Insoluble "brown carbon" emitted by marine engines: relevance to a warming Arctic

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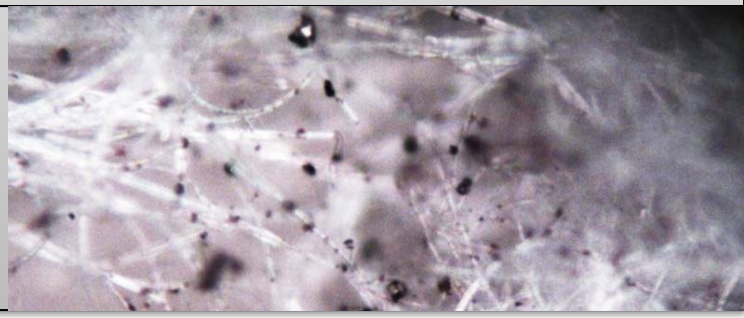

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Outline

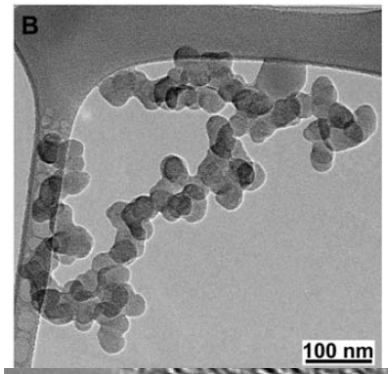
1. Light-absorbing carbon (LAC)
2. “brown carbon” (brC) in heavy fuel oil (HFO) PM
3. Identity of brC in heavy fuel oil PM
4. Optical properties of brC in heavy fuel oil PM

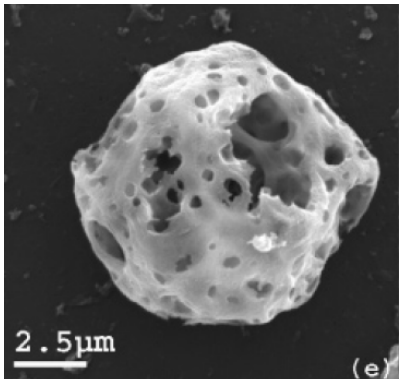
Types of light-absorbing carbon (LAC)

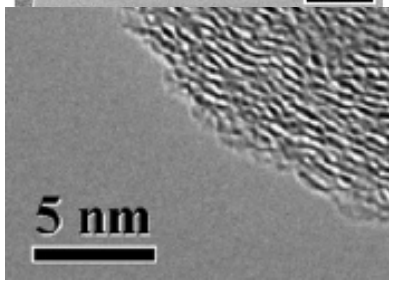
Corbin et al., in prep. 2018

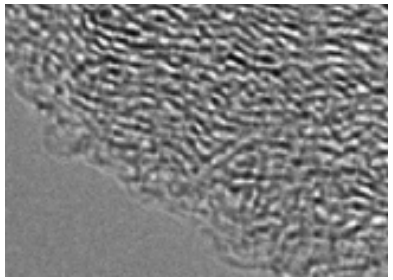
	Soot BC	Char BC	"Tar"	Brown carbon (brC)
Solubility	Insoluble in any common solvent			Soluble
Substantial solar absorption at λ =	300–1000 nm (black)			300–500 nm (yellow/brown)
Chemical state	Contorted graphene layers (sp2 bonding)		**Amorphous solid (sp3 and sp2 bonding)**	Distinct sp2-bonded organic molecules
Vapourization at	~4000 K		**~1000 K**	~600 K
Produced by	Flame synthesis	Fuel-droplet pyrolysis	Partial pyrolysis	Oxidation, partial pyrolysis, …

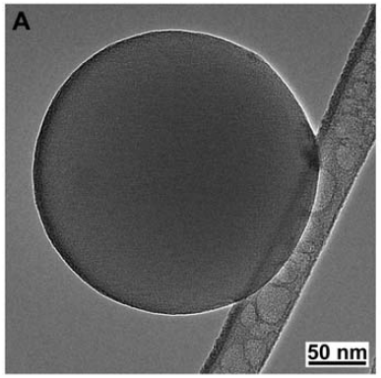
[1] Soot: Alexander et al., Science 2008
[2] Char: Chen, Shah et al. Energy Fuels 2005
[3] brC: Laskin et al., Chem Rev. 2015



