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Real-time detection of tar brown carbon by light-scattering and laser-induced incandescence

Joel C. Corbin [1,2] and Martin Gysel-Beer [2]

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Outline

npj | Climate and Atmospheric Science www.nature.com/npjclimatsci

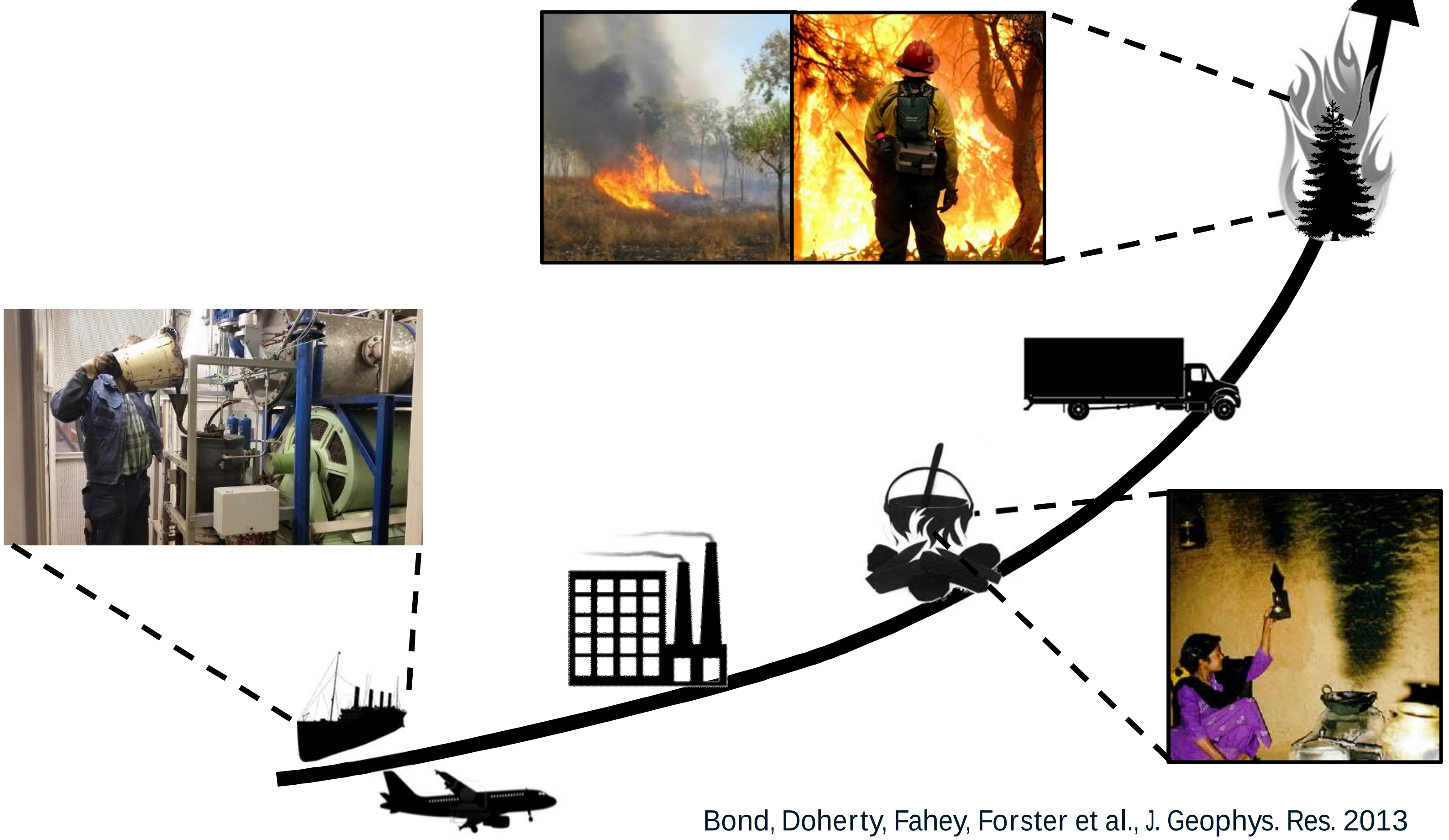
ARTICLE OPEN

Infrared-absorbing carbonaceous tar can dominate light absorption by marine-engine exhaust

J. C. Corbin[1,2], H. Czech[3,10], D. Massabò[4,5], F. Buatier de Mongeot[4], G. Jakobi[6,7], F. Liu[2], P. Lobo[2], C. Mennucci[4], A. A. Mensah[8], J. Orasche[3,7], S. M. Pieber[1,11], A. S. H. Prévôt[1], B. Stengel[6,9], L.-L. Tay[2], M. Zanatta[1,12], R. Zimmermann[3,6,8], I. El Haddad[1] and M. Gysel[1]

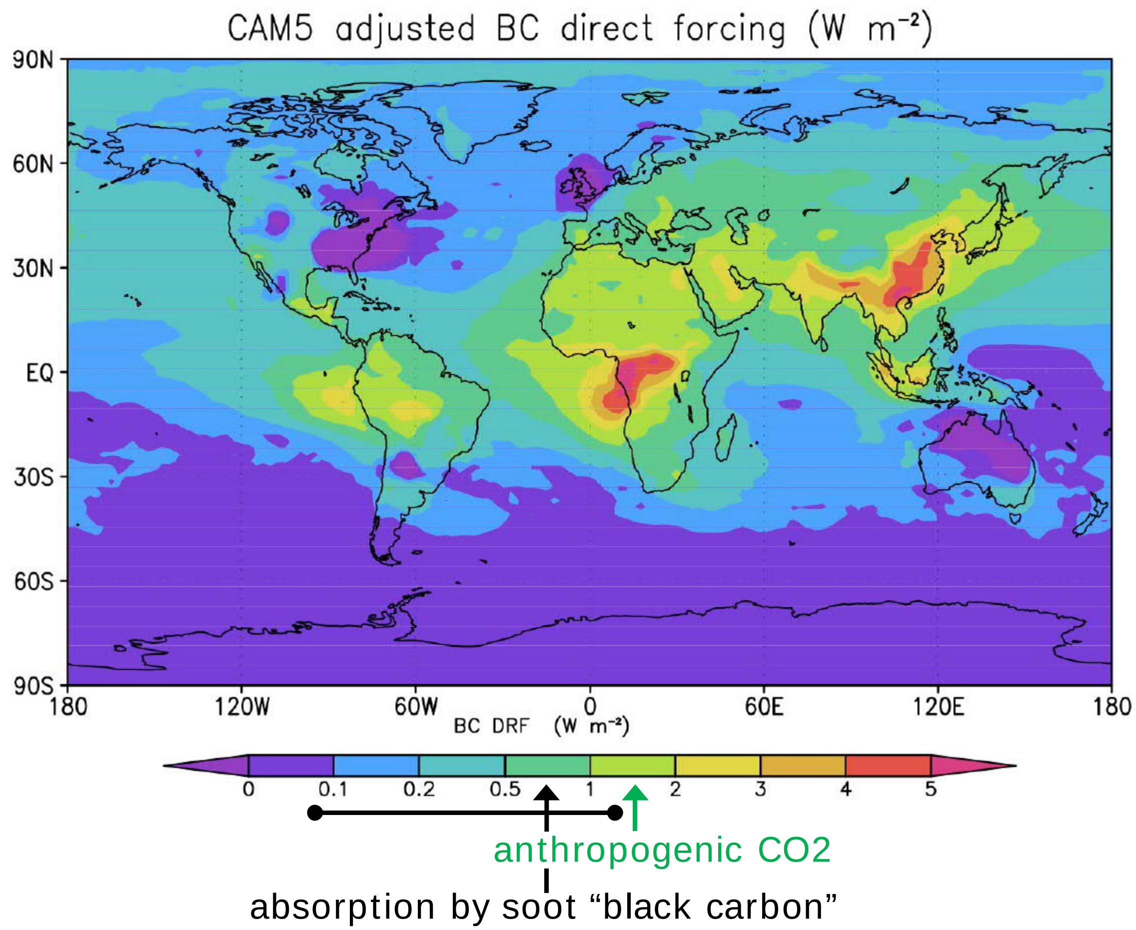
1. **Background**
   - black carbon and not-black-carbon
2. **Technique**
   - Single-Particle “Soot” Photometry (SP2)
3. **Results**
   - Using the SP2 to characterize non-soot black carbon

