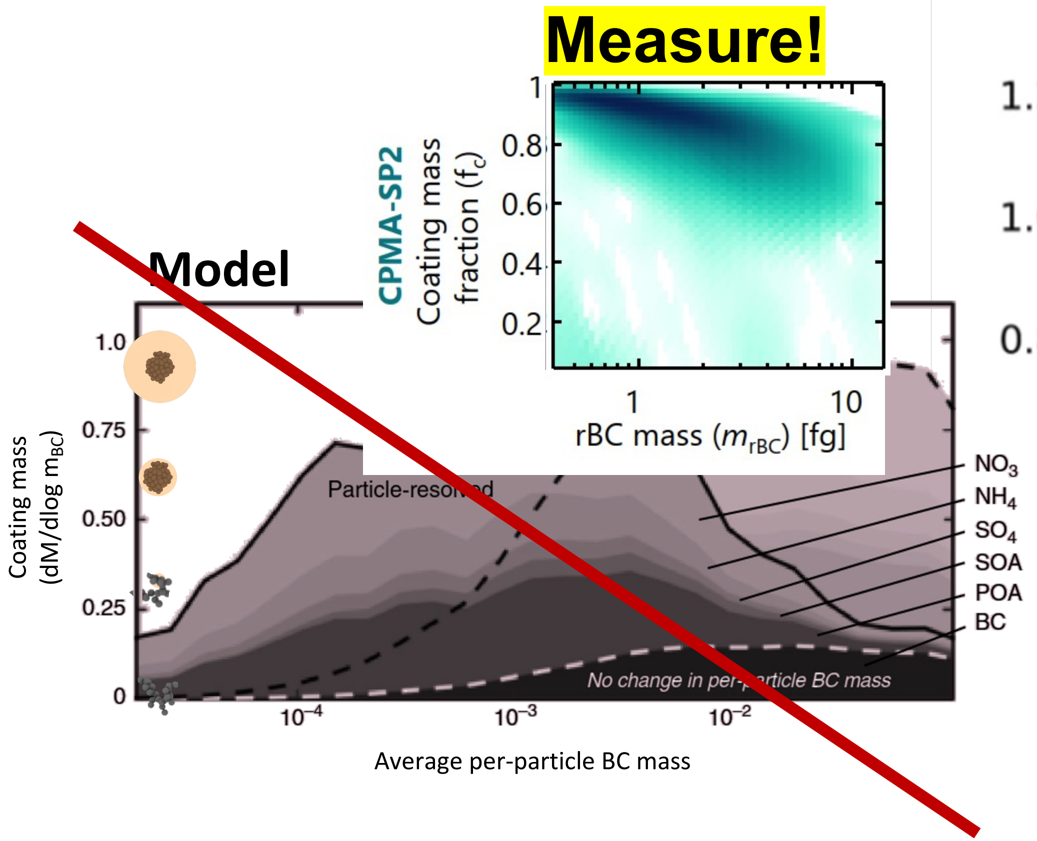


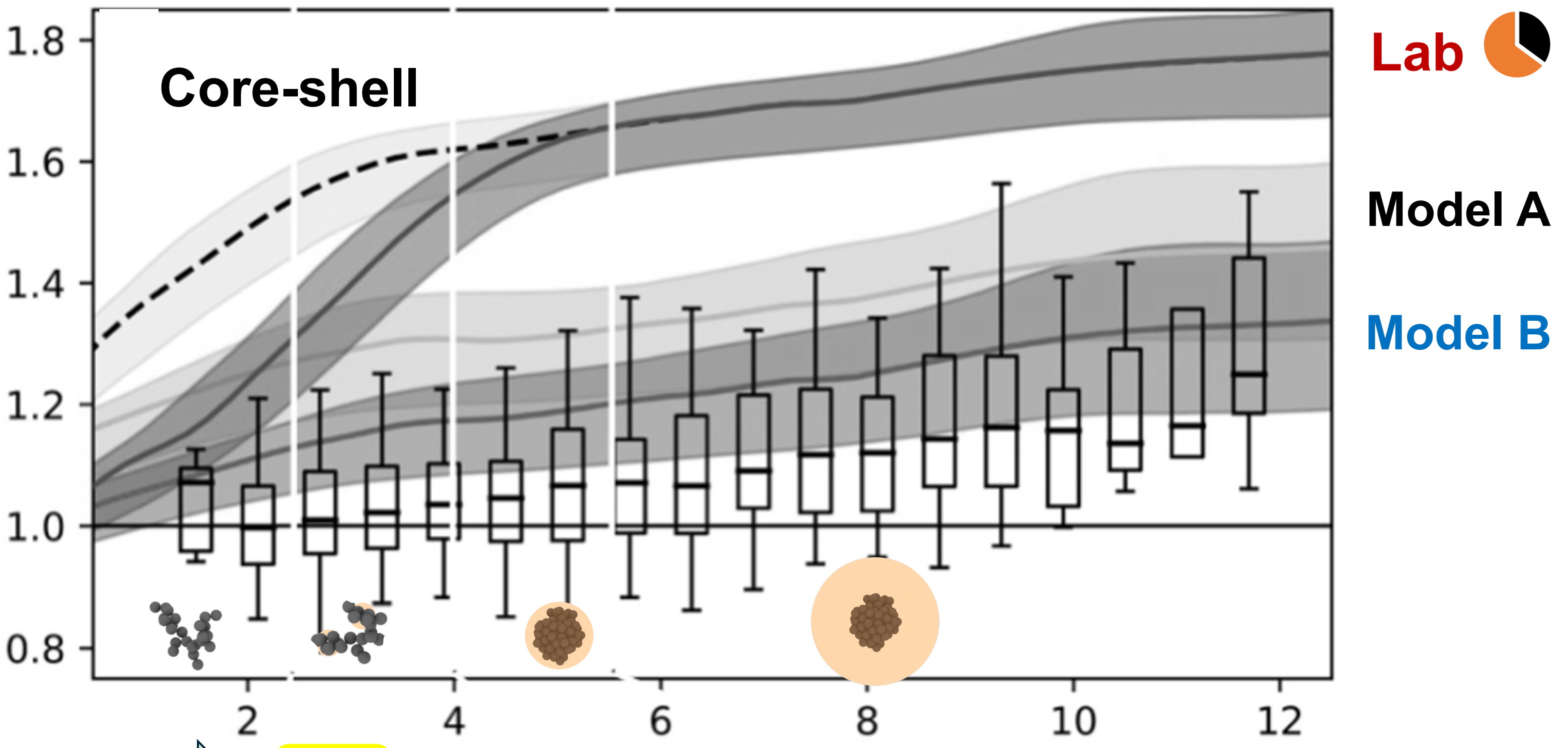


R = Coating mass / soot mass

Fierce et al., Nature Comm 2016; PNAS 2020

This talk: measure R using CPMA-SP2

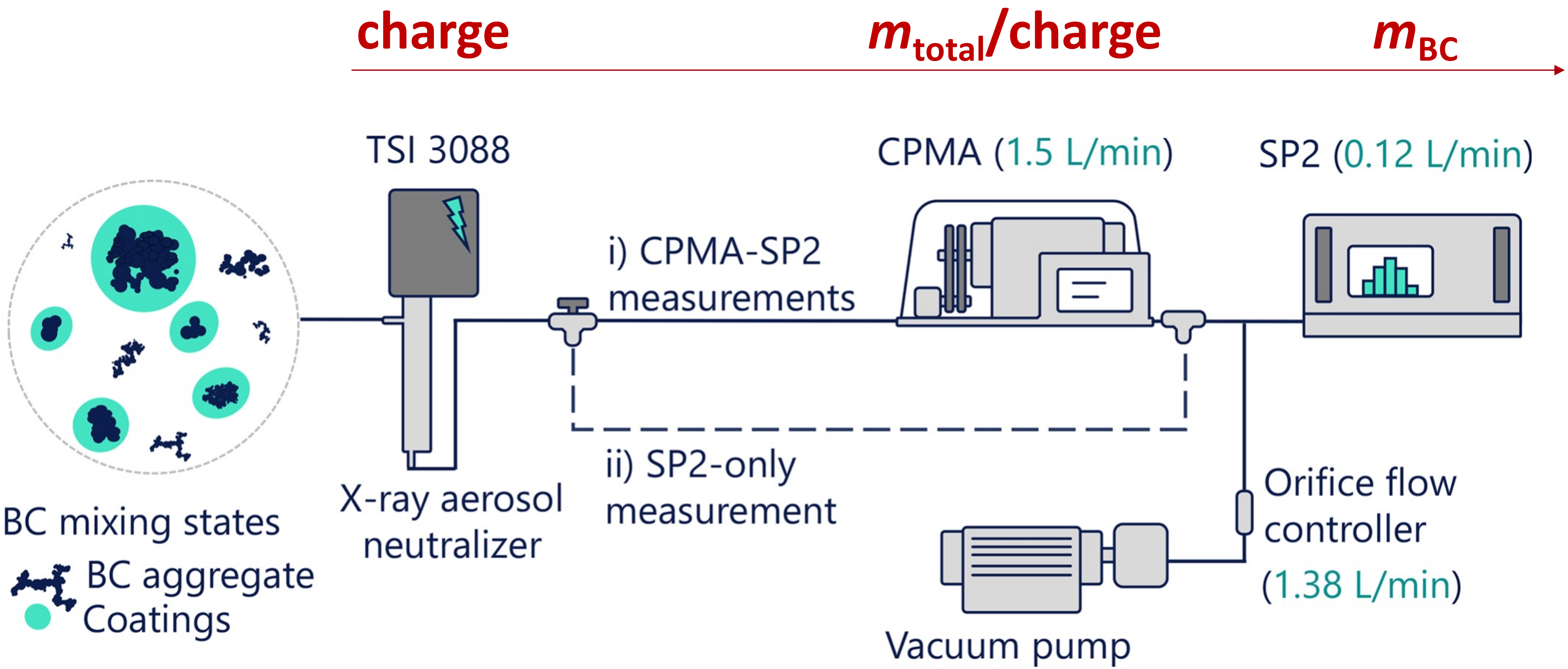




R = Coating mass / soot mass

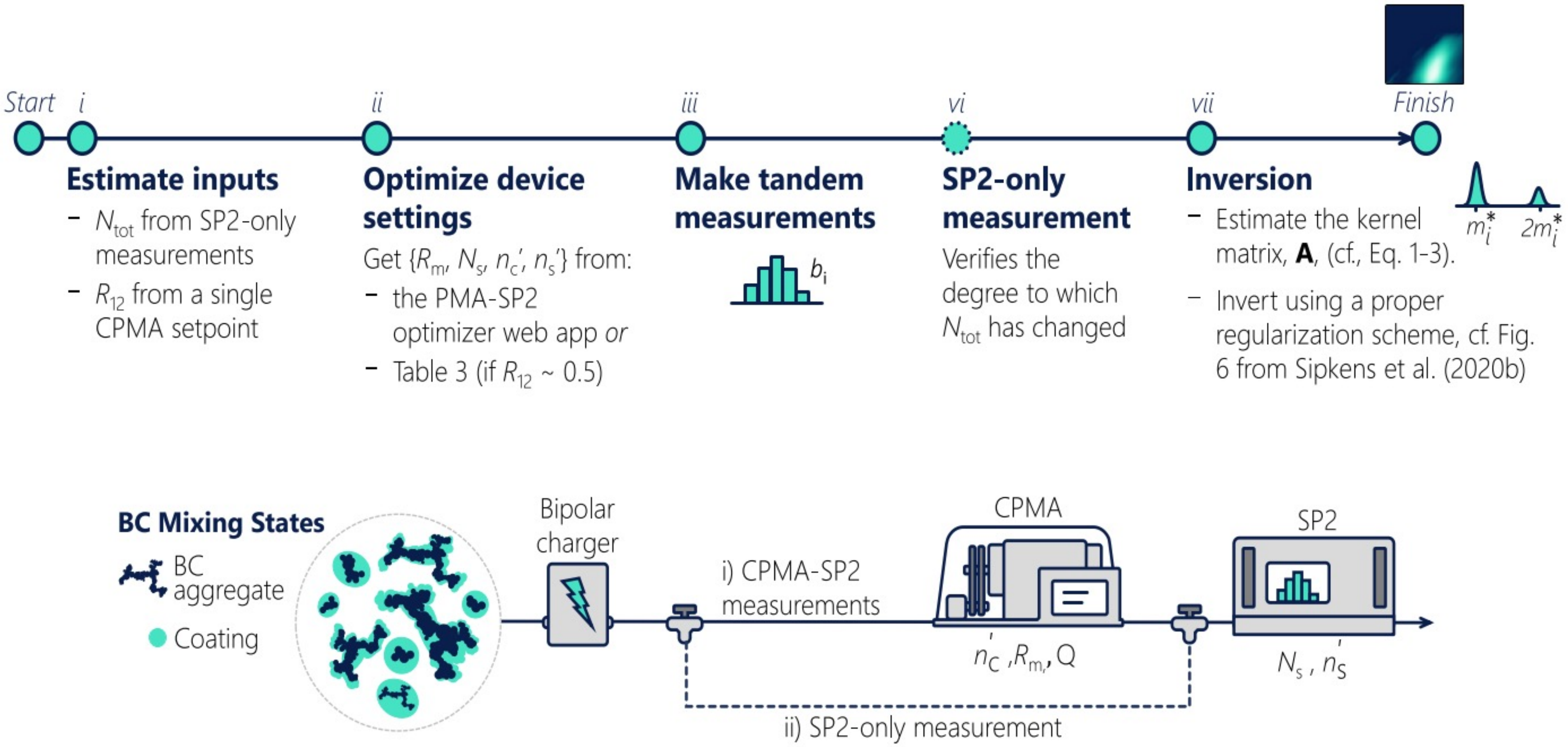
Fierce et al., Nature Comm 2016; PNAS 2020

Method to measure soot mixing state: CPMA-SP2



Naseri, Corbin and Olfert. AMT 2024

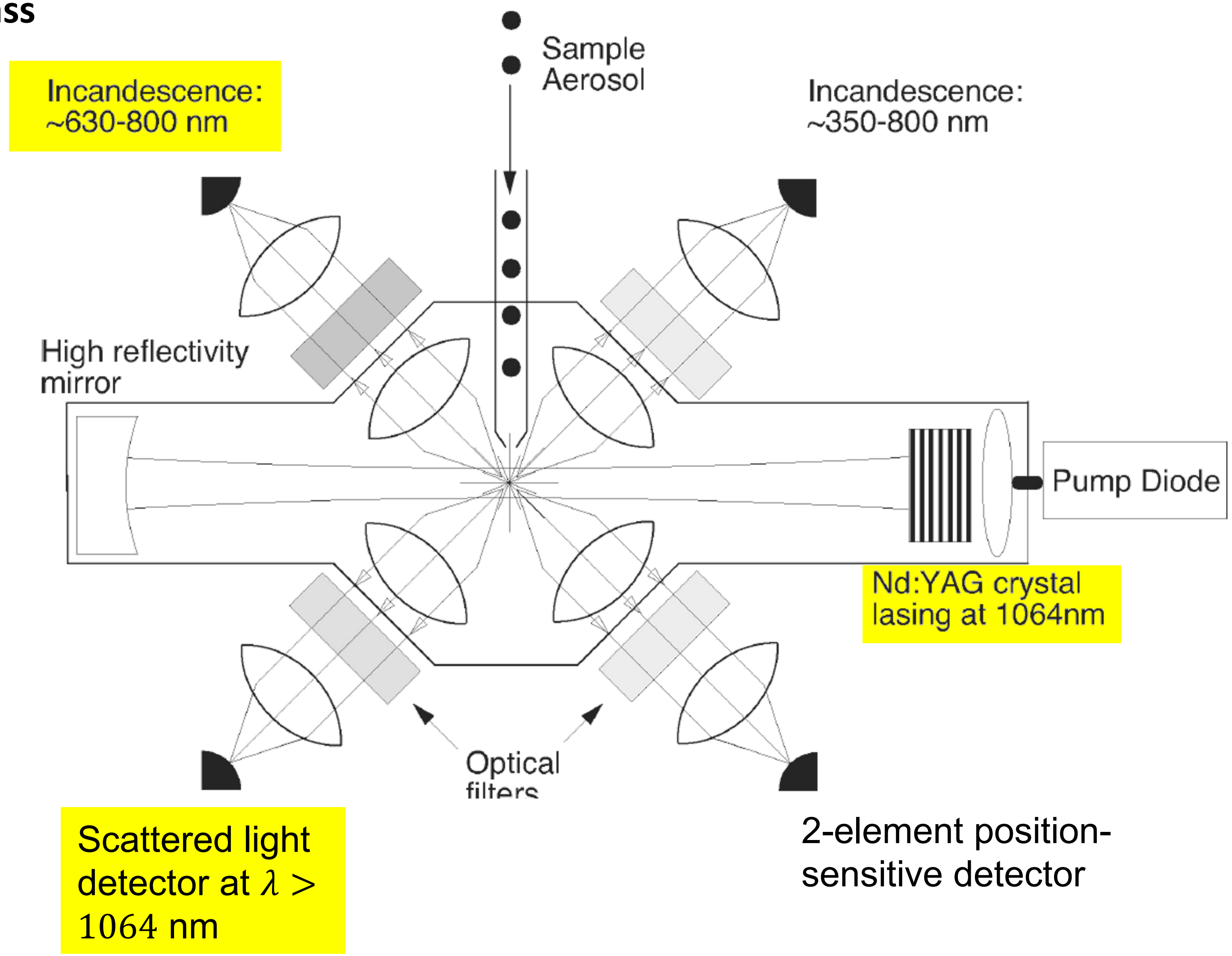
CPMA-SP2 procedure



Naseri, Sipkens, Rogak, Olfert JAS 2022

Single Particle Soot Photometer (SP2)