Global sources of black carbon (BC) & light-absorbing carbon (LAC):



Bond, Doherty, Fahey, Forster et al., J. Geophys. Res. 2013

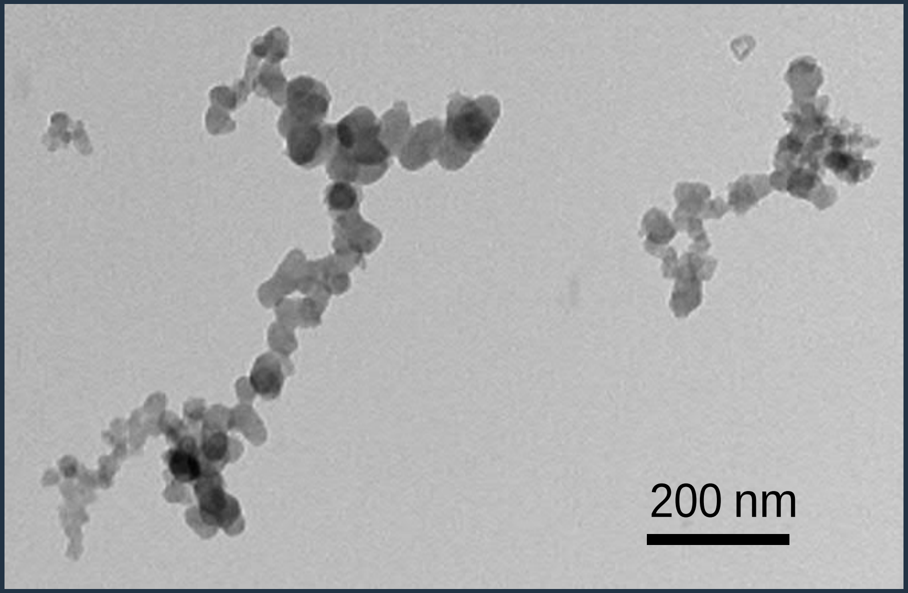
Black carbon (BC): an important atmospheric absorber

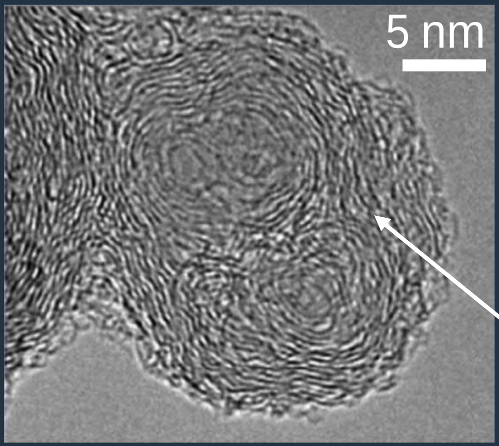


Bond, Doherty, Fahey, Forster et al., J. Geophys. Res. 2013; Ghan ACP 2013

Black carbon (BC):

Flame-synthesized nano-aggregates of nearly-graphitic carbon spherules.





Curved graphene-like layers

200nm image from Trivanovic, Corbin et al., 2019
5nm image from Vander Wal et al., 2014

Smoke does not just contain BC!

1. **Heavy fuels (~1000 Da) form carbonized particles known as tarballs [1,2]**

2. **Heavy fuels are:**
   - Biomass (wood, …)
     - *Home heating, wildfires*
   - Residual fuels
     - *Marine engines*

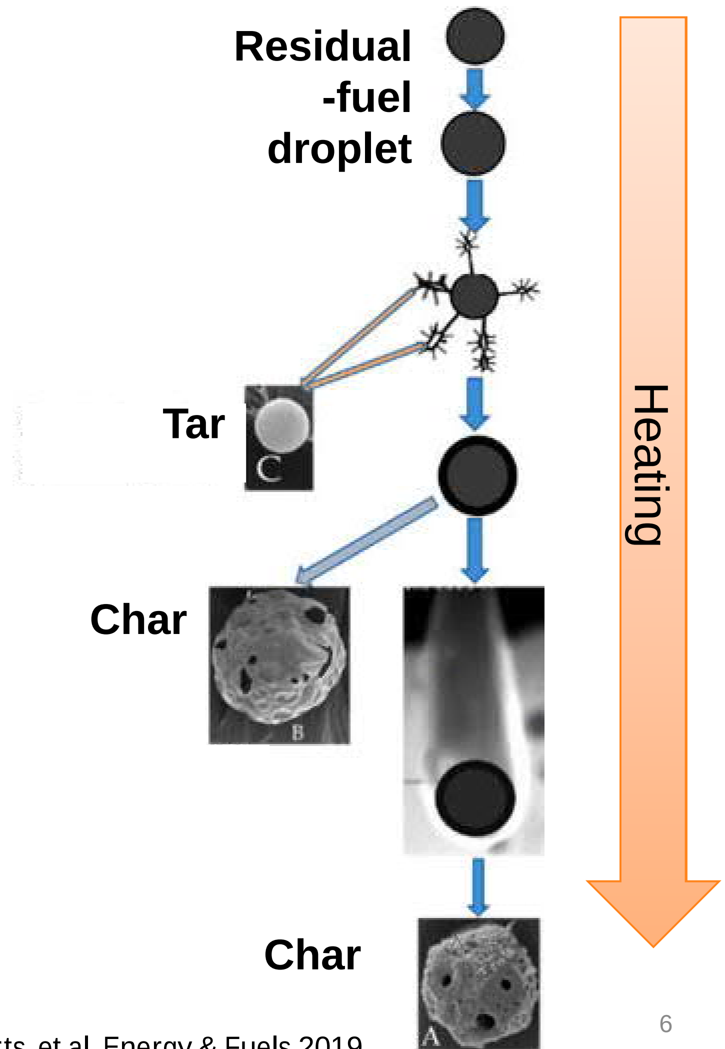


IMAGE: Jiang, Roberts, et al. Energy & Fuels 2019

[1] Corbin et al., Nature npj Clim Atmos Sci 2019
[2] Corbin and Gysel, Atmos Chem Phys Discuss 2019

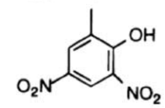
Corbin et al., Nature npj Clim Atmos Sci 2019

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

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

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 ●
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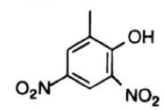
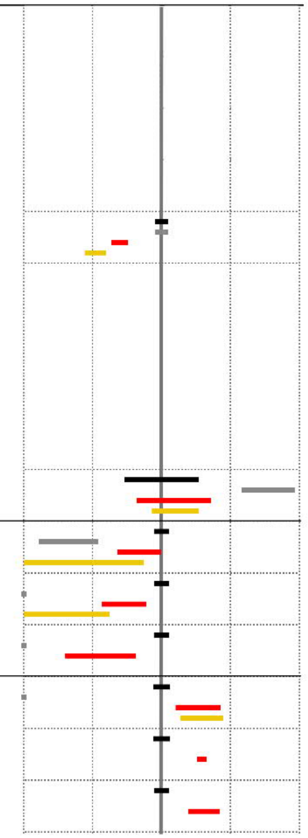
Chemical state	Contorted graphene layers		Amorphous	Distinct molecules
Carbon bonding	sp^2 dominated		sp^2 and sp^3	sp^2 and sp^3
Vapourization at[b]	~ 4000 K [EC, rBC]		~ 1000 K [EC]	< 600 K
Produced by	Flame synthesis	Fuel-droplet pyrolysis	Partial pyrolysis	Oxidation, pyrolysis, ...
Morphology				
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	$\ll$0.1–6.0
MAE (550 nm)[d] [m^2/g]	7.5 ± 1.2	0.2–1.3	1.1–4.1	$\ll$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.

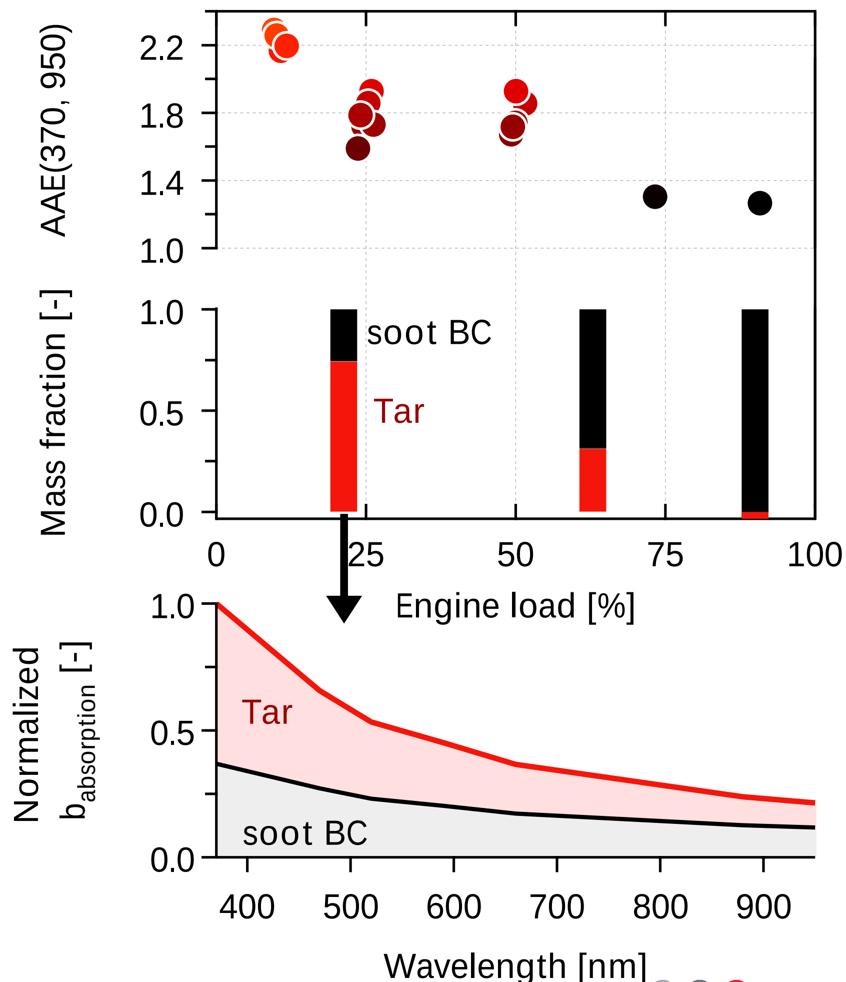
Tar ≫ soot-BC at low engine loads

Low loads (<40%) used for safety in presence of ice
[Lack and Corbett, ACP 2012]

Our data explain tar-like particles identified in previous studies

- AAE of 2.2 measured by Doherty et al., ACP 2010 for insoluble LAC in snow.
- Alexander et al. (Science 2008) could not identify source of tar-like particles over Yellow Sea.

Corbin et al., Nature npj Clim Atmos Sci 2019



Outline

1. **Background**
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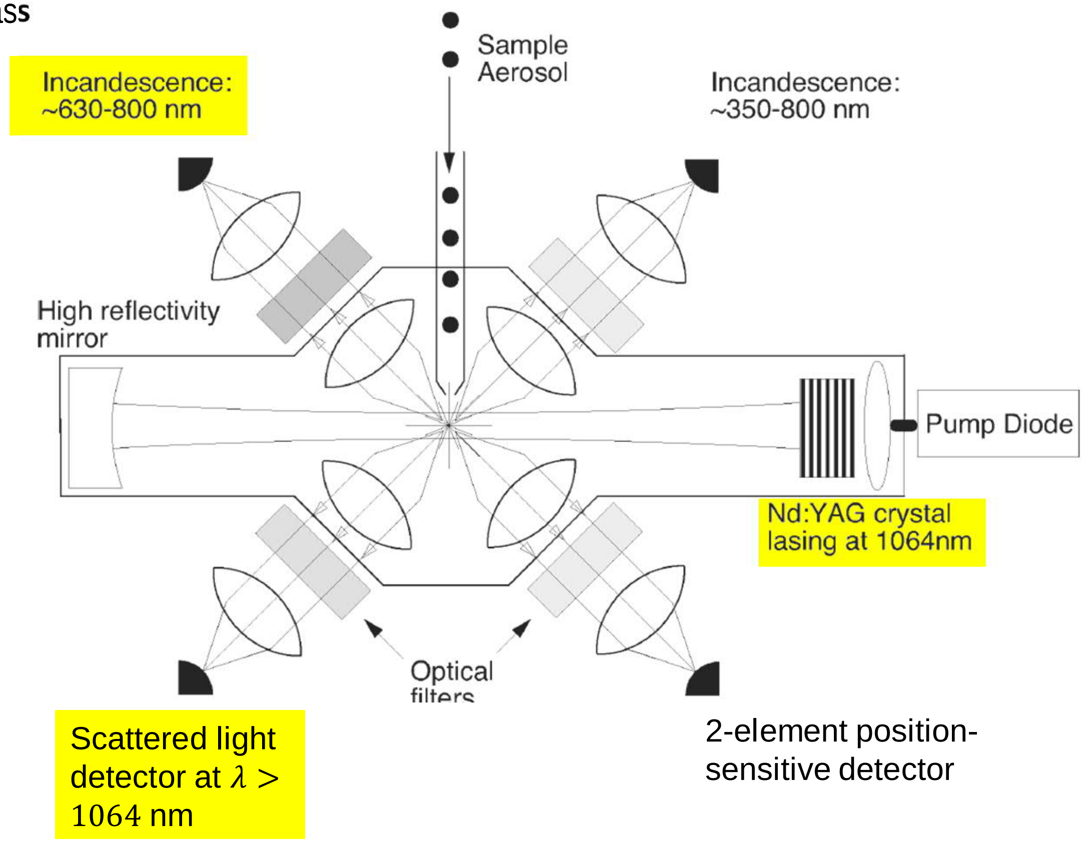
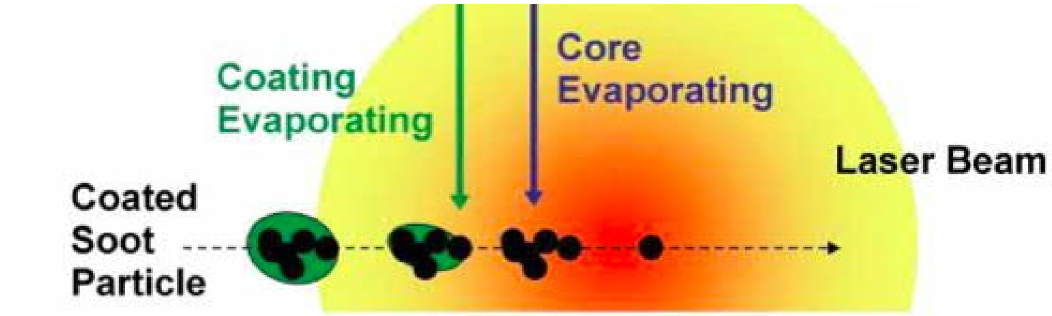
Single Particle Soot Photometer (SP2)