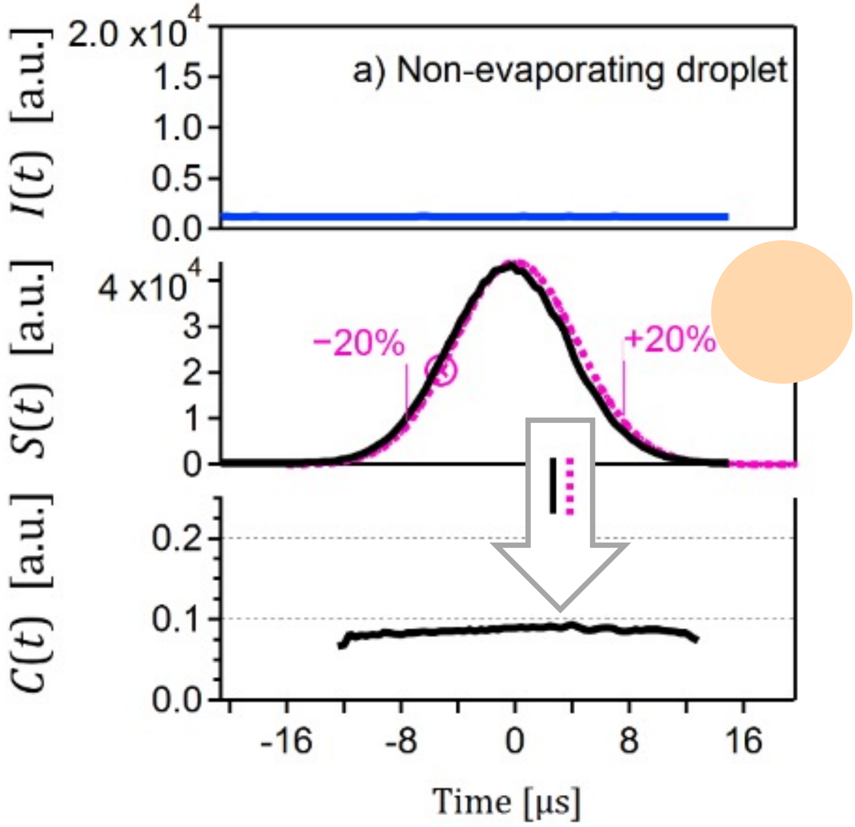
→ **designed to measure rBC mass**



Stephens et al., 2003; Schwarz et al., JGR 2006

SP2 signals for soot

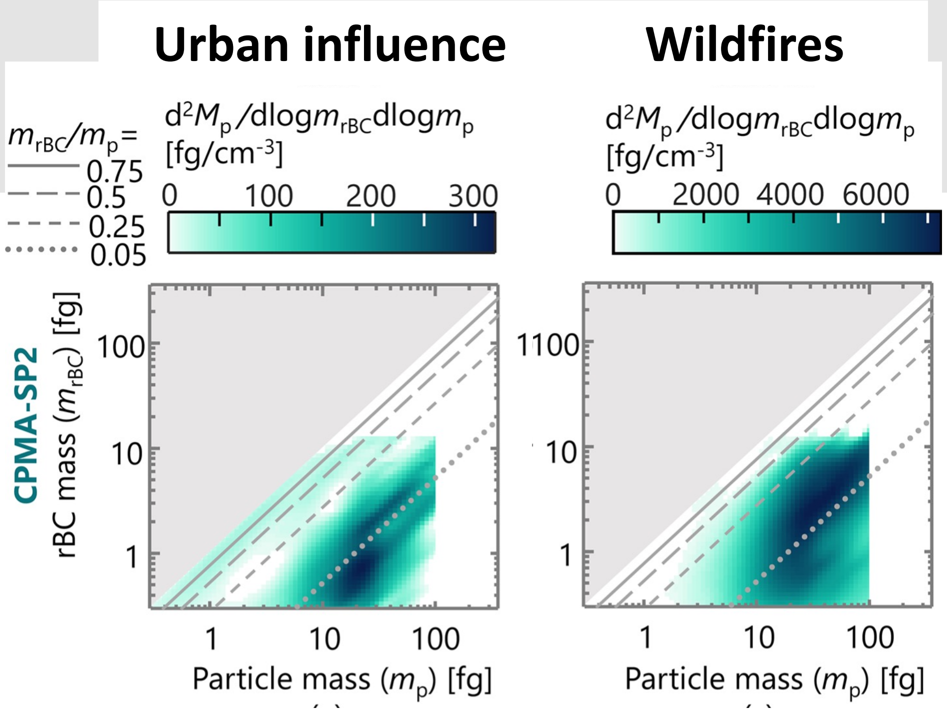
SP2 modelling at the poster of
F. Liu, T. A. Sipkens, and J. C. Corbin
at this conference.



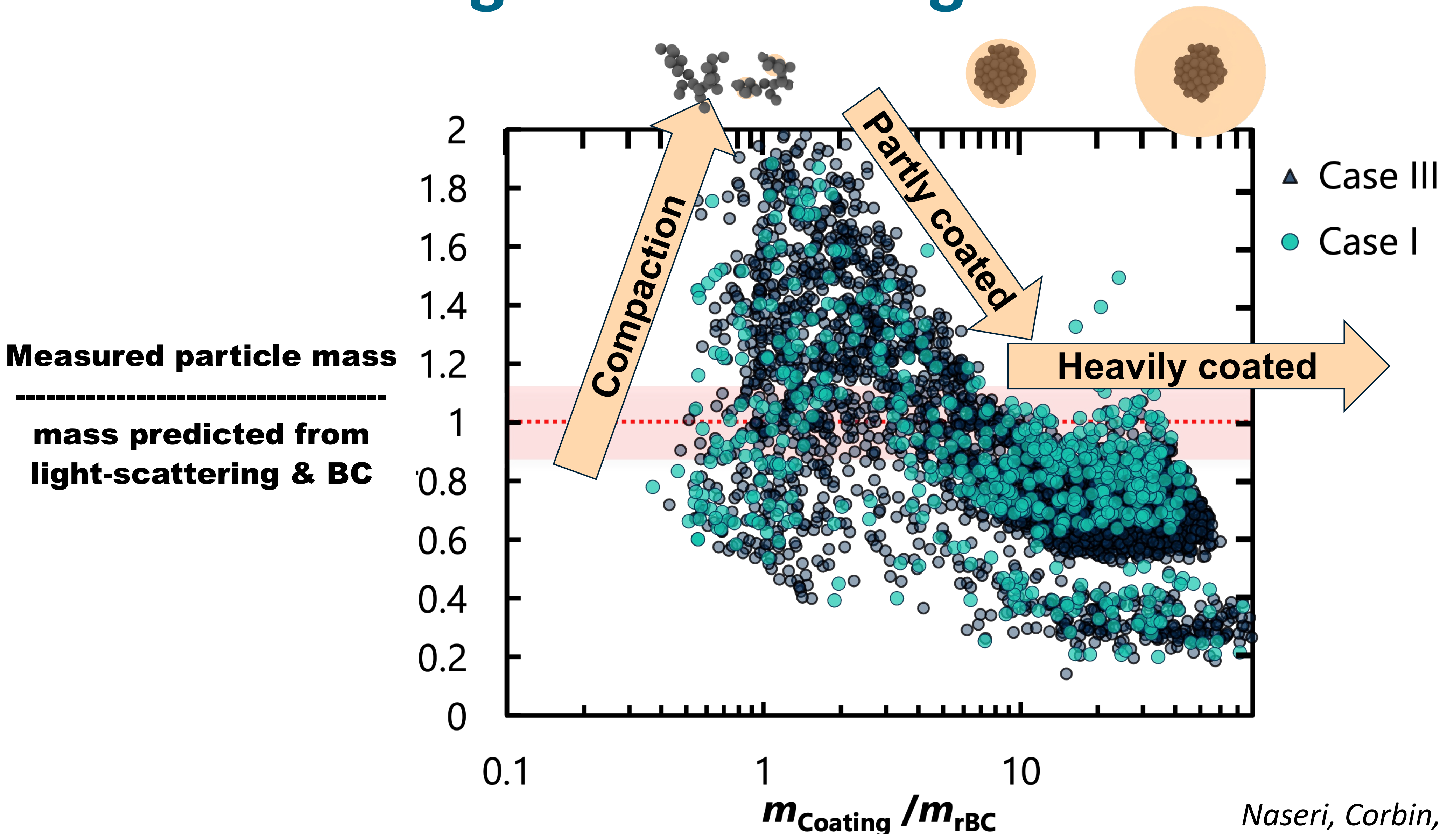
Corbin and Gysel-Beer, ACP 2019

CPMA-SP2 **Results**

Direct measurement of soot mixing state.



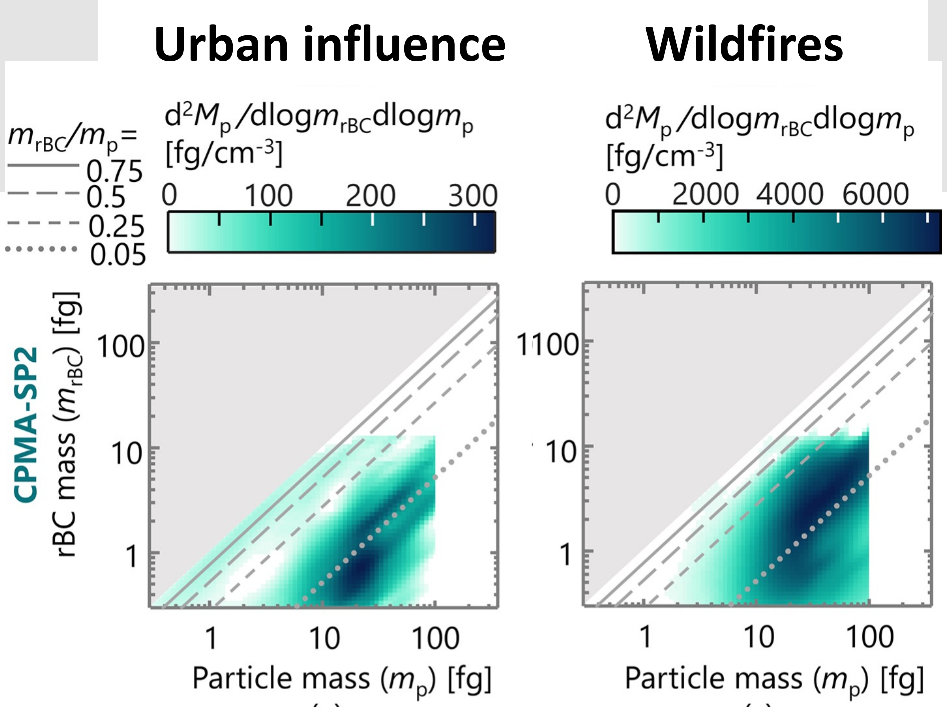
CPMA-SP2 **insights into mixing state**



Naseri, Corbin, Olfert AMT 2024
Corbin, Modini, Gysel-Beer AS&T 2022

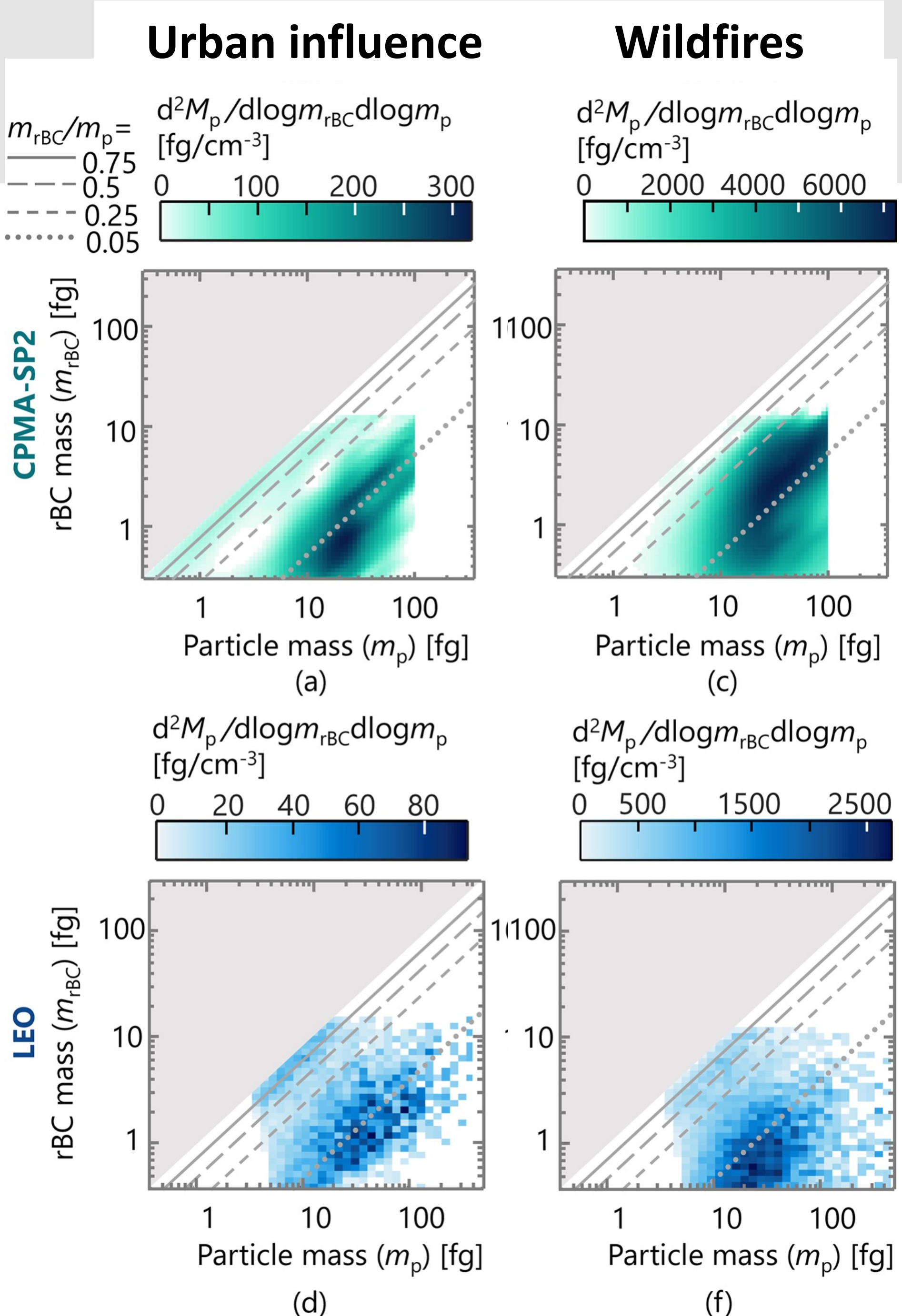
CPMA-SP2 **Results**

Direct measurement of soot mixing state.