→ designed to measure rBC mass



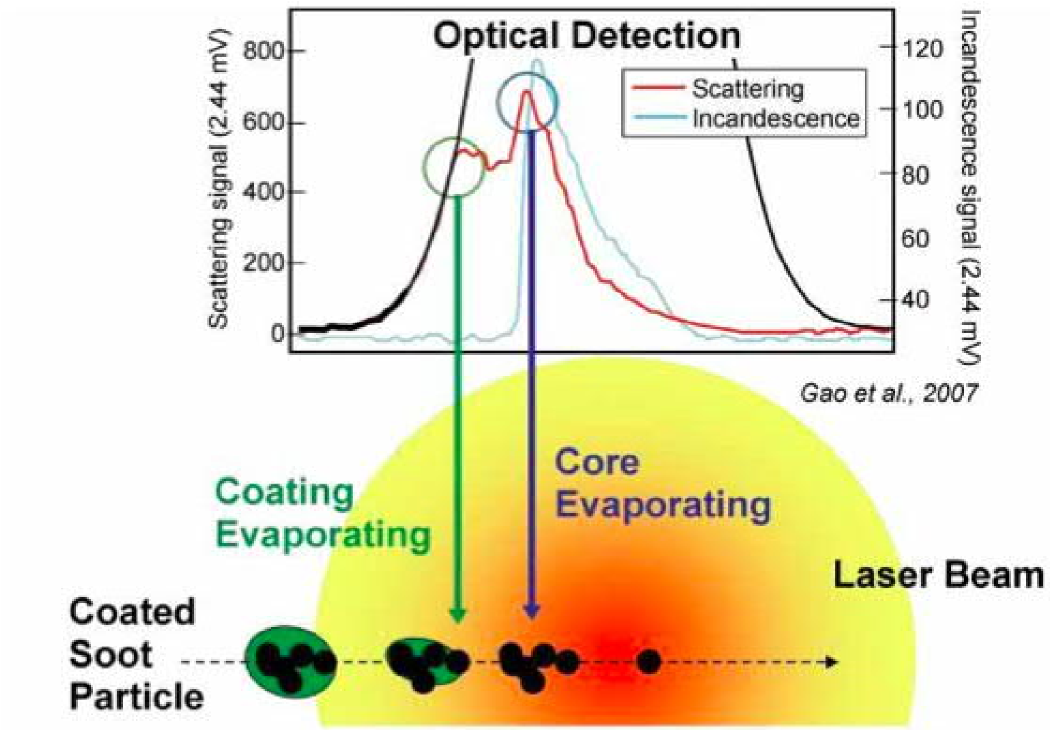
Schwarz et al., JGR 2006

Soot within the SP2 laser



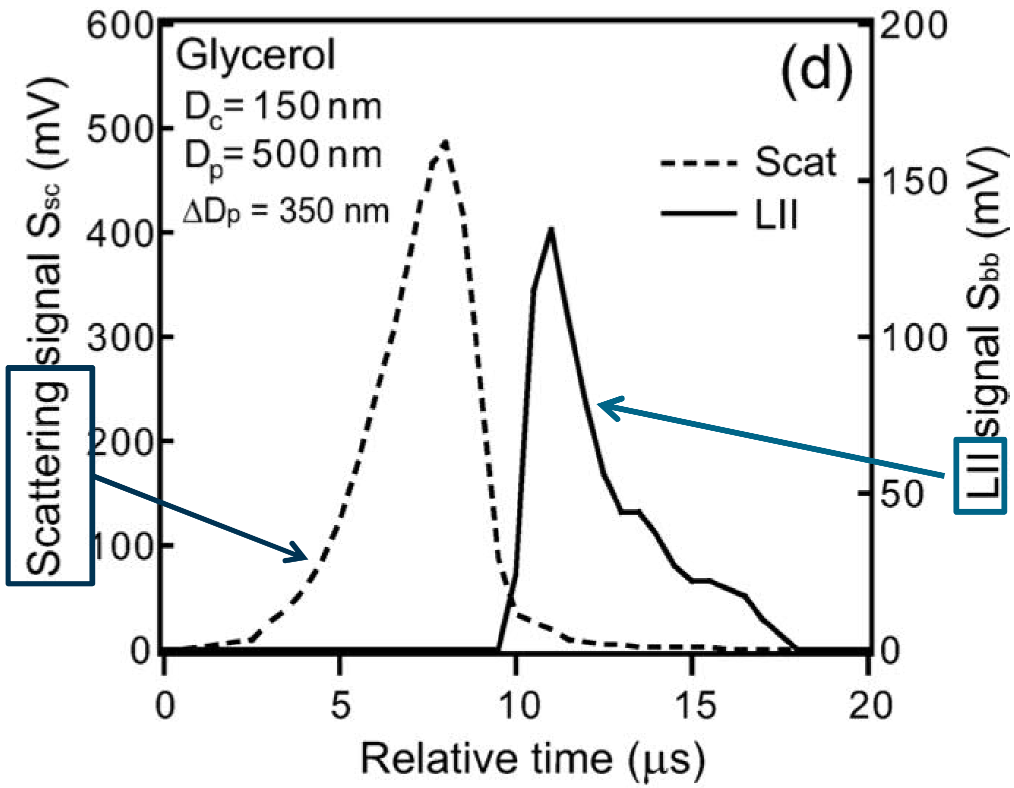
Onasch et al., 2011

Soot within the SP2 laser



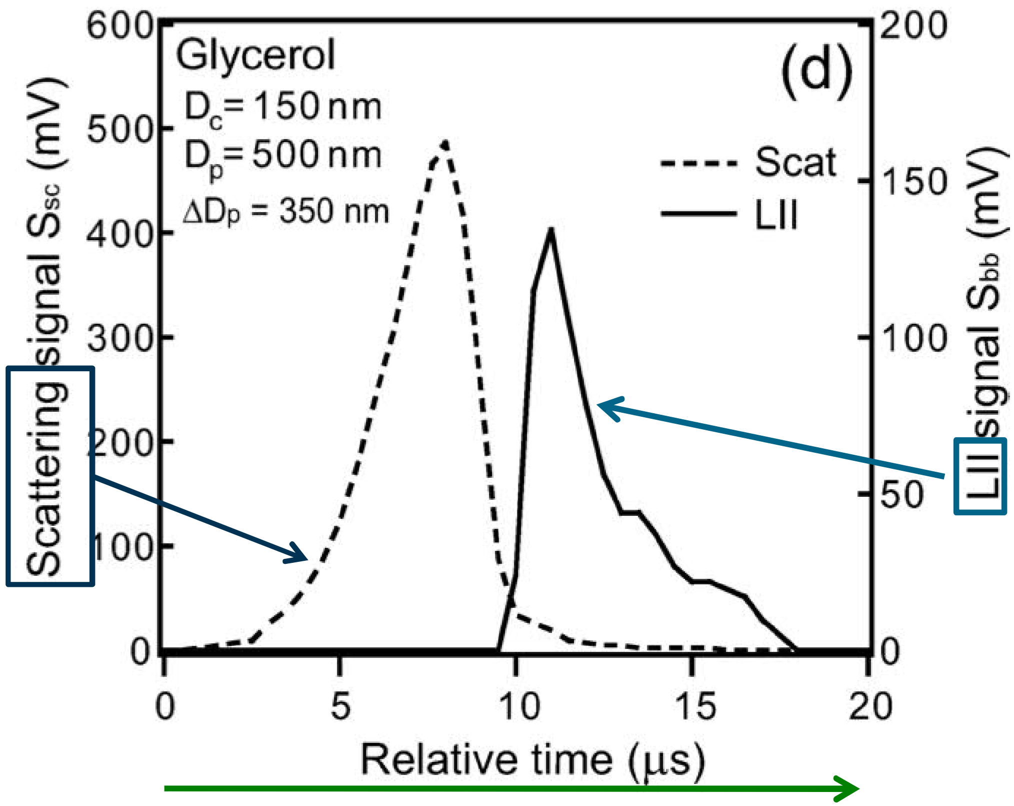
Onasch et al., 2011

Interpreting SP2 spectra



Moteki and Kondo, AS & T 2007

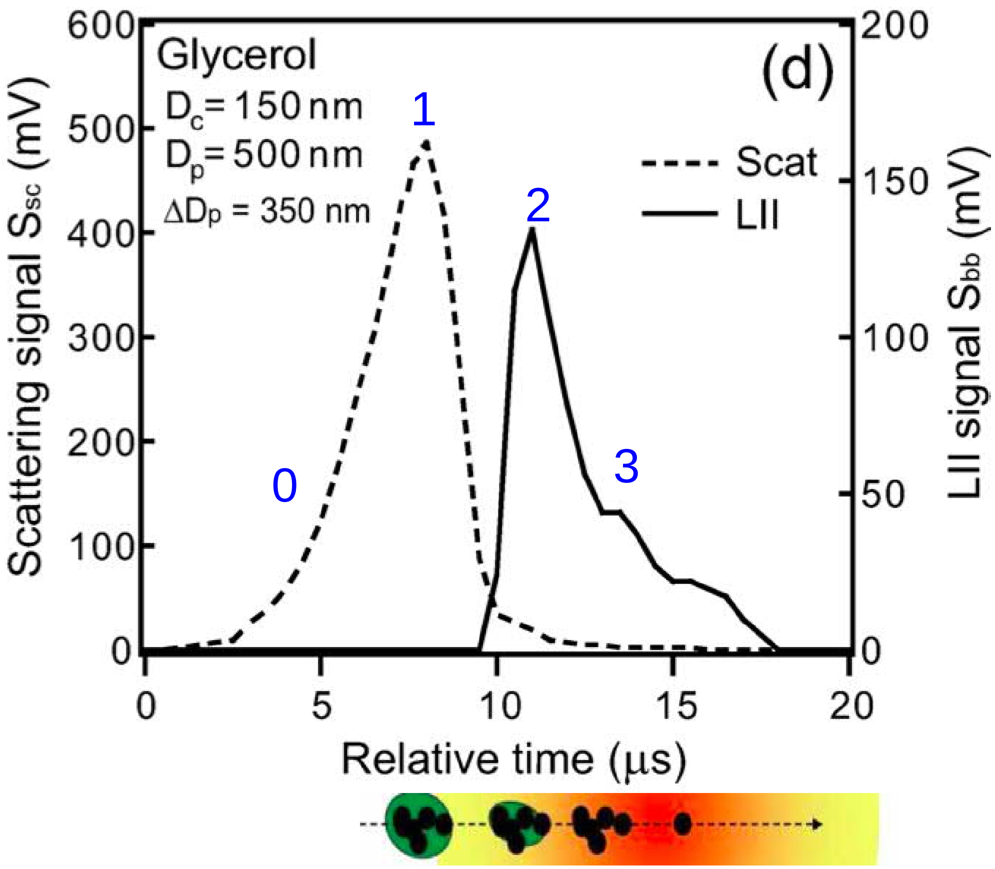
Interpreting SP2 spectra



Laser Width = “13 μs” = 630 μm (99.7% of Gaussian)

Interpreting SP2 spectra

0. Particle beginning to cross Gaussian laser beam
1. Coating evaporates
2. BC incandesces
3. BC vapourizes



Outline

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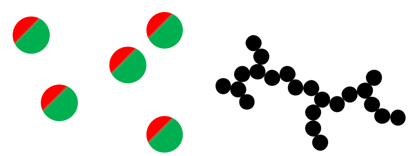
Experiment Overview

80kW ship engine → porous-tube dilutor, 12x → ejector dilutors, 100x

porous-tube dilutor, 12x → filter samples

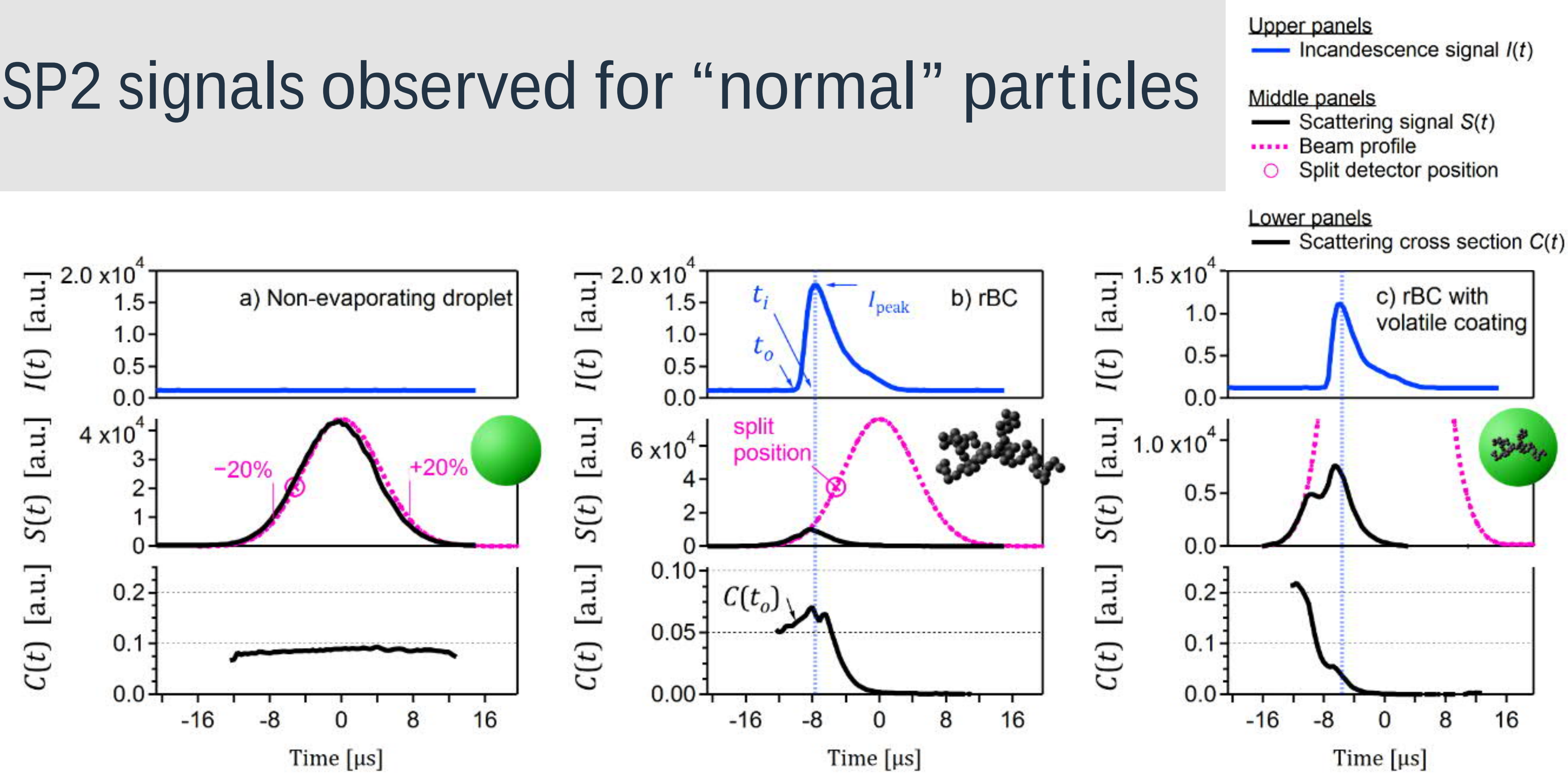
- **SP2** (focus of this talk)

- Many other instruments, measurements, to characterize emissions and fuel dependence
  - *Corbin et al., J. Geophys. Res. 2018*
  - *Corbin et al., Environ. Sci. Technol. 2018*
  - *Corbin et al., Nature Clim Atmos Sci 2019*