CPMA-SP2 **vs. SP2-LEO**

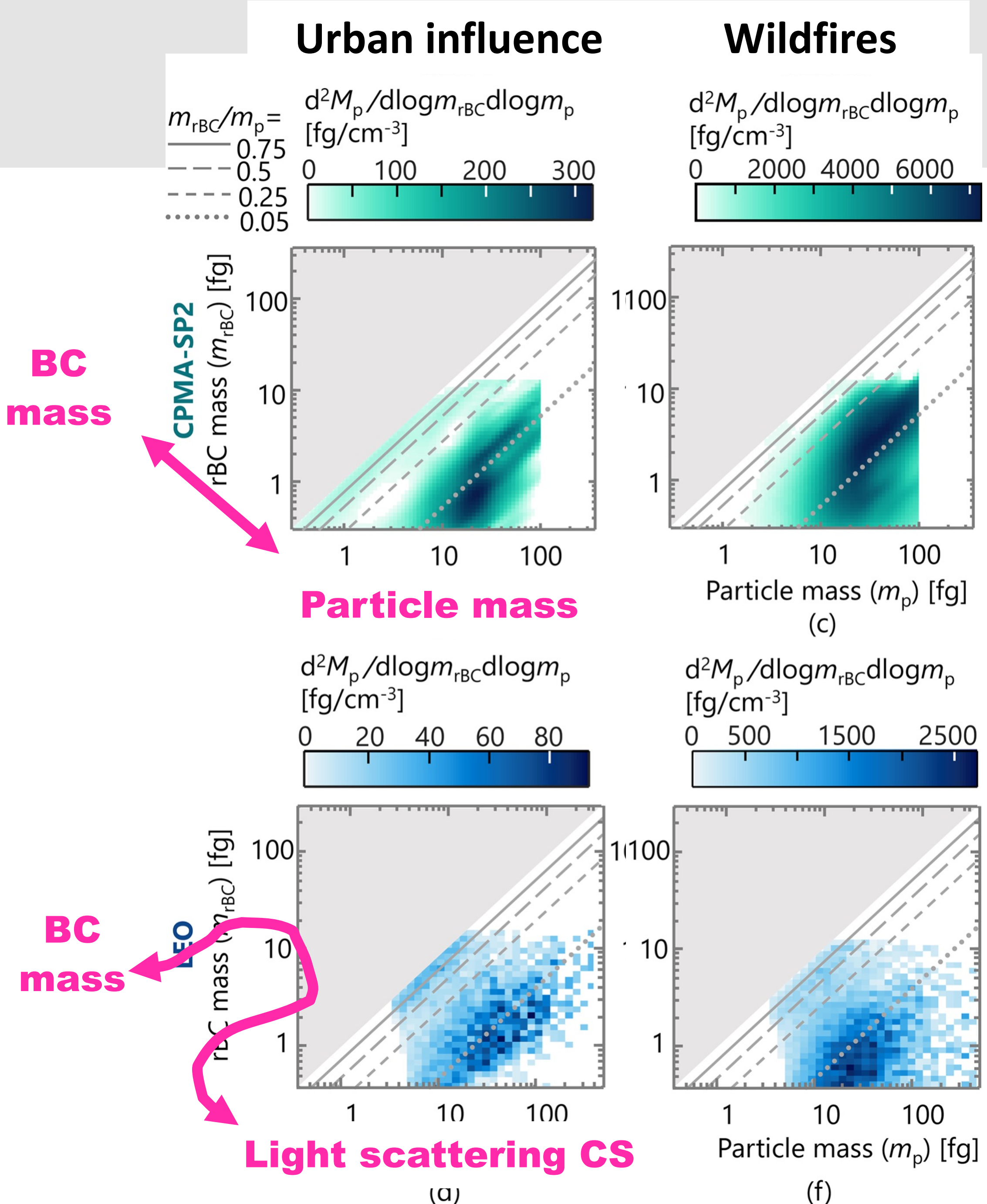
Indirect "LEO" estimation biased towards thicker coatings, larger particles.



CPMA-SP2 **vs. SP2-LEO**

Indirect "LEO" estimation biased towards thicker coatings, larger particles:

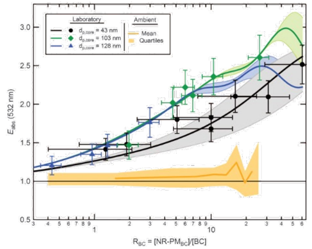
LEO = total mass from initial light-scattering, assuming core-shell BC.

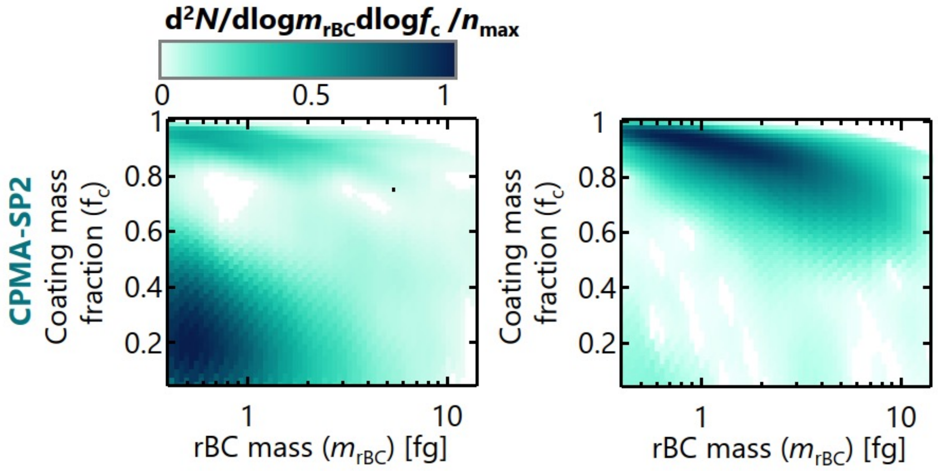


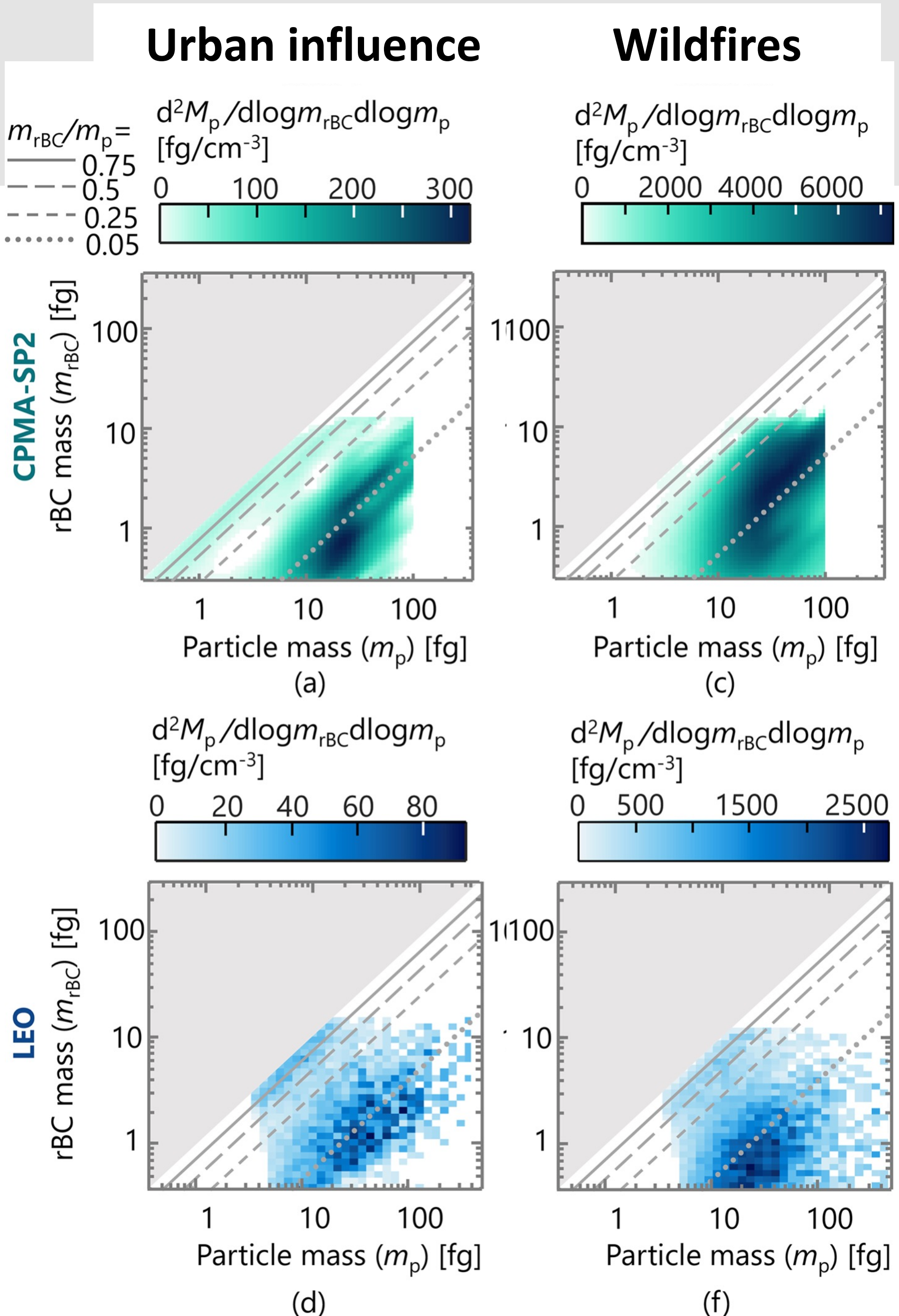
CPMA-SP2 Results

Can directly calculate $f_{coating,}$

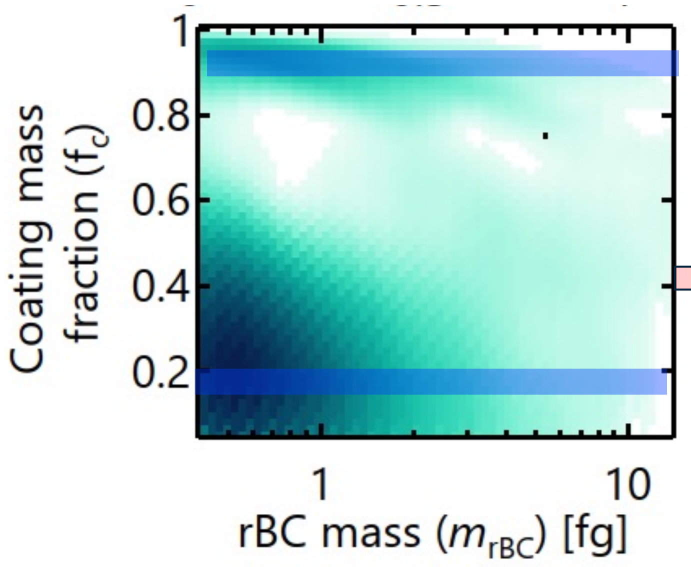
therefore

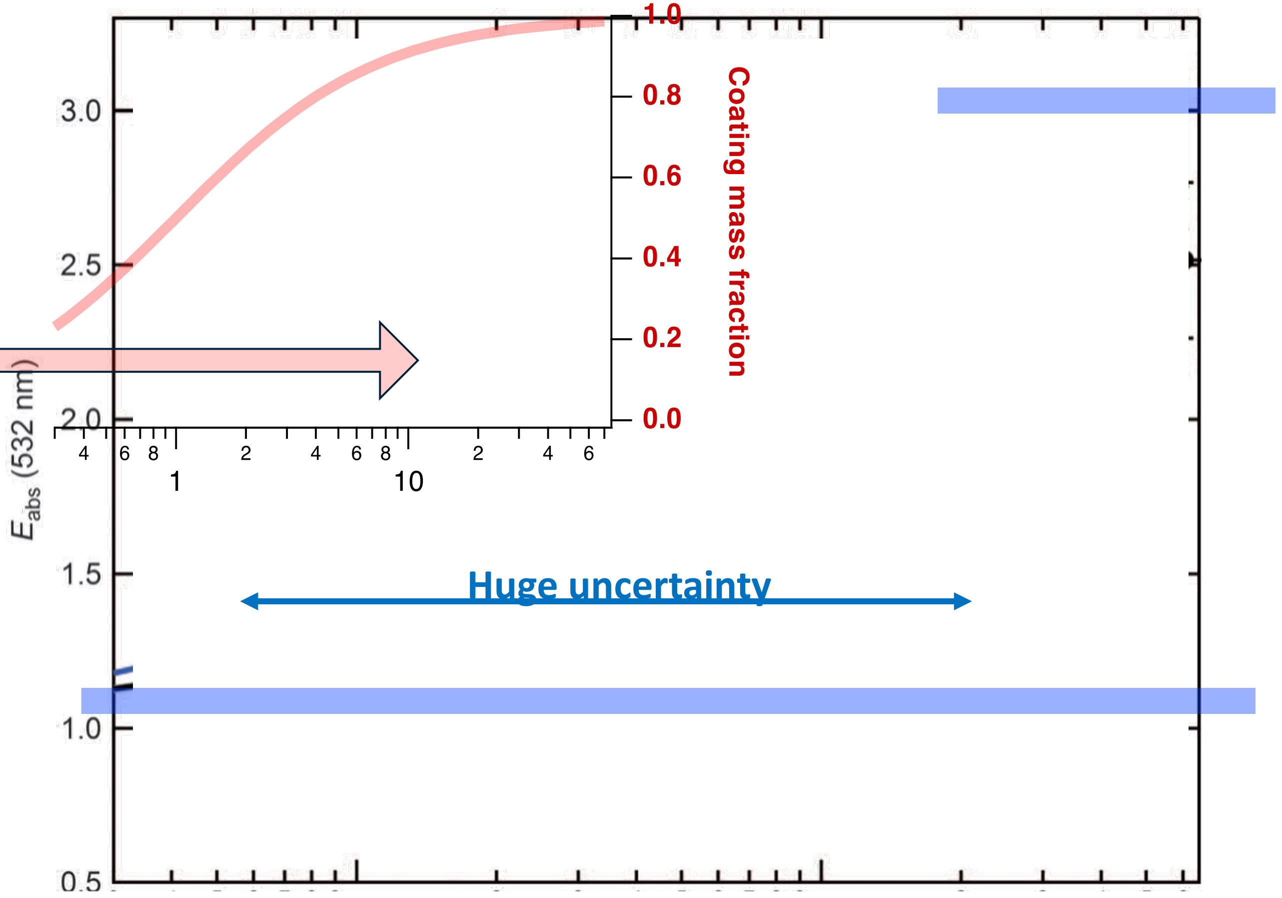






(Coating mass fraction) $f_c = c/(c + \mathrm{BC})$ vs. $\mathbf{R} = \mathrm{c/BC}$

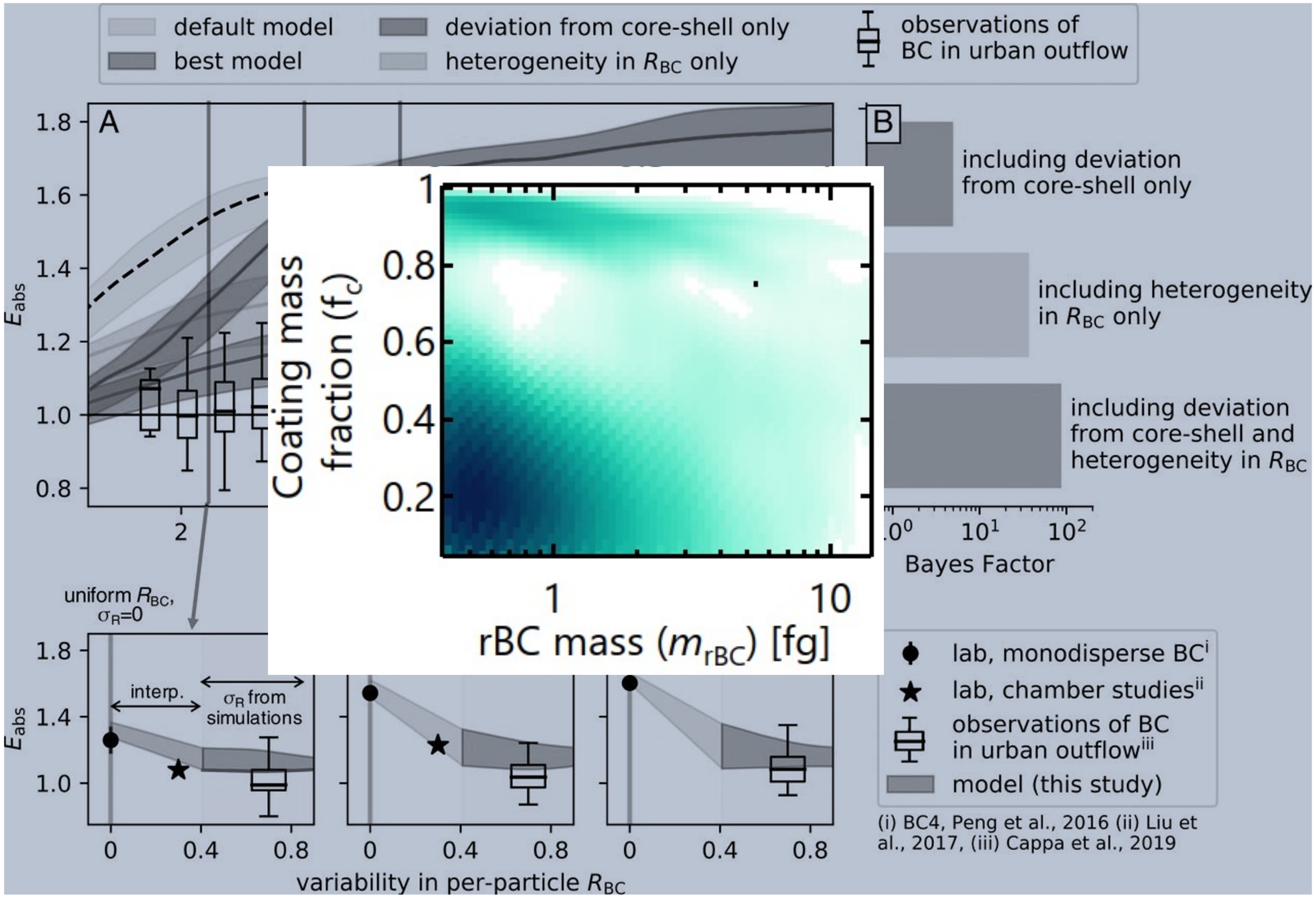




R = Coating mass / soot mass

Corbin, Sipkens, Moallemi, Olfert et al., in prep

We need these measurements across the globe!