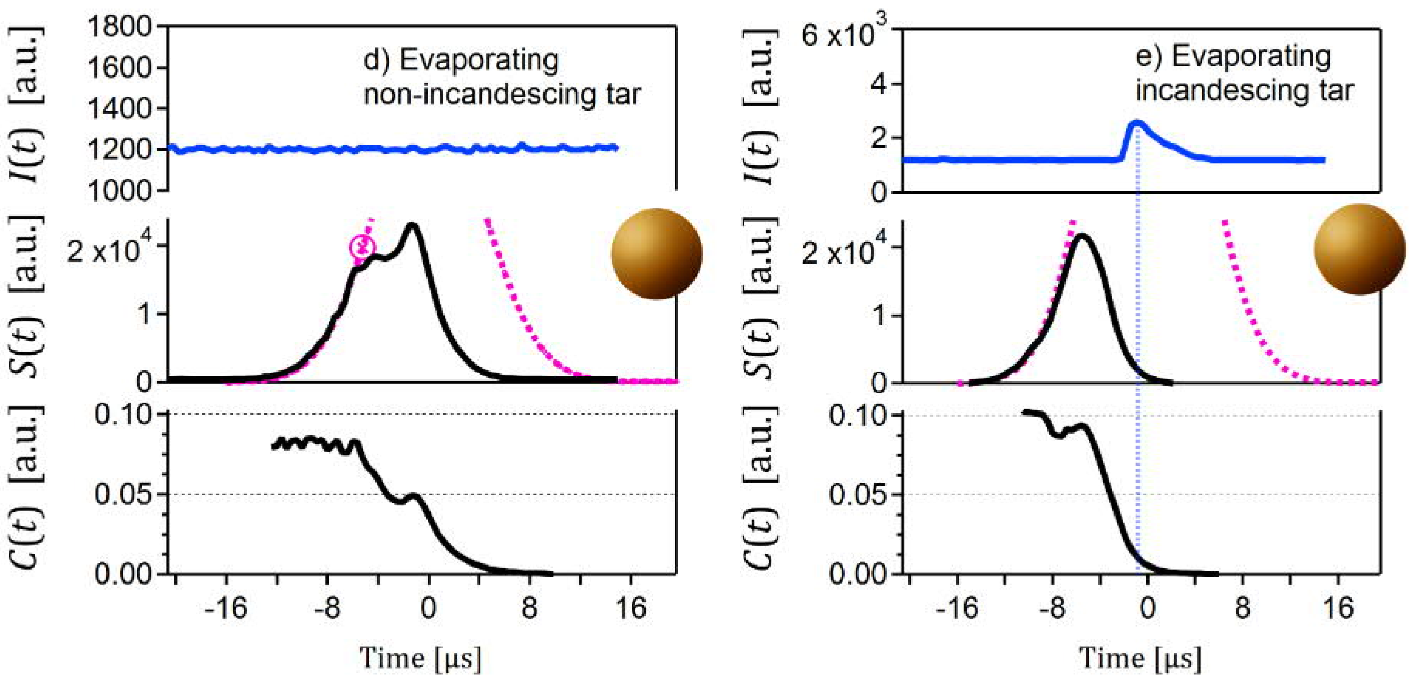


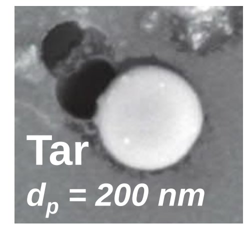
Particulate mixture of
BC, OM, sulfate
& associated gases

SP2 signals observed for “normal” particles



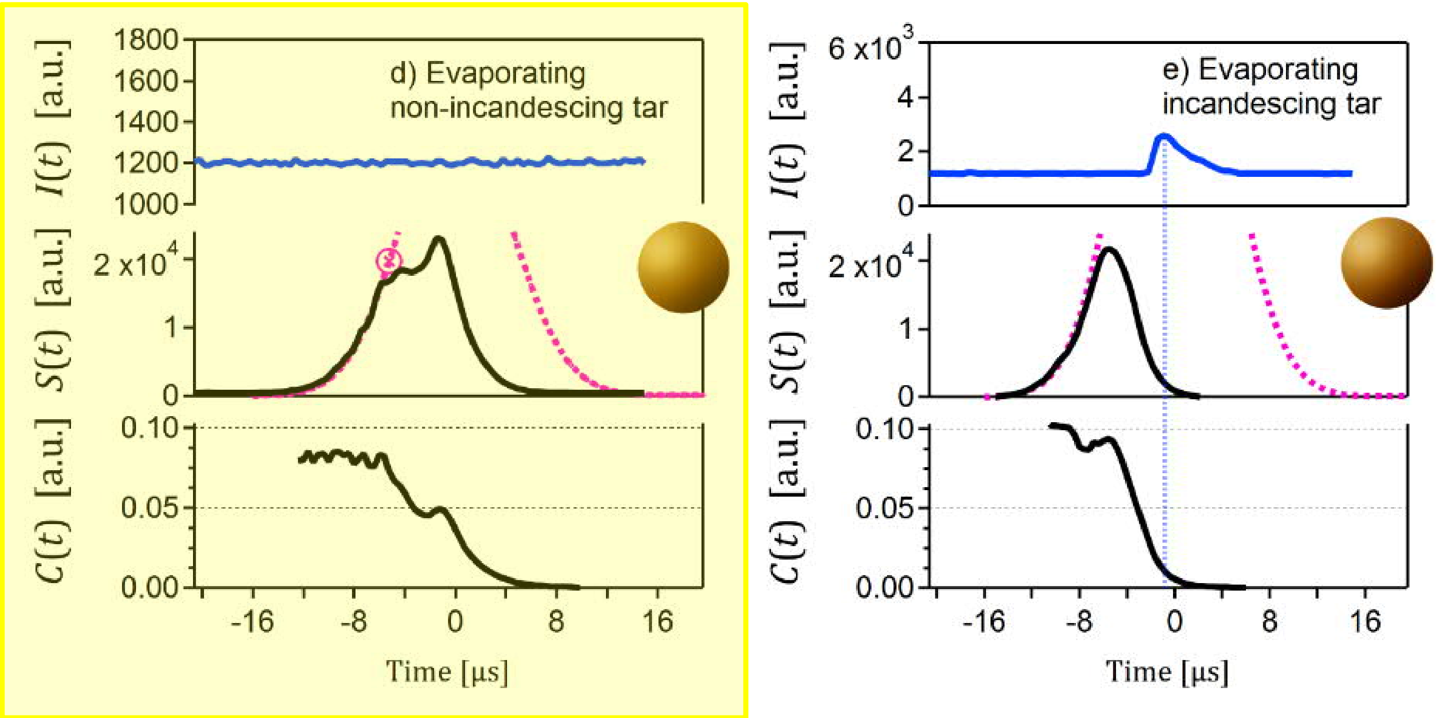
Anomalous SP2 signals: identified as tar



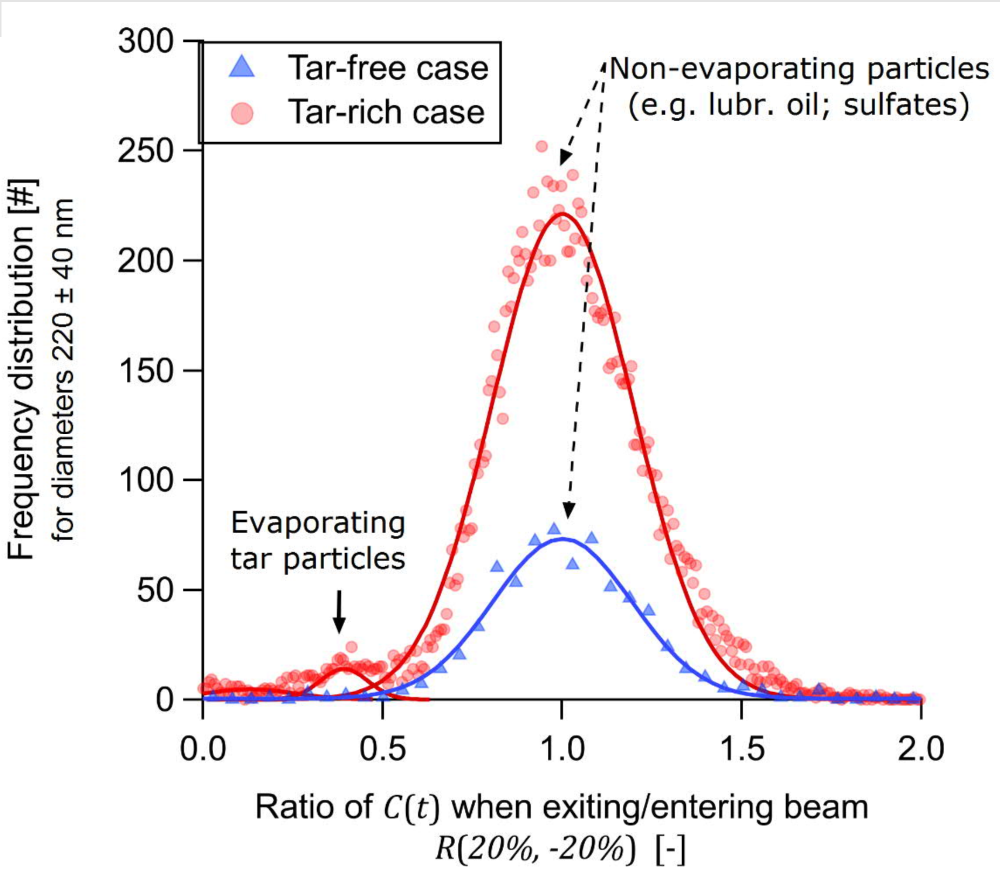


Identification as tar described in Corbin et al. [Nature npj Climate & Atmos. Science 2019]

Anomalous SP2 signals: identified as <u>tar</u>



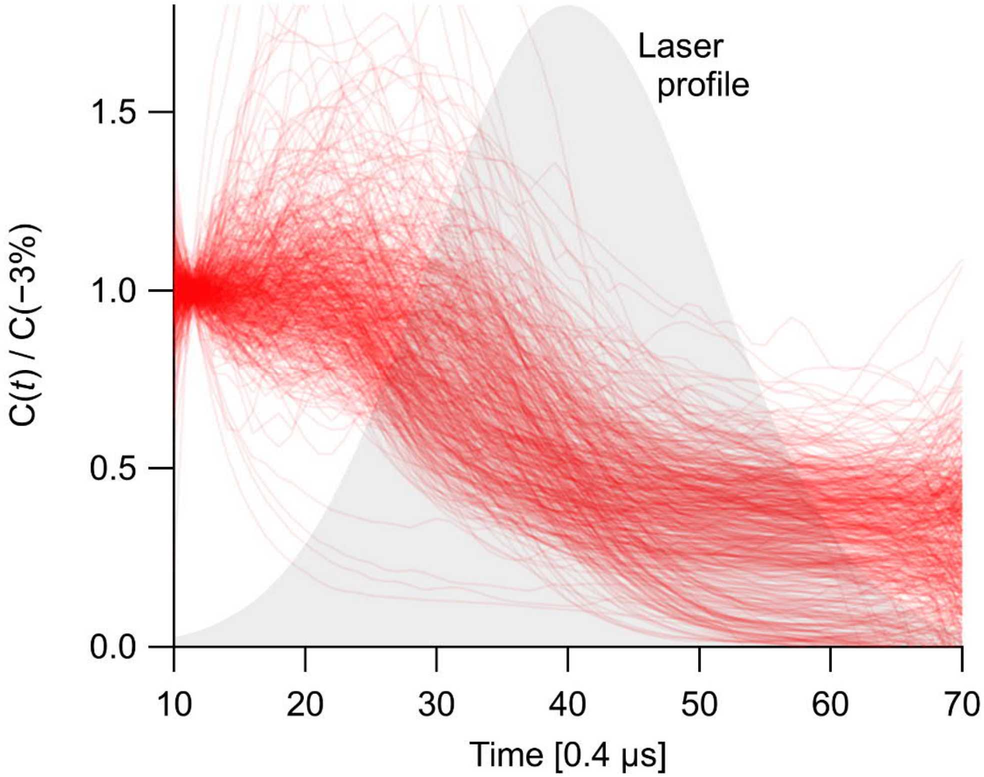
Evaporating, non-incandescing tar [1/2]



578 of 2.5×10^5 particles partially evaporated.

False negatives not quantified.

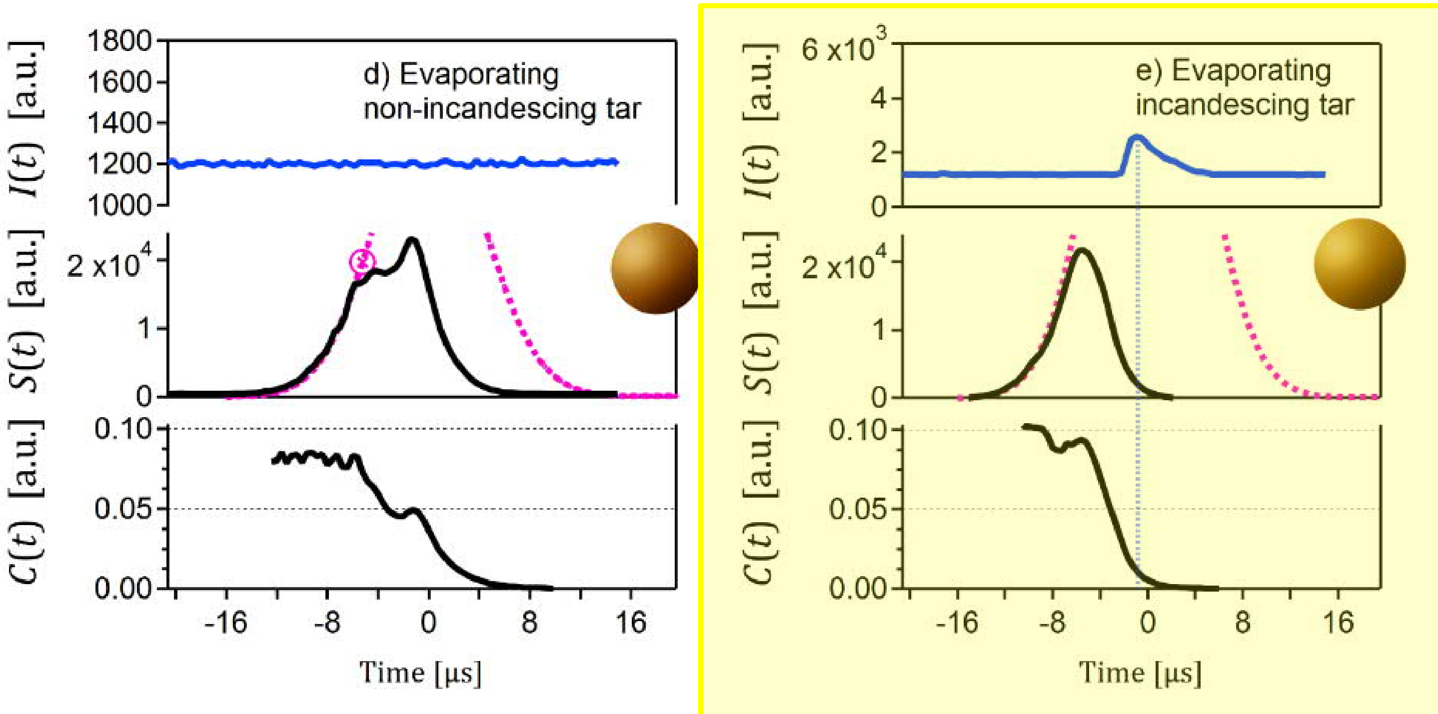
Evaporating, non-incandescing tar [2/2]