1. **Different climates**
2. **Cloud processing**
3. **Wildfires**

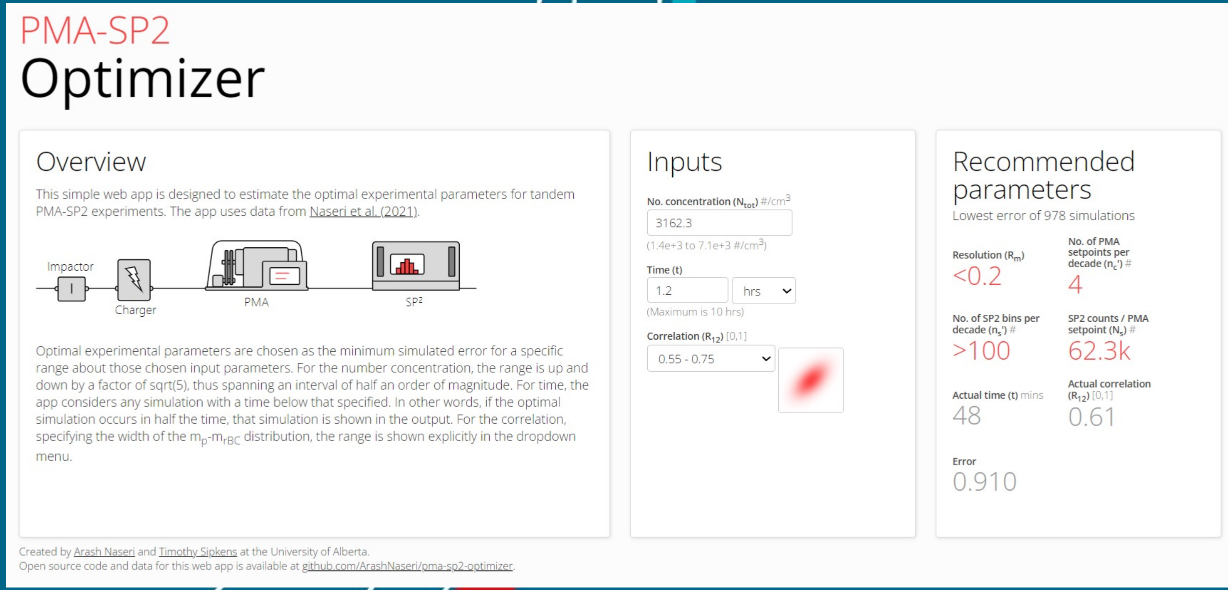
Thank you!

Joel.Corbin@nrc-cnrc.gc.ca

Code:

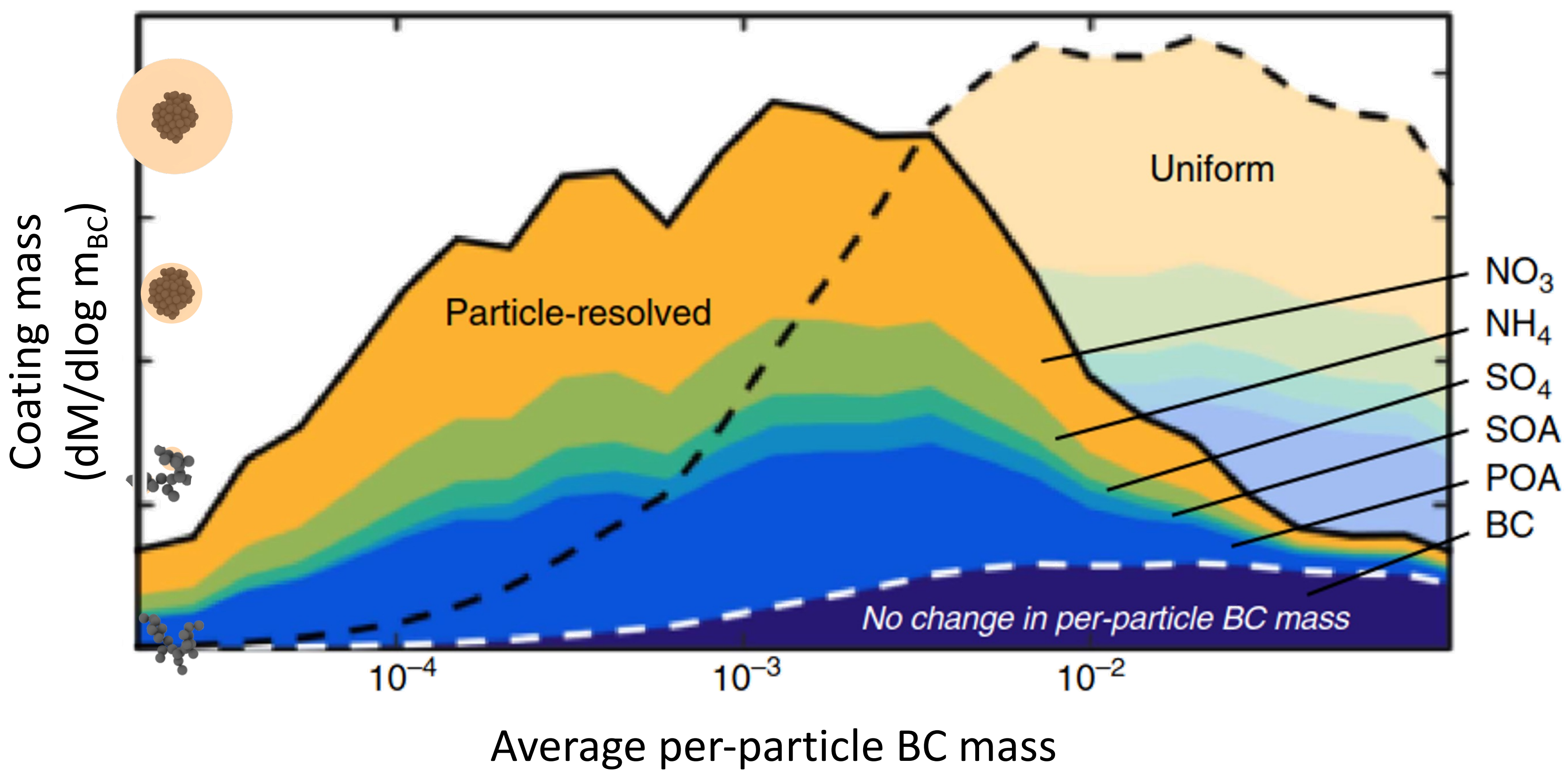
https://arashnaseri.github.io/empirical-cpma-tfer/

https://arashnaseri.github.io/pma-sp2-optimizer/



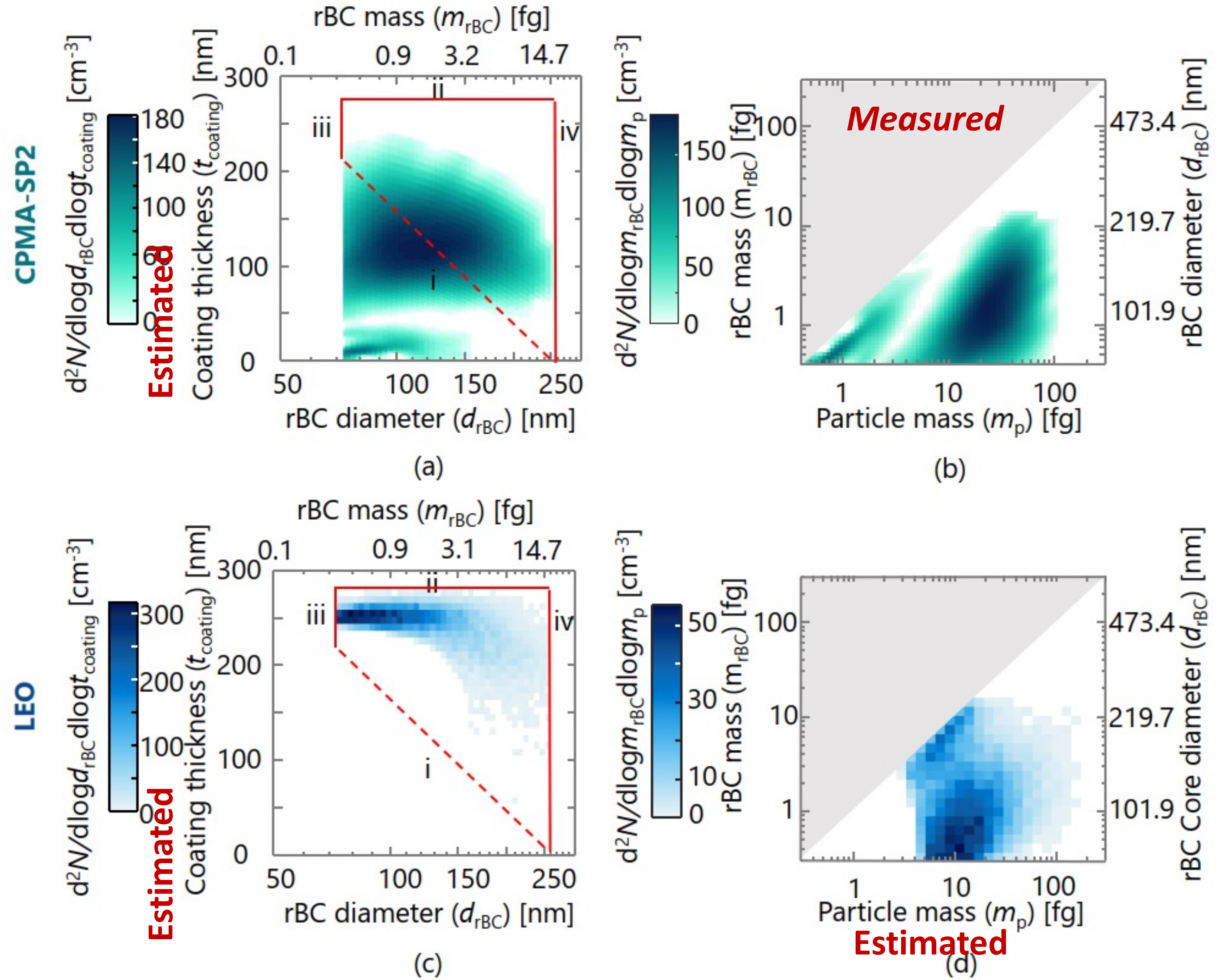
Backup

Condensation + coagulation → variability in BC coating



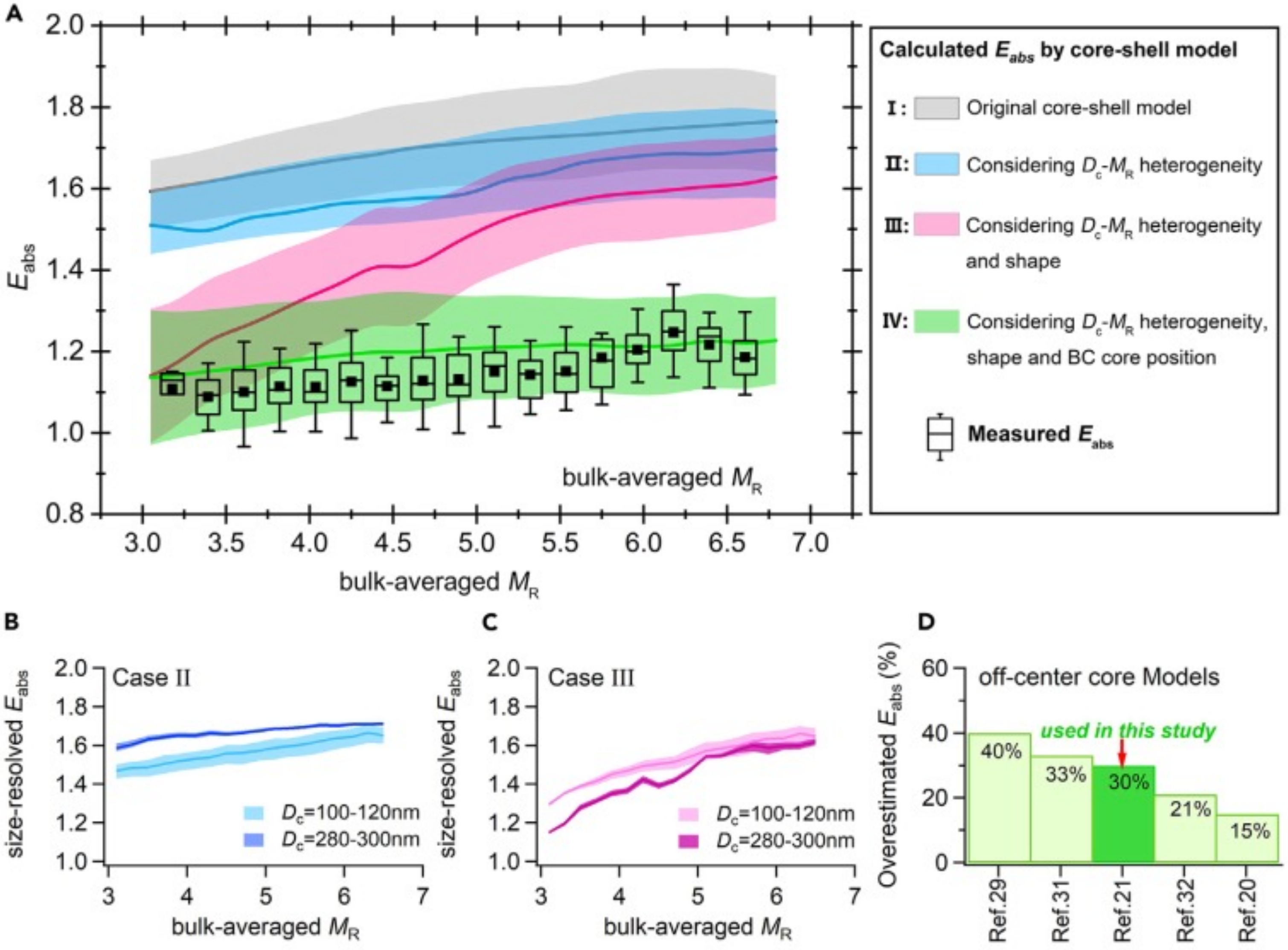
Model results *(Fierce et al., N Comm 2016)*

“SP2” view


CPMA-SP2
LEO
rBC mass (m_{rBC}) [fg]
Coating thickness ($t_{coating}$) [nm]
rBC diameter (d_{rBC}) [nm]
$d^2N/dlogd_{rBC}dlogt_{coating}$ [cm^{-3}]
$d^2N/dlogm_{rBC}dlogm_p$ [cm^{-3}]
rBC mass (m_{rBC}) [fg]
Particle mass (m_p) [fg]
rBC diameter (d_{rBC}) [nm]
rBC Core diameter (d_{rBC}) [nm]
Measured
Estimated
Estimated
Estimated
i
ii
iii
iv
(a)
(b)
(c)
(d)

DMA-SP2 method:

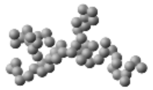
Unknown accuracy



Xiao-Feng Huang et al., One Earth 2024

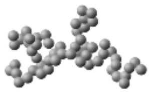
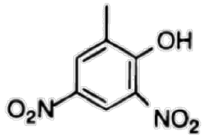
Corbin et al., Nature npj Clim Atmos Sci 2019

Defining and measuring ~~BC~~ Light-Absorbing Carbon

Property	**Soot BC**	**Tar brC**
Solubility[a]	Negligible solubility in common solvents	
Light absorption	300–1000 nm [detected as **eBC** at NIR λ]	
Chemical state	Contorted graphene layers	
Carbon bonding	sp^2 dominated	
Vapourization at[b]	$\sim$ 4000 K [**EC**, **rBC**]	
Produced by	Flame synthesis	
Morphology		
Diameter[c] [μm]	0.02–0.2	0.03–0.3

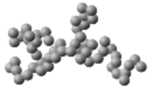
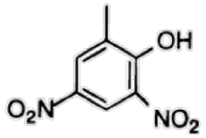
Corbin et al., Nature npj Clim Atmos Sci 2019

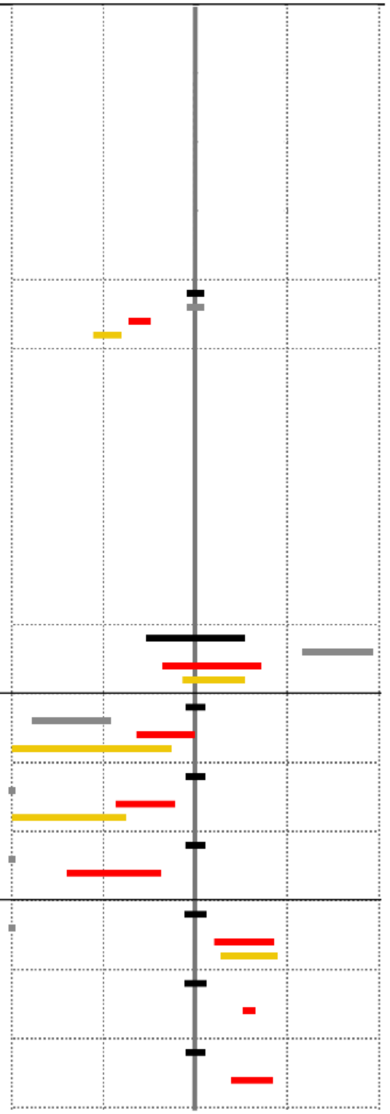
Defining and measuring Light-Absorbing Carbon

Property	LAC type: Soot BC	Char BC	Tar brC	Soluble brC
Solubility[a]	Negligible solubility in common solvents			Soluble
Light absorption	300–1000 nm [detected as **eBC** at NIR λ]			300–600 nm
Chemical state	Contorted graphene layers		Amorphous	Distinct molecules
Carbon bonding	sp^2 dominated		sp^2 and sp^3	sp^2 and sp^3
Vapourization at[b]	$\sim$ 4000 K [**EC**, **rBC**]		$\sim$ 1000 K [**EC**]	$<$ 600 K
Produced by	Flame synthesis	Fuel-droplet pyrolysis	Partial pyrolysis	Oxidation, pyrolysis, ...
Morphology				
Diameter[c] [μm]	0.02–0.2	1–5	0.03–0.3	0.05–0.2

Corbin et al., Nature npj Clim Atmos Sci 2019

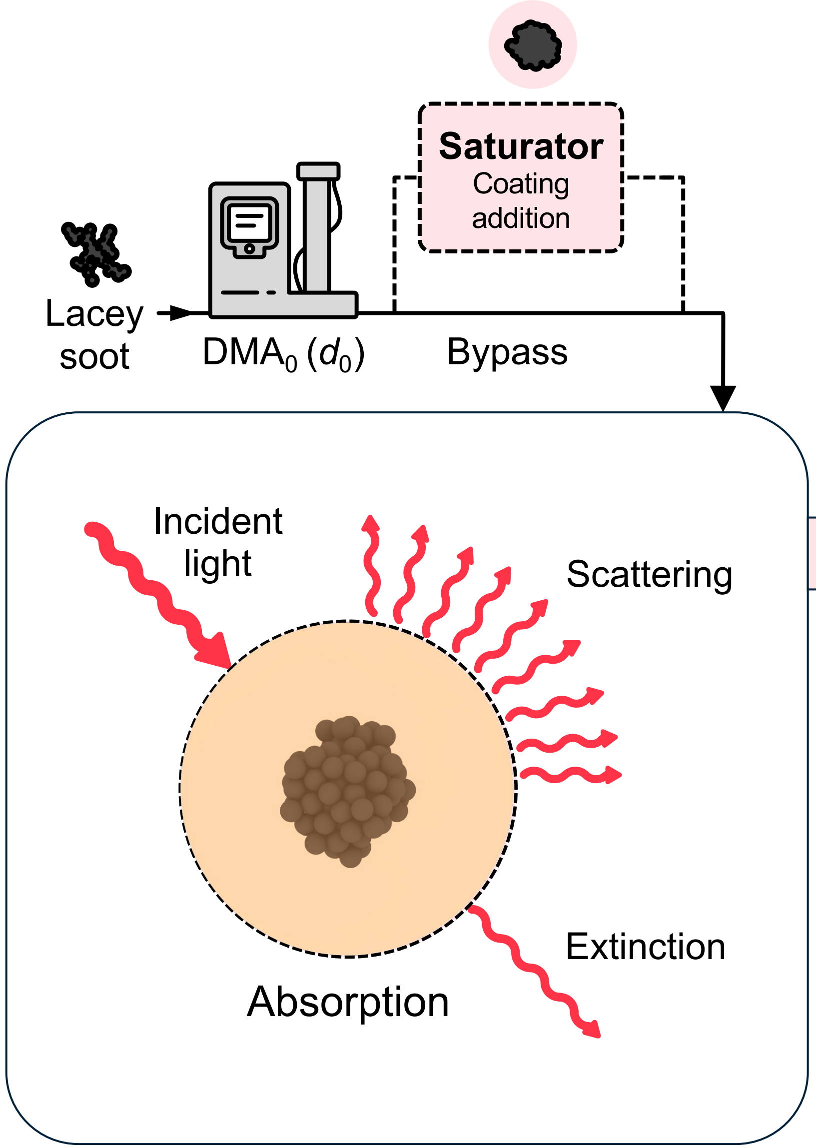
Defining and measuring Light-Absorbing Carbon

Property	LAC type: Soot BC ●	Char BC ●	Tar brC ●	Soluble brC ●
Solubility[a]	Negligible solubility in common solvents			Soluble
Light absorption	300–1000 nm [detected as **eBC** at NIR λ]			300–600 nm
Chemical state	Contorted graphene layers		Amorphous	Distinct molecules
Carbon bonding	sp^2 dominated		sp^2 and sp^3	sp^2 and sp^3
Vapourization at[b]	~ 4000 K [EC, rBC]		~ 1000 K [EC]	< 600 K
Produced by	Flame synthesis	Fuel-droplet pyrolysis	Partial pyrolysis	Oxidation, pyrolysis, ...
Morphology				
Diameter[c] [μm]	0.02–0.2	1–5	0.03–0.3	0.05–0.2
MAE (370 nm)[d] [m^2/g]	11.1 ± 1.8	0.2–1.2	2.7–9.9	≪0.1–6.0
MAE (550 nm)[d] [m^2/g]	7.5 ± 1.2	0.2–1.3	1.1–4.1	≪0.1–1.2
MAE (880 nm)[d] [m^2/g]	4.7 ± 0.8	0.2–1.5	0.2–1.8	n.a.[e]
AAE (370, 530 nm)[d]	0.8–1.2	-0.3 to -0.1	1.7–6.5	2–7
AAE (370, 950 nm)[d]	0.8–1.2	-0.2 to 0.0	3.5–4.0	n.a.[e]
AAE (880, 950 nm)[d]	0.8–1.1	-0.3 to 0.0	2.5–6	n.a.[e]

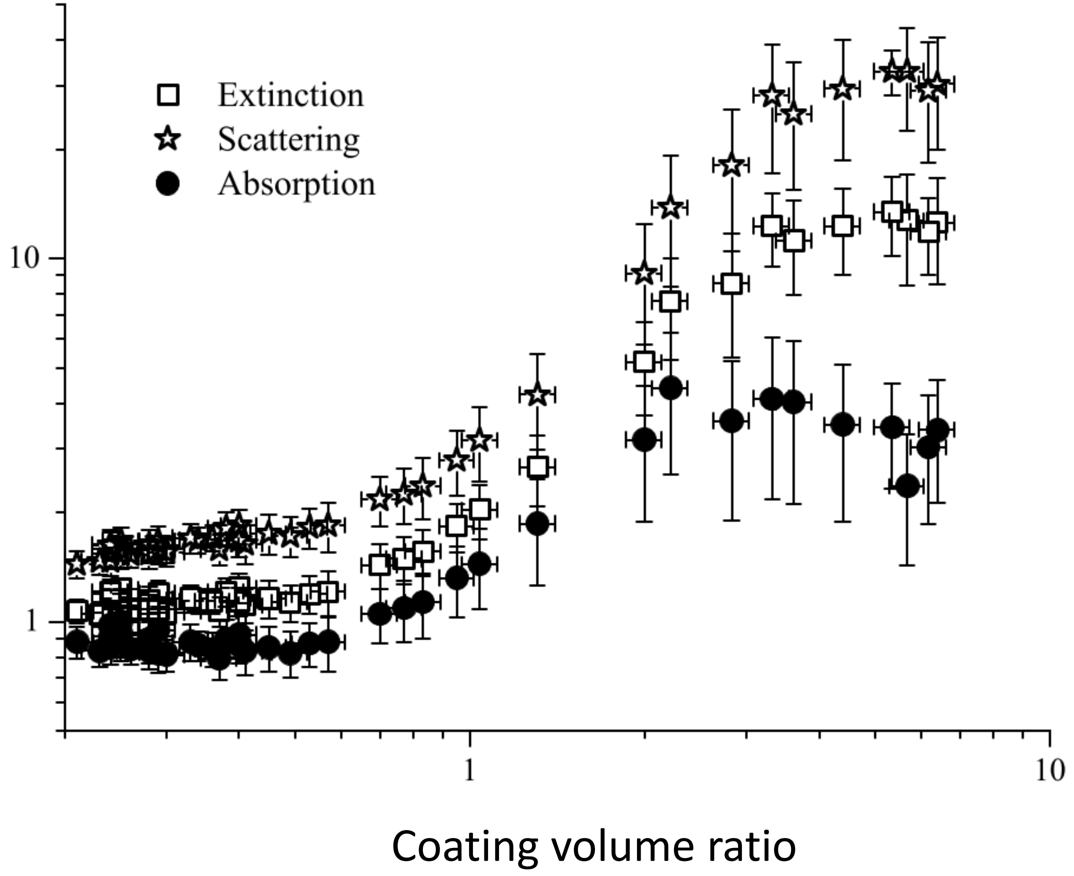


 New categorization of light-absorbing carbon (LAC) in the atmosphere.

Soot coating experiments → E_{abs} 1…10

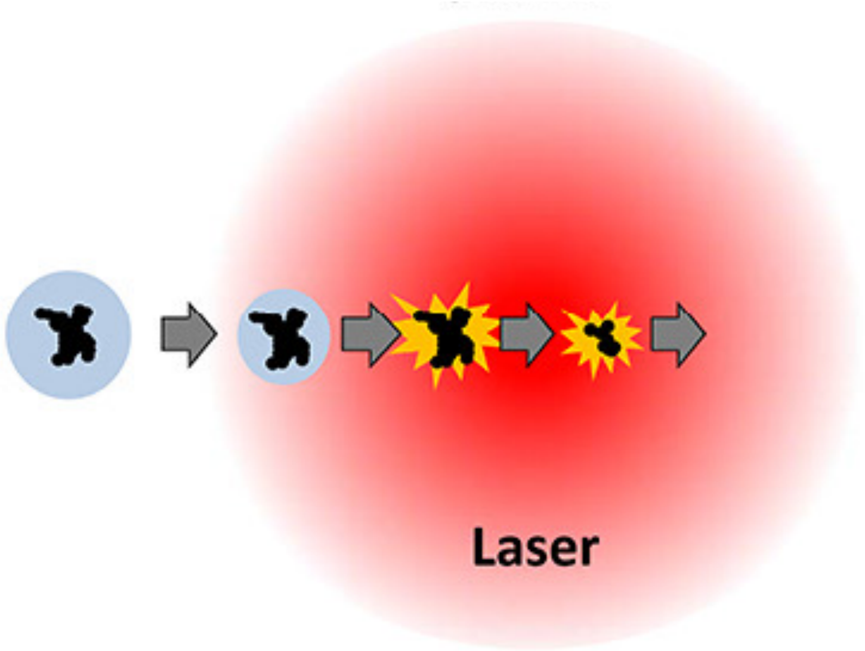


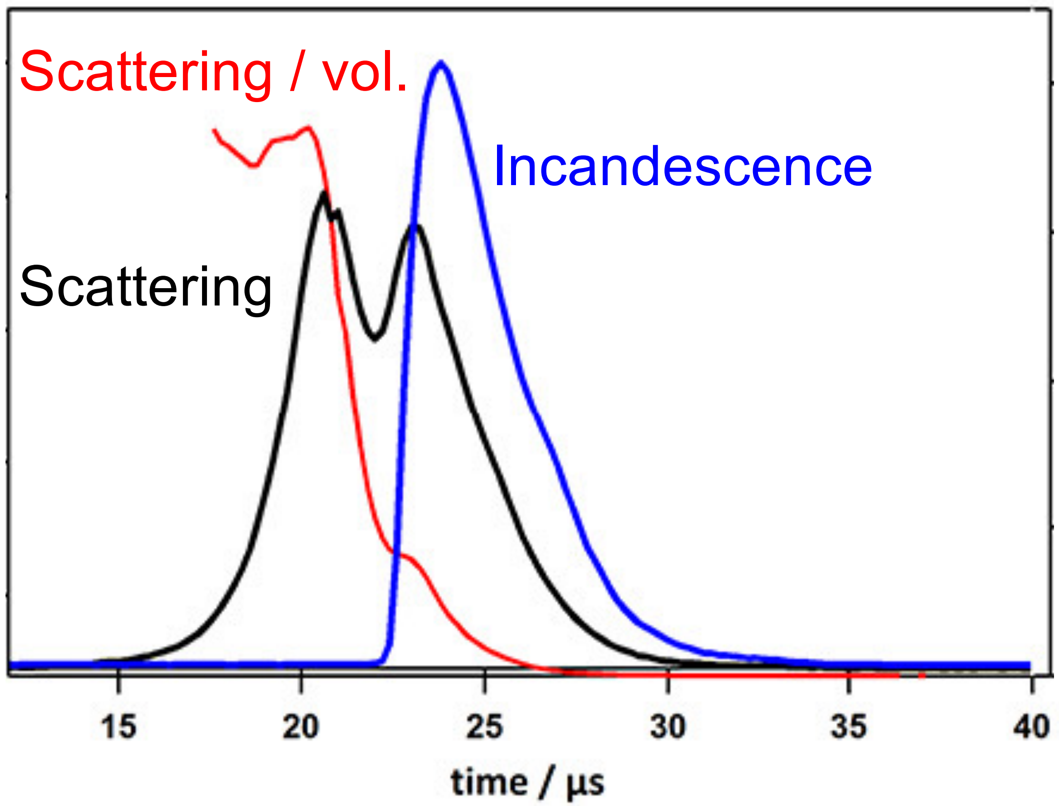
$$E_{abs} = \frac{\text{coated absn}}{\text{initial absn}}$$



Mikhailov et al, GRL 2006. Coating thickness via mass change.