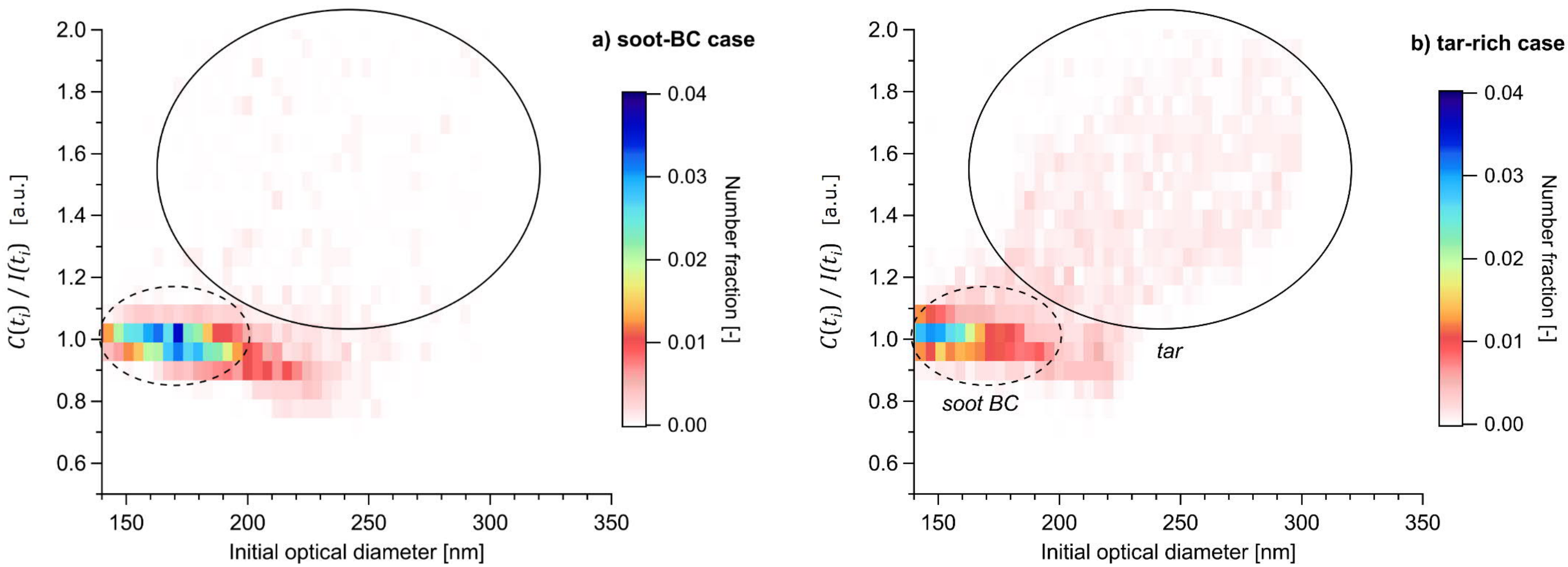
Overall trends show similar behaviour.

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

Anomalous SP2 signals: identified as <u>tar</u>



Incandescing tar identified in combination with light-scattering analysis



Conclusions

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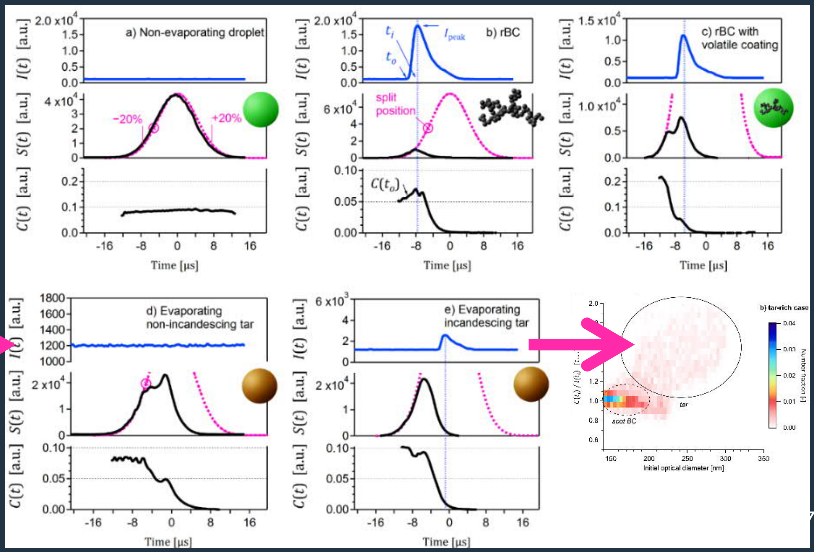
Atmos Chem Phys Discuss 2019
doi:10.5194/acp-2019-568

1. **Tar brC, not just soot, matters for climate warming by smoke from wildfires and marine engines**
2. **Real-time tar identification was possible by combining time-resolved light-scattering and laser-induced incandescence.**

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 rBC 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				Spheres or coatings
Diameter[c] [μm]	0.02–0.2	1–5	0.03–0.3	0.05–0.2



Acknowledgements

Prem Lobo, NRC

Martin Gysel, NRC

BLACARAT EU Grant

Corbin et al., Nature npj Clim Atmos Sci 2019

Defining and measuring BC

Proxies for 

Property	Soot BC
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

→ 'eBC': Light absorption equivalent
based on literature
mass absorption efficiency (MAE)

→ 'EC': Refractory carbon at 900-1200 K
slow heating in helium
optical absorption correction for org. pyrolysis

→ 'rBC': Refractory carbon at ~3500 K
rapid laser heating,
measure incandescence (LII)

Background: ship fuels

➢ "Heavy Fuel Oil" HFO:

- Cheap, crude-oil residual
- Heavy metal impurities
- High S (2.3% = 23,000 ppm)

Emissions may exceed SECA limits →

Existing & future Sulfur Emission Control Areas (SECA)

➢ "Distillate fuels" fuels:

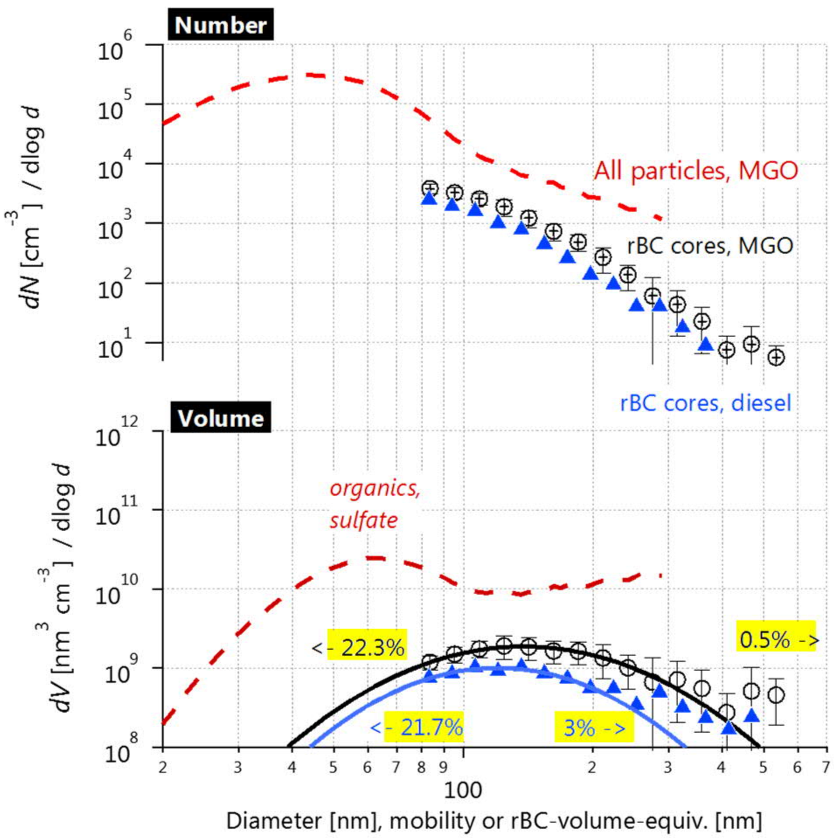
- Marine Gas Oil (MGO, 780 ppm S)
- Diesel (DF, 7 ppm S)

➢ Different fuels, different

- PM emissions and composition
- Climate effects
- Health effects for HFO and DF [1]

[1] Oeder et al., PLoS One 2015 [2] Jonson et al., ACP 2015

Marine gas oil (MGO) and diesel (DF) size distributions



- rBC GSD~2.1

Note: $d_{\text{mobility}} \geq d_{\text{vol-equiv}}$