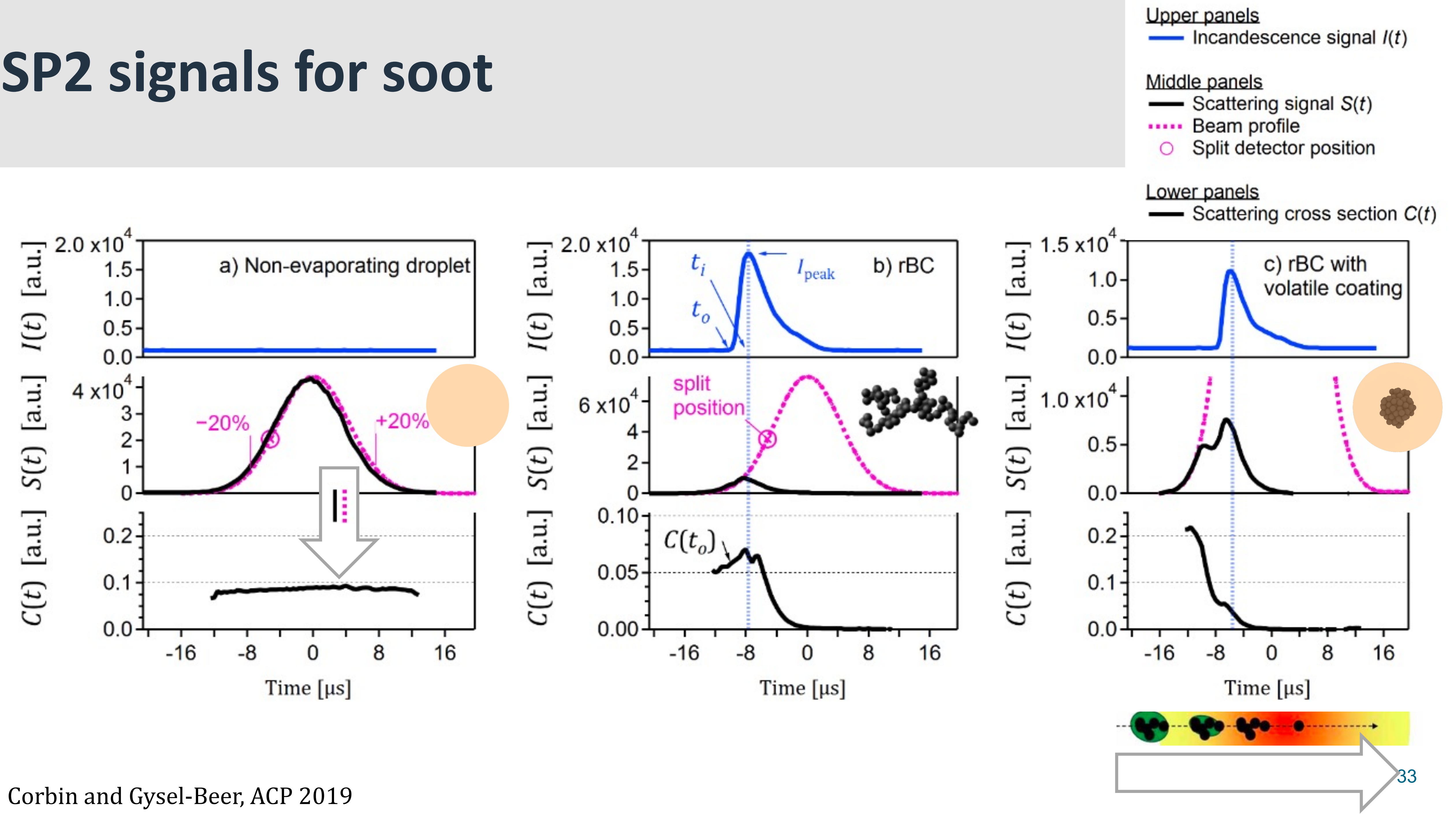
SP2





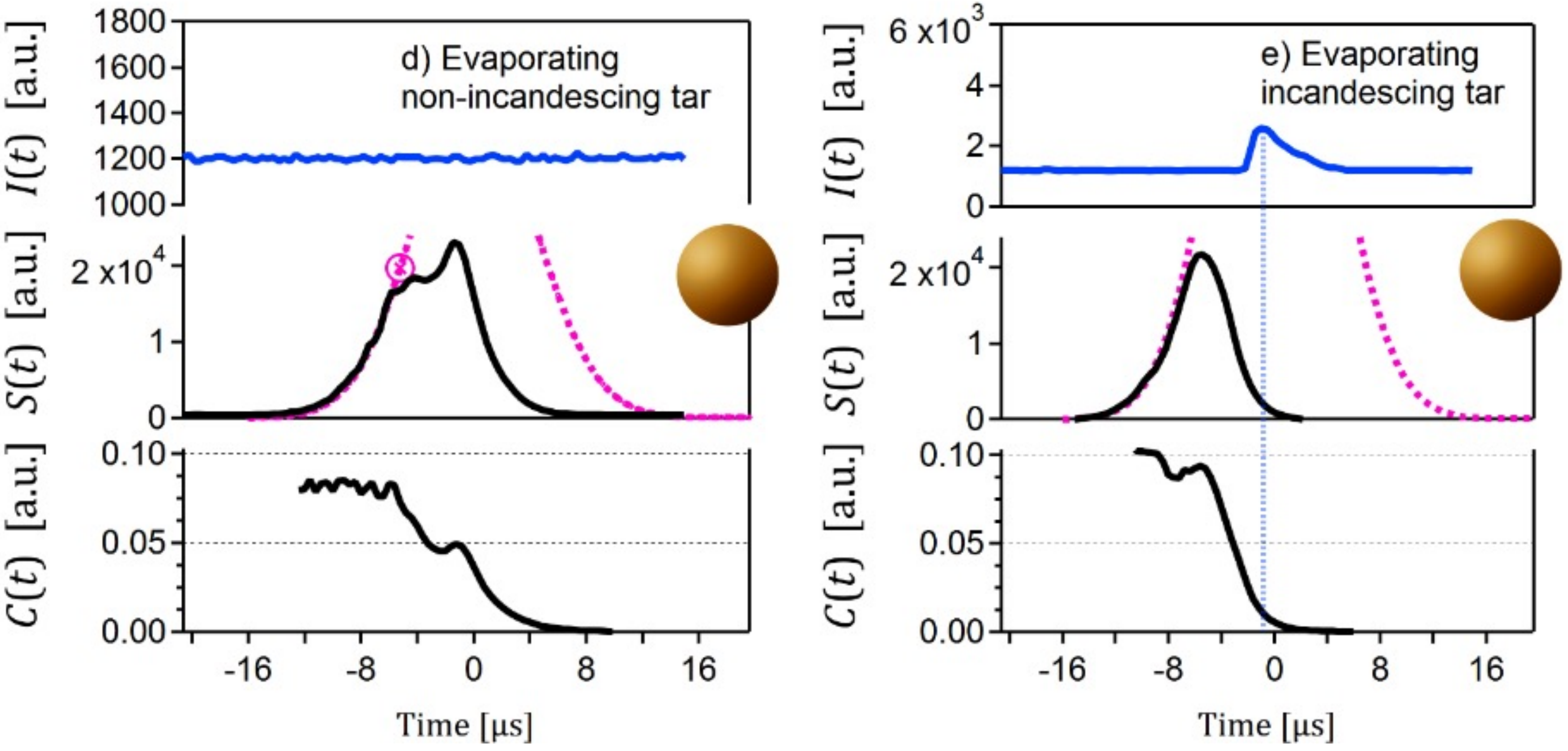
Modified from M. Gysel, PSI Switzerland

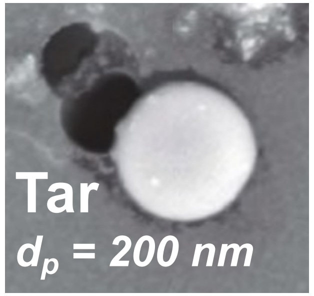
SP2 signals for soot



Corbin and Gysel-Beer, ACP 2019

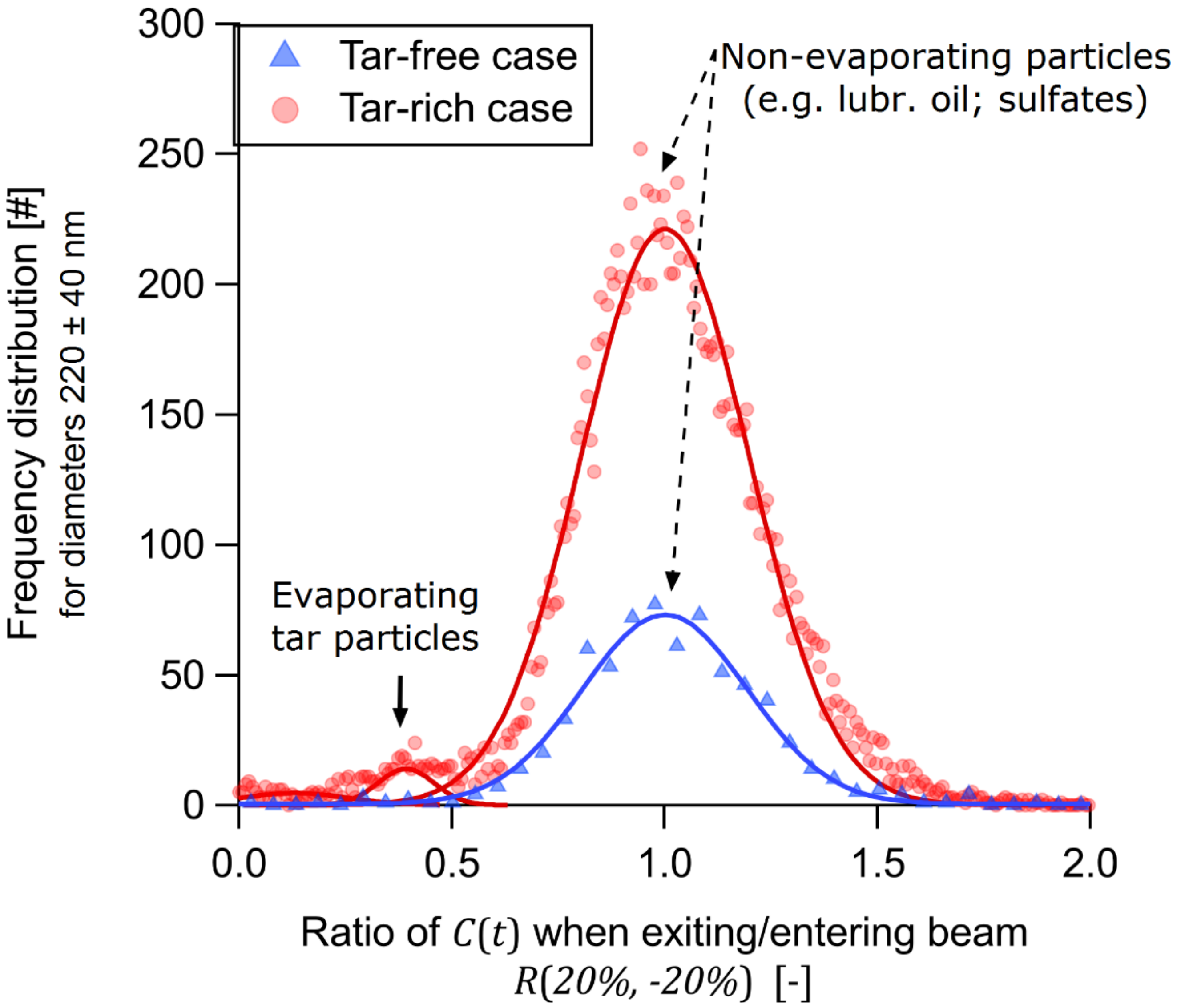
Anomalous SP2 signals: identified as tar





Identification as tar described in ***Corbin et al.*** [*Nature npj Climate & Atmos. Science 2019*]

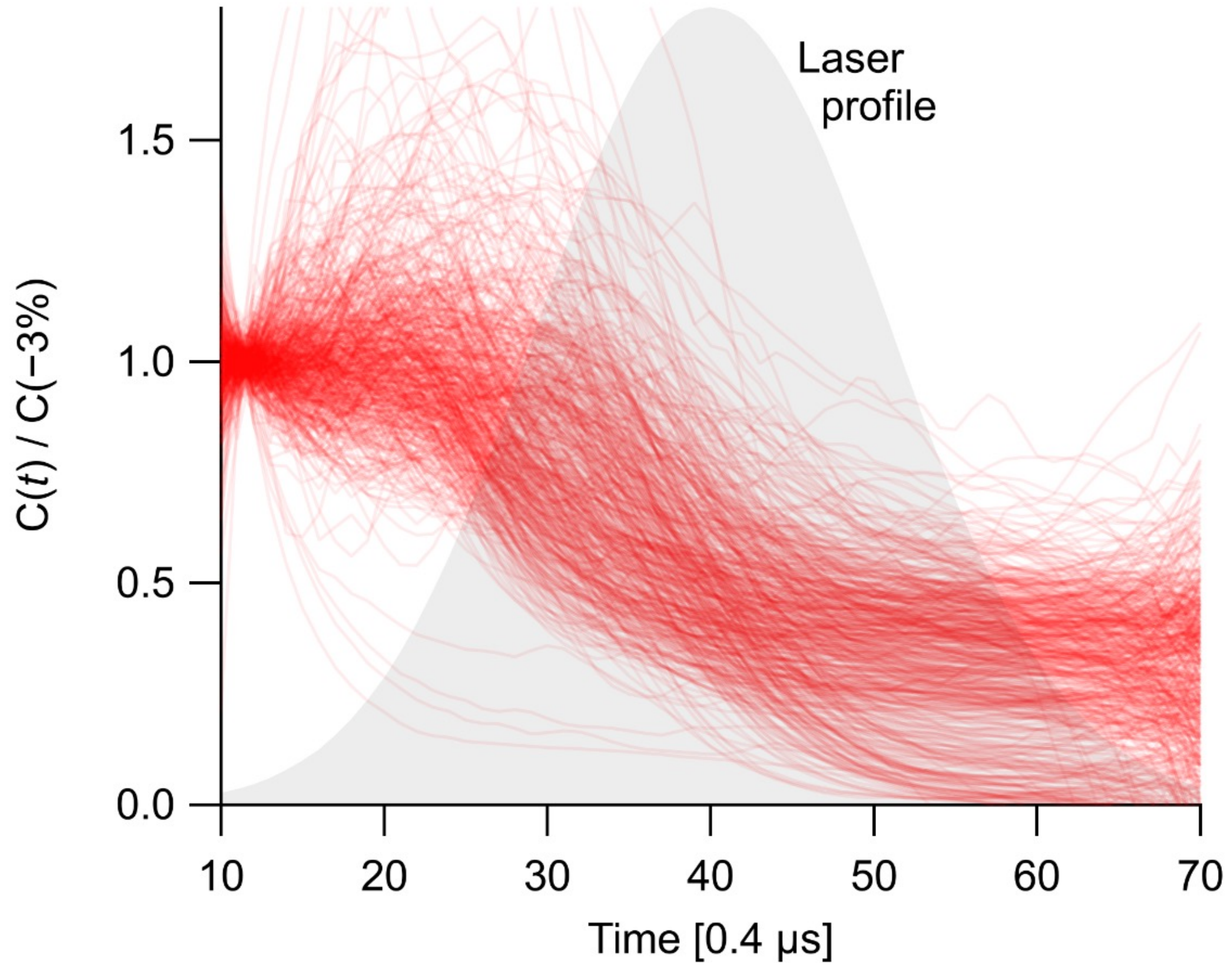
Evaporating, non-incandescing tar [1/2]



578 of 2.5×10^5 particles partially evaporated.

False negatives not quantified.

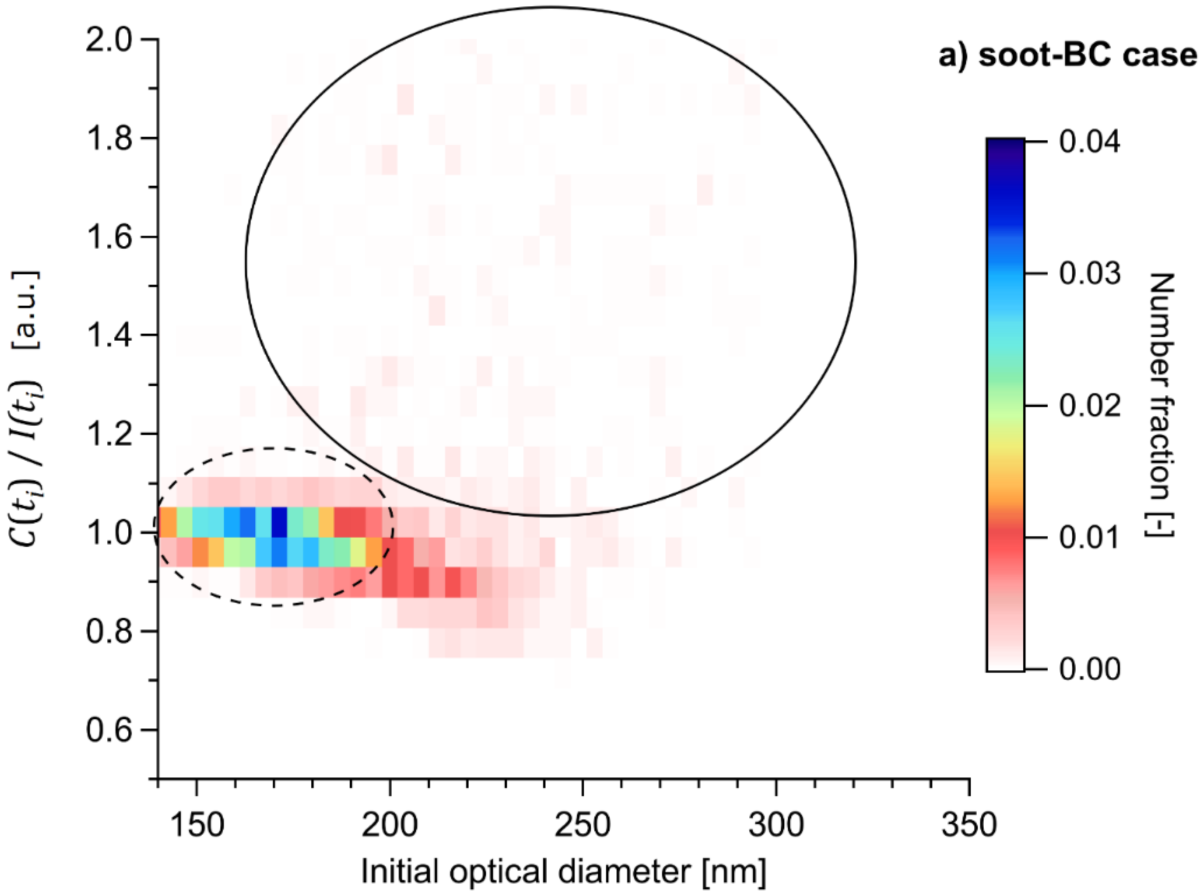
Evaporating, non-incandescing tar [2/2]

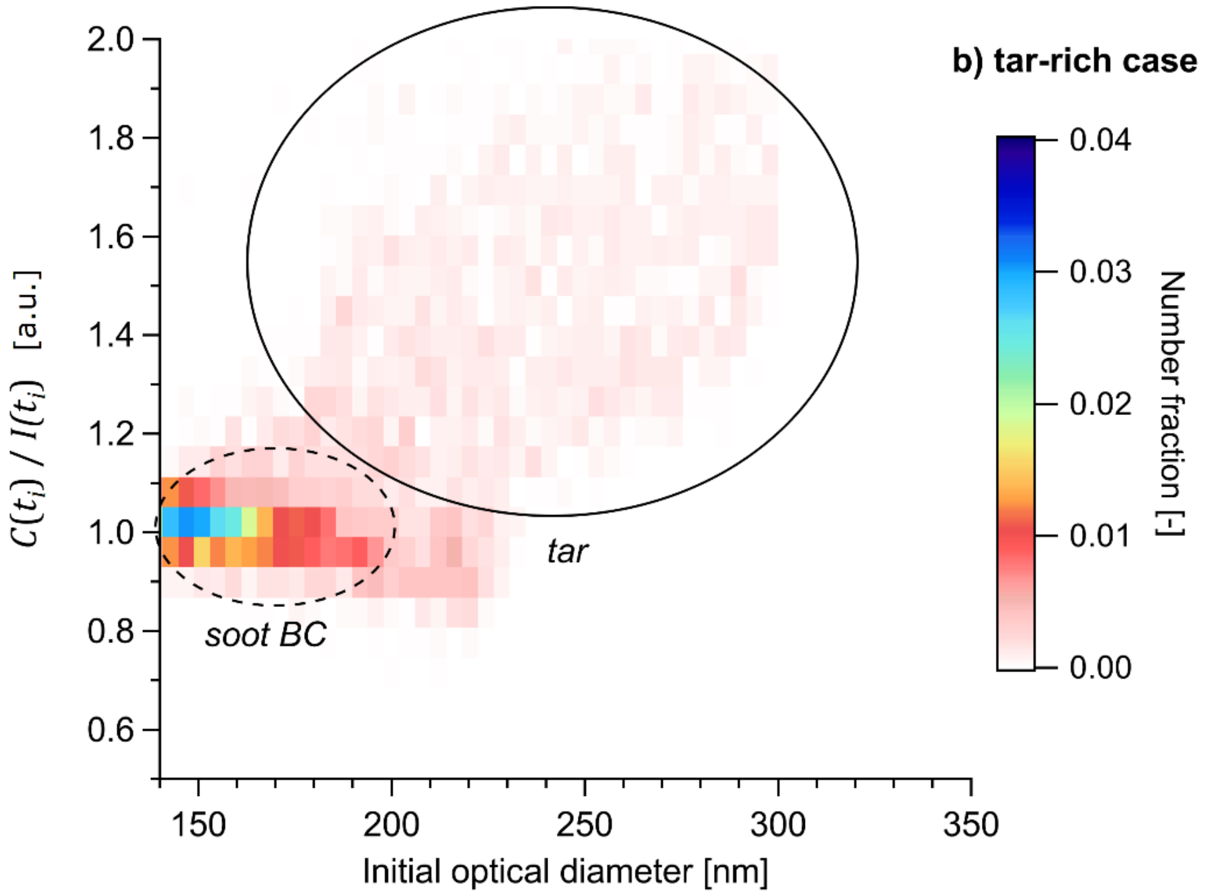


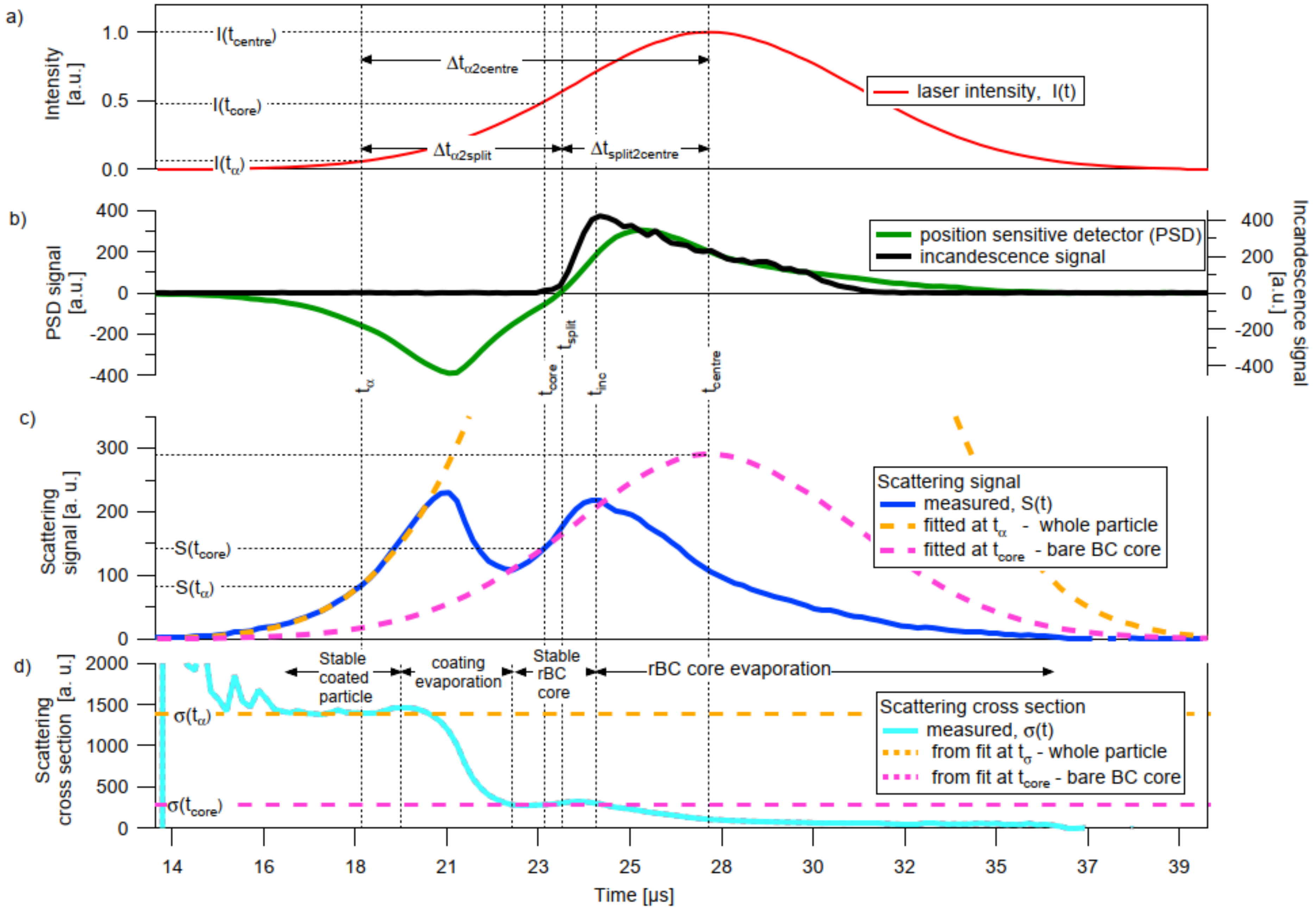
Overall trends show similar behaviour.

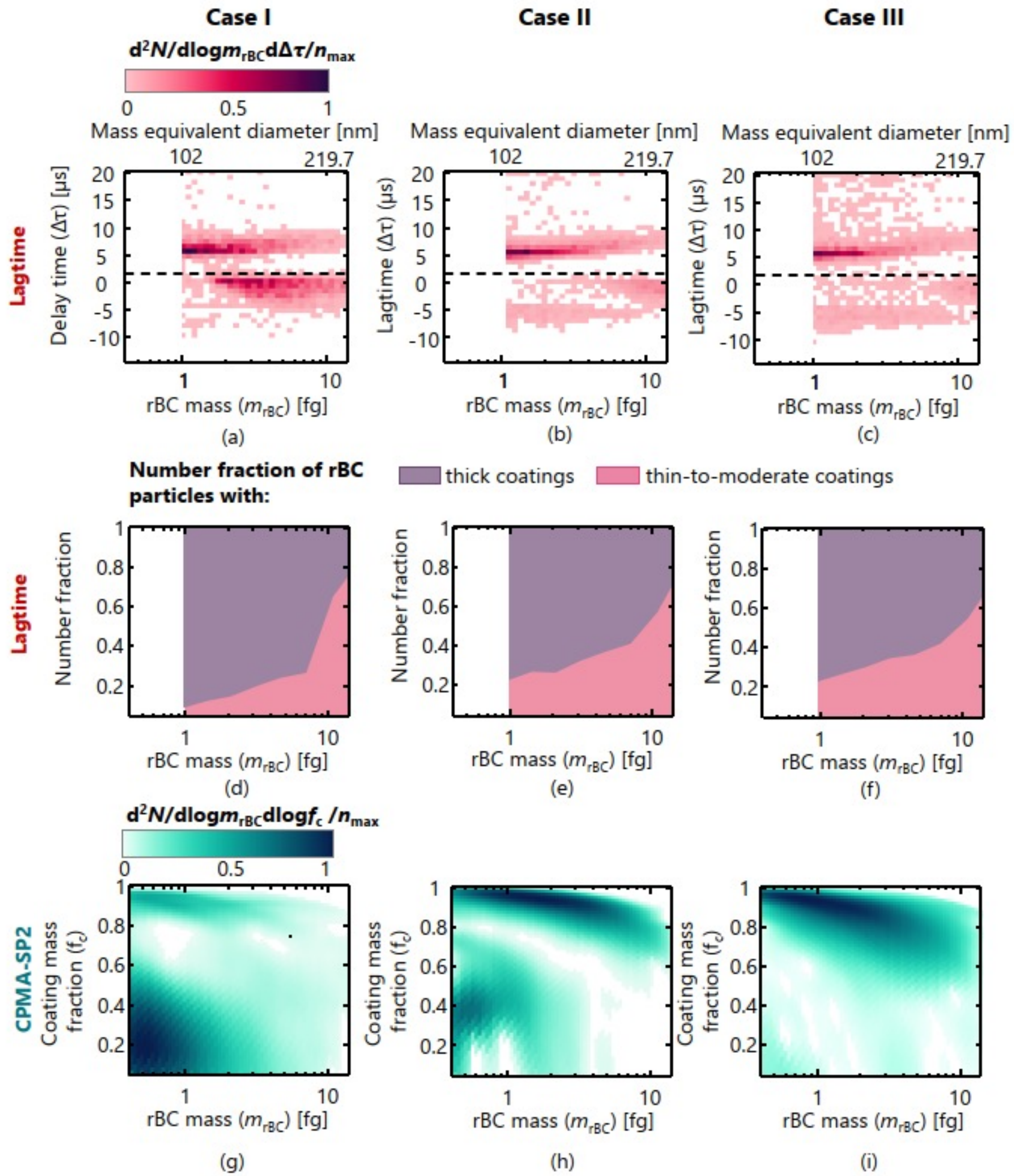
All normalized to $C(-3\%)$.

Incandescing tar identified in combination with light-scattering analysis

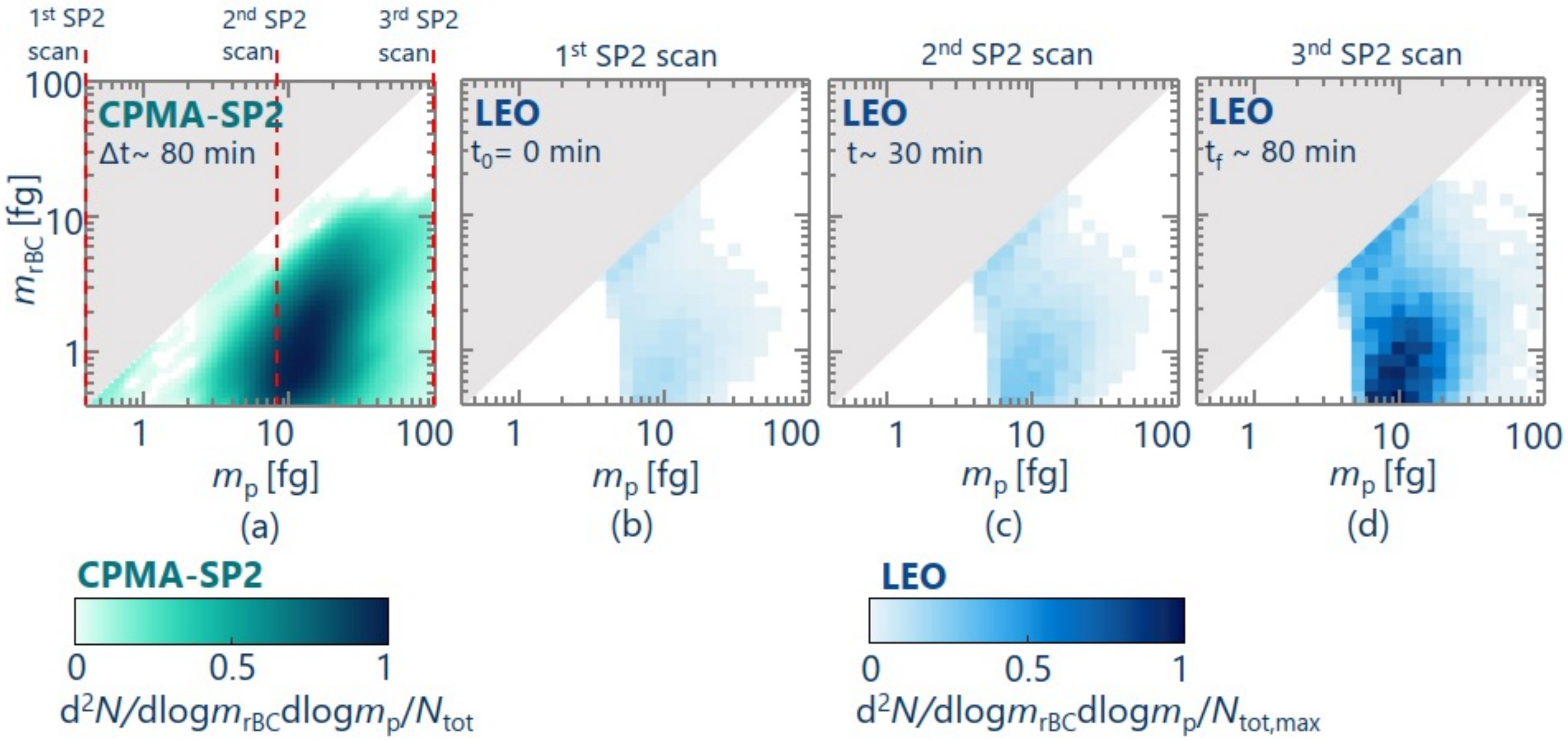




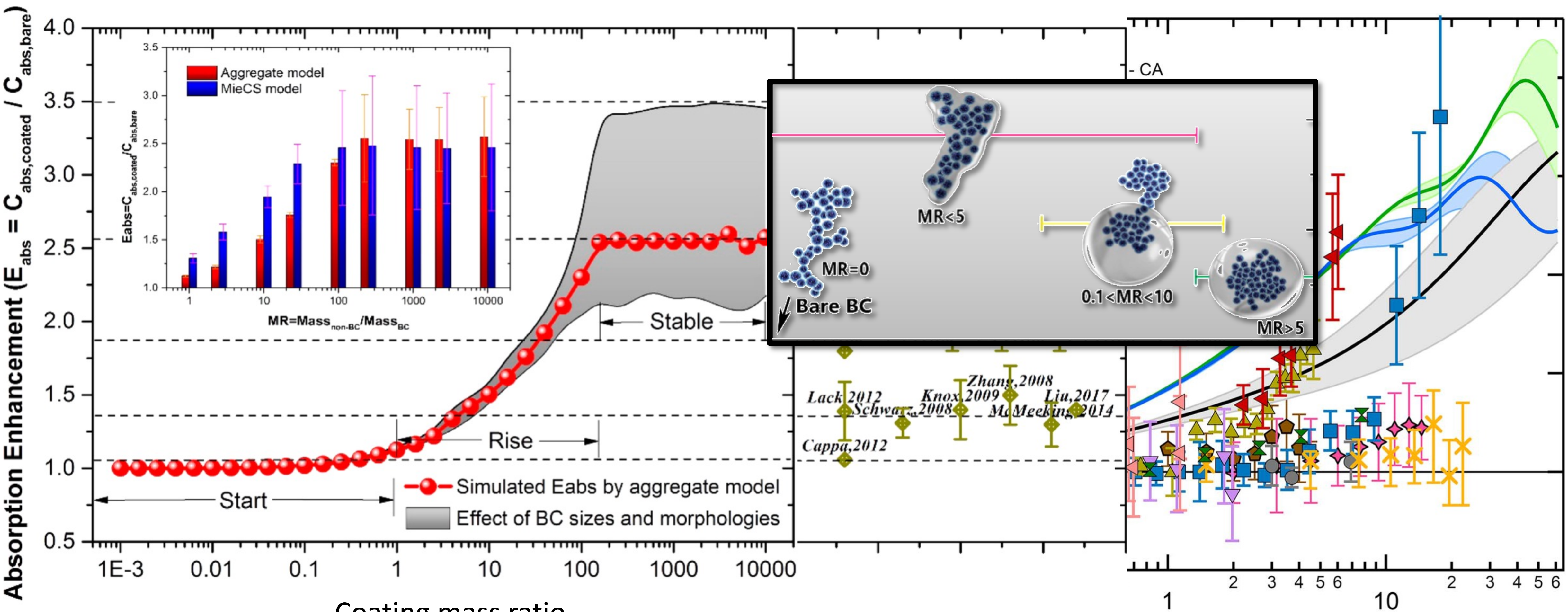

a)
Intensity [a.u.]
I(t_centre)
I(t_core)
I(t_α)
Δt_α2centre
Δt_α2split
Δt_split2centre
laser intensity, I(t)
b)
PSD signal [a.u.]
Incandescence signal [a.u.]
position sensitive detector (PSD)
incandescence signal
t_α
t_core
t_split
t_inc
t_centre
c)
Scattering signal [a. u.]
S(t_core)
S(t_α)
Scattering signal
measured, S(t)
fitted at t_α - whole particle
fitted at t_core - bare BC core
d)
Scattering cross section [a. u.]
σ(t_α)
σ(t_core)
Stable coated particle
coating evaporation
Stable rBC core
rBC core evaporation
Scattering cross section
measured, σ(t)
from fit at t_σ - whole particle
from fit at t_core - bare BC core
Time [µs]


Case I
Case II
Case III
$d^2N/dlogm_{rBC}d\Delta\tau/n_{max}$
0
0.5
1
Mass equivalent diameter [nm]
102
219.7
Lagtime
Delay time (Δτ) [μs]
Lagtime (Δτ) (μs)
rBC mass (m_{rBC}) [fg]
(a)
(b)
(c)
Number fraction of rBC particles with:
thick coatings
thin-to-moderate coatings
Number fraction
(d)
(e)
(f)
$d^2N/dlogm_{rBC}dlogf_c/n_{max}$
CPMA-SP2
Coating mass fraction (f_c)
(g)
(h)
(i)

CPMA-SP2 slower than SP2-LEO



Variability in atmospheric E_{abs}



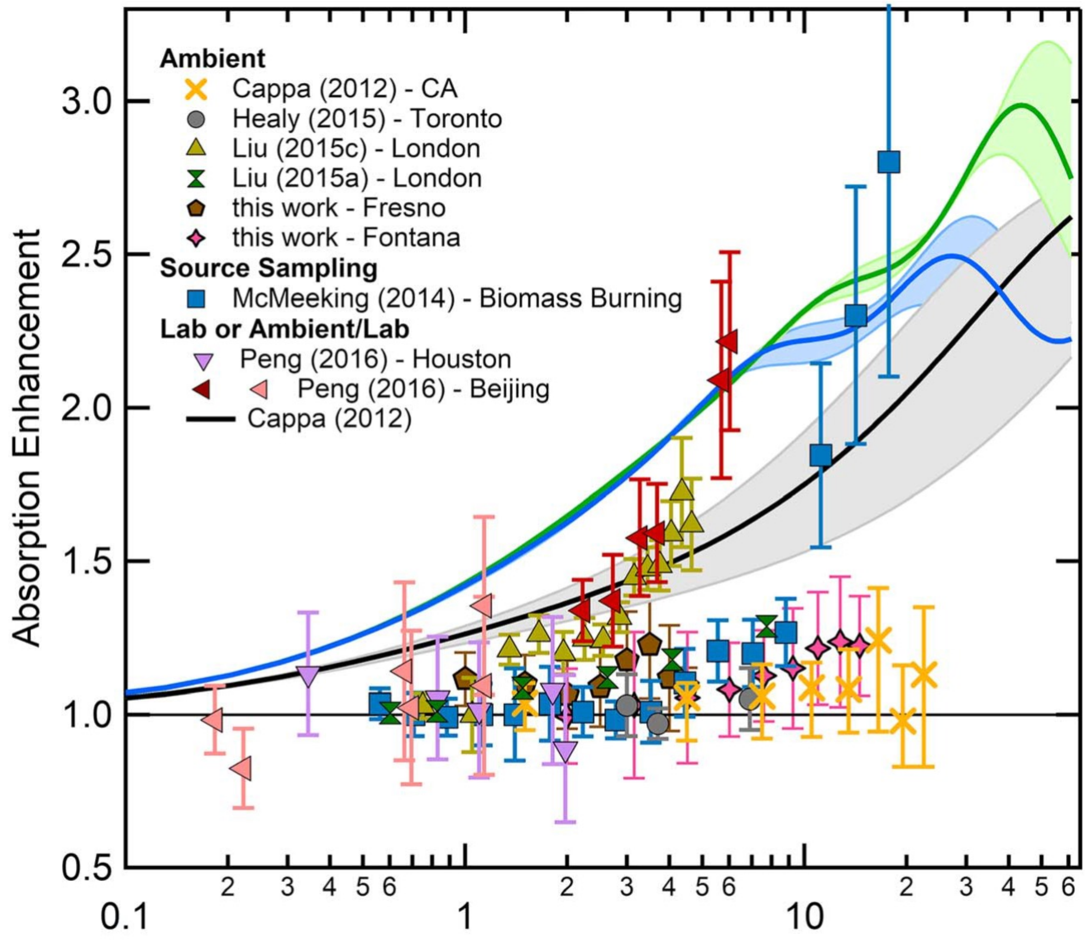
Coating mass ratio

Coating mass ratio

Yu Wu, Tianhai Cheng et al., EST 2012

Cappa et al., Science 2012; JGR 2019.

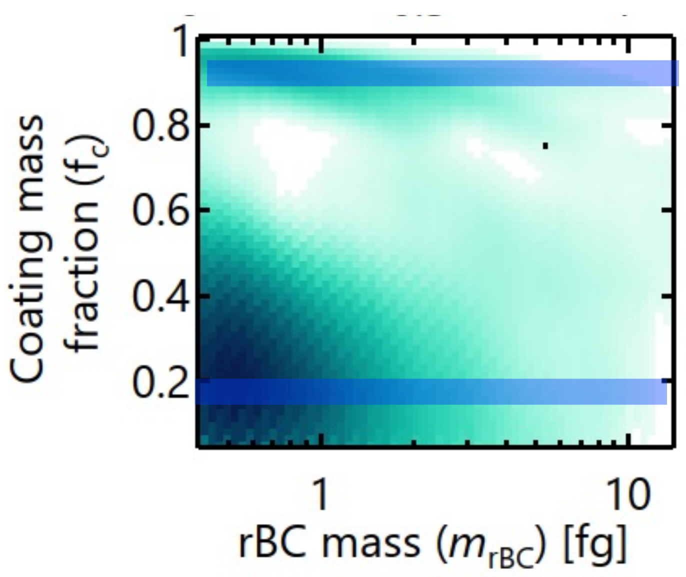
E_{abs} atm < lab

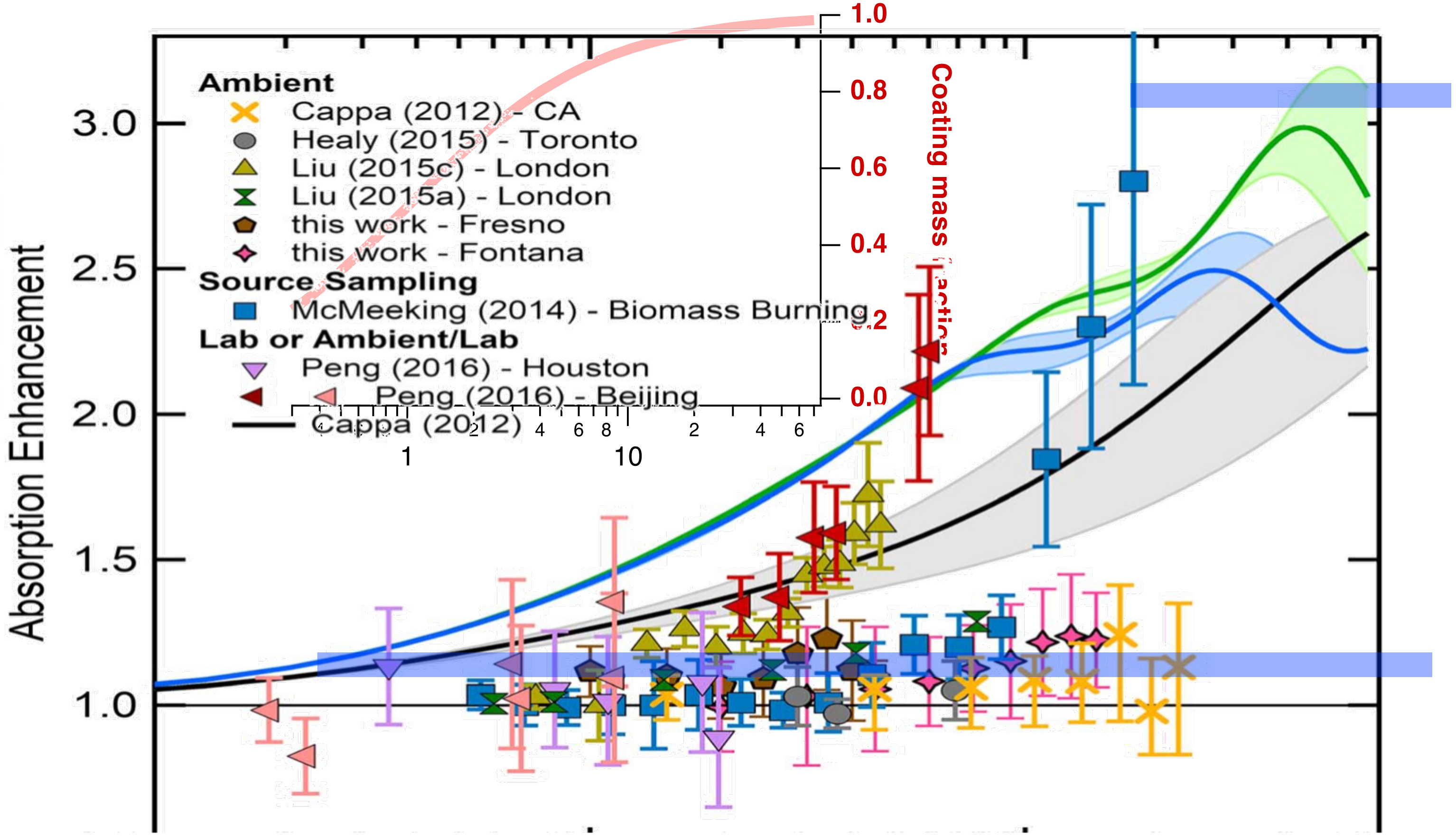


Coating mass ratio

Cappa et al., Science 2012; JGR 2019.

(Coating mass fraction) f_c vs. R (coating/BC ratio)





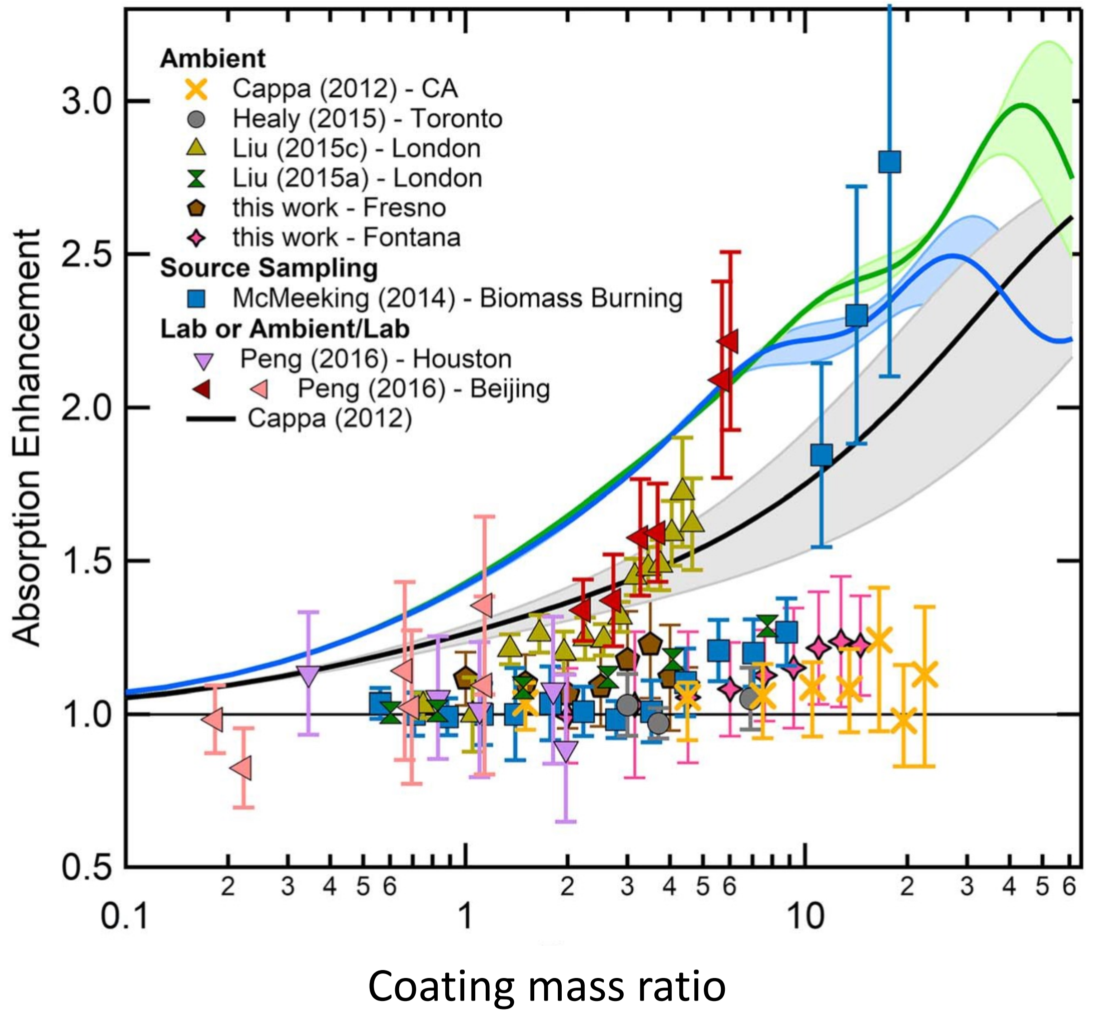
Coating mass ratio

Severe X-axis bias from bulk measurements of R.
CPMA-SP2 provides a solution.

Corbin, Sipkens, Moallemi, Olfert et al., in prep

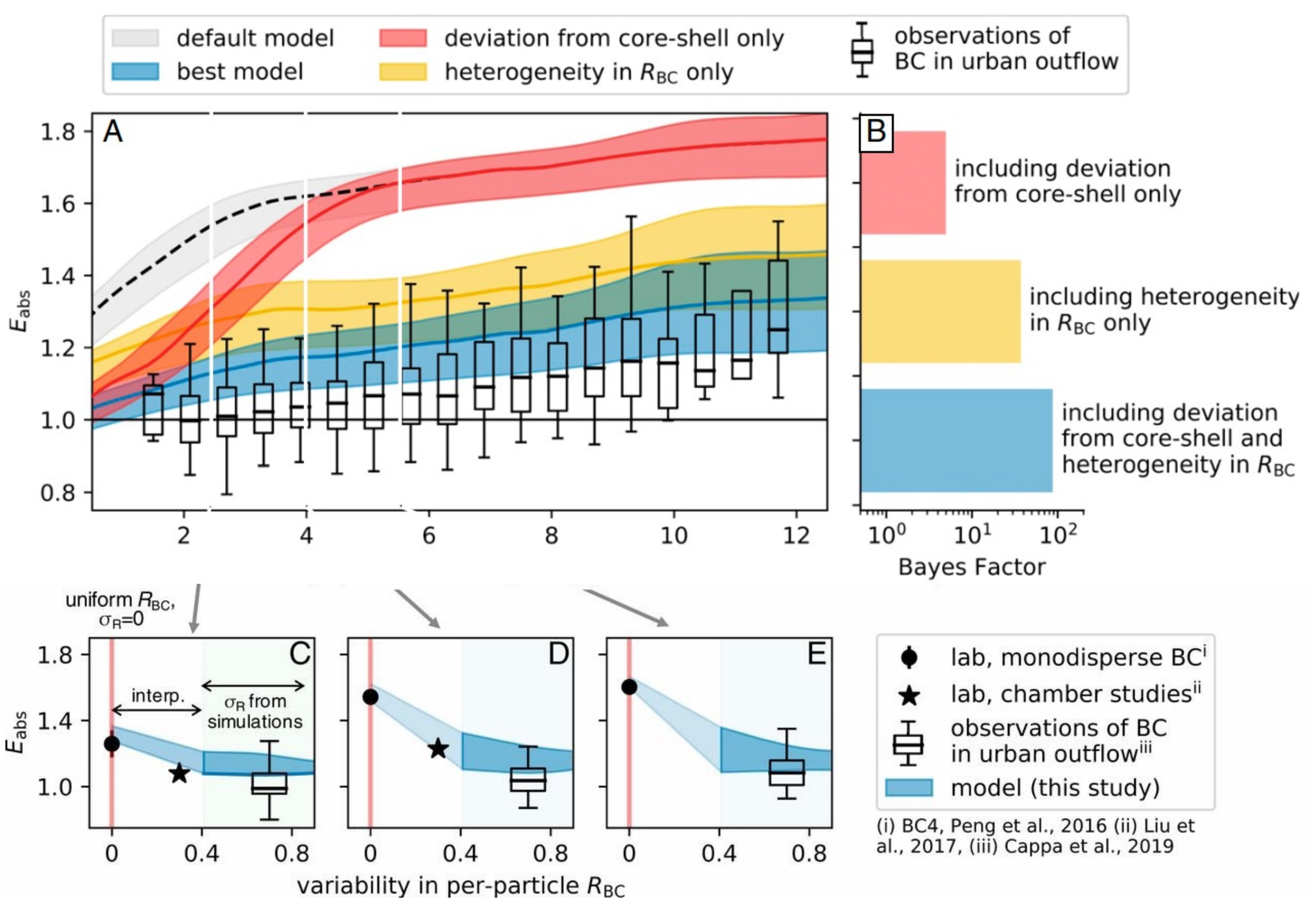
Cappa et al., Science 2012; JGR 2019.

E_{abs} atm < lab



Cappa et al., Science 2012; JGR 2019.

Fierce 2020


default model
best model
deviation from core-shell only
heterogeneity in R_{BC} only
observations of BC in urban outflow
A
E_{abs}
1.8
1.6
1.4
1.2
1.0
0.8
2
4
6
8
10
12
B
including deviation from core-shell only
including heterogeneity in R_{BC} only
including deviation from core-shell and heterogeneity in R_{BC}
10^0
10^1
10^2
Bayes Factor
uniform R_{BC}, σ_R=0
C
D
E
interp.
σ_R from simulations
0
0.4
0.8
variability in per-particle R_{BC}
lab, monodisperse BC[i]
lab, chamber studies[ii]
observations of BC in urban outflow[iii]
model (this study)
(i) BC4, Peng et al., 2016 (ii) Liu et al., 2017, (iii) Cappa et al., 2019