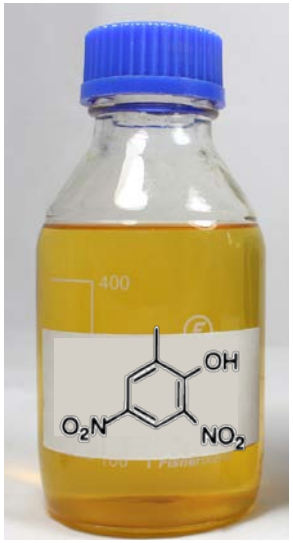






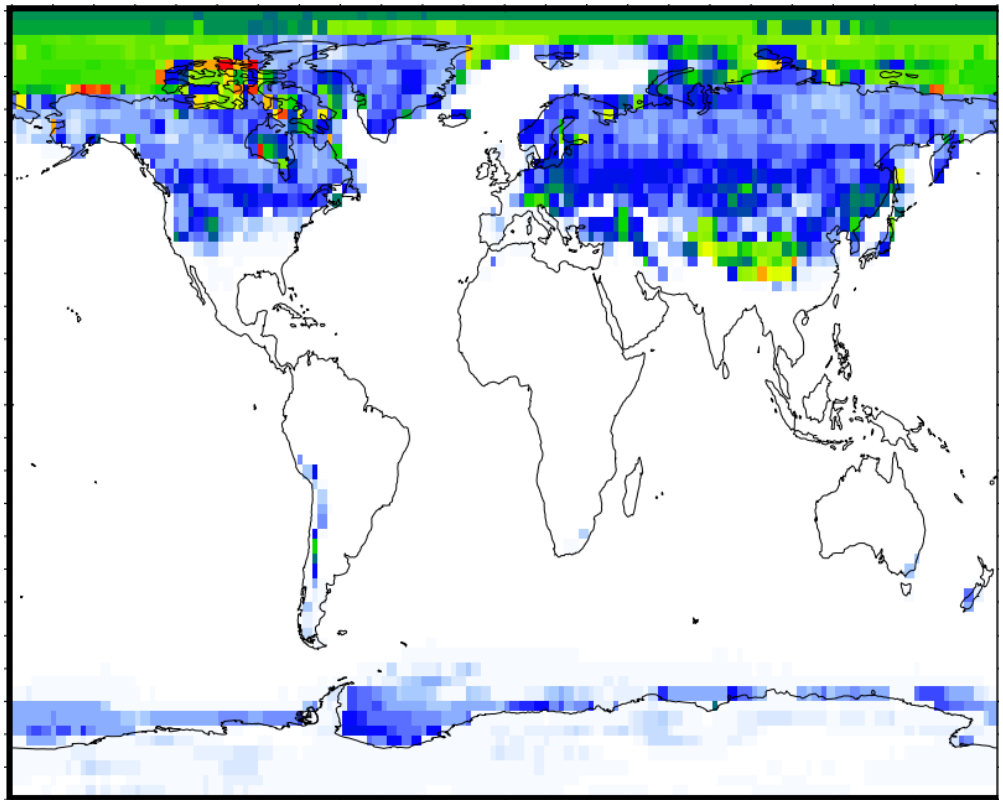


"Tar balls": previously identified only in biomass-burning smoke [3]

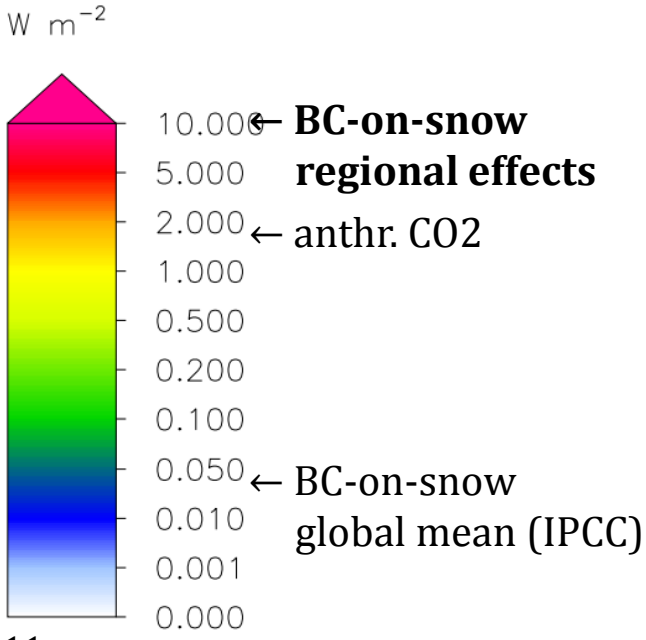


Importance of LAC emitted by shipping in the Arctic

1. 1µg of LAC emitted in Arctic gives 5x more Arctic warming than 1µg of LAC emitted in midlatitudes [1]
2. Less Arctic sea ice will lead to more Arctic shipping [2]
3. Arctic particularly sensitive to BC-on-snow climate forcing [3]:



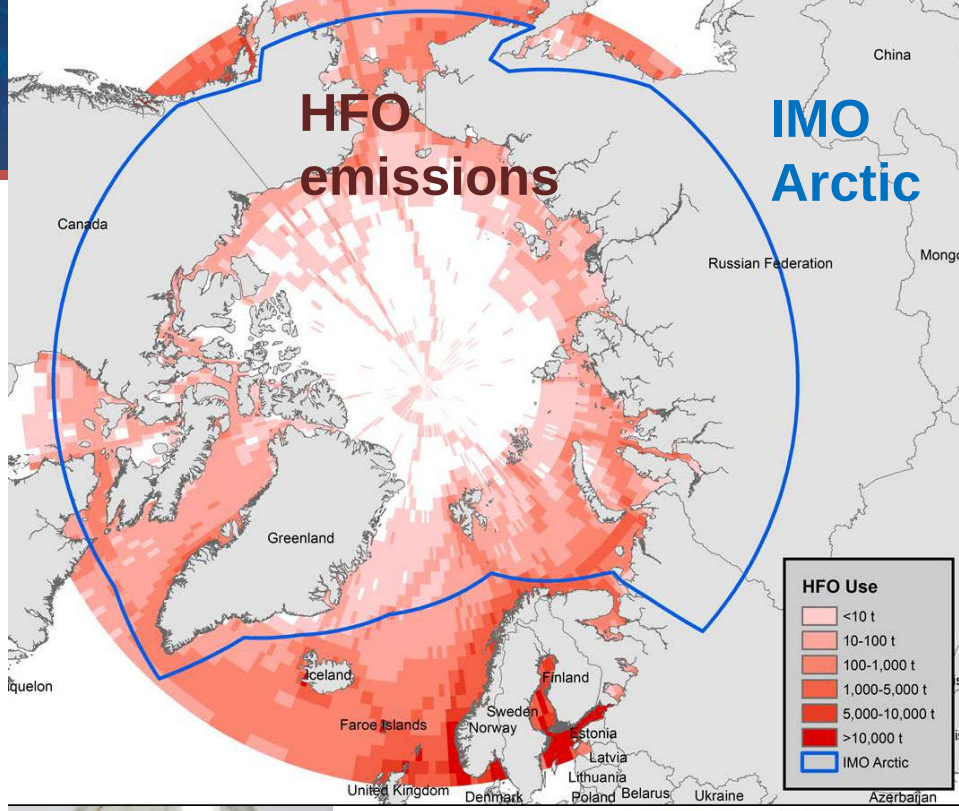
1750 vs. 2000

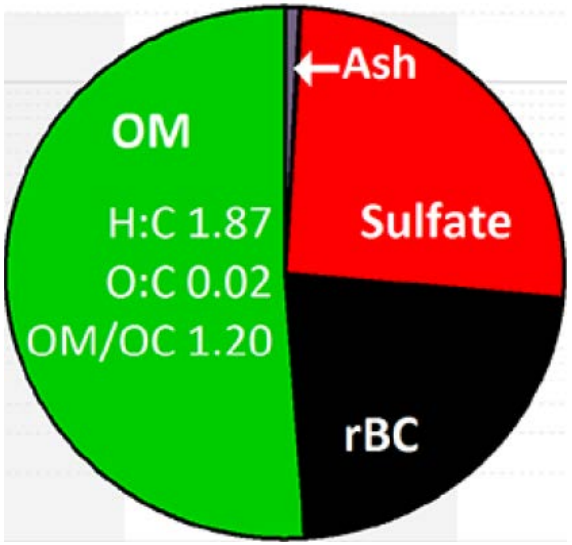


[1] Sand et al., J Geophys. Res. 2013; [2] AMAP 2015 [2] Skeie et al, ACP 2011

Heavy fuel oil (HFO) & HFO emissions (HFO-PM)

- HFO most widely used (57%) Arctic marine fuel [1]
- 1-2% sulfur content (→ sulfur scrubbers will be required globally in 2020)
- HFO-PM emissions high in organic PM (**OM**) and **BC**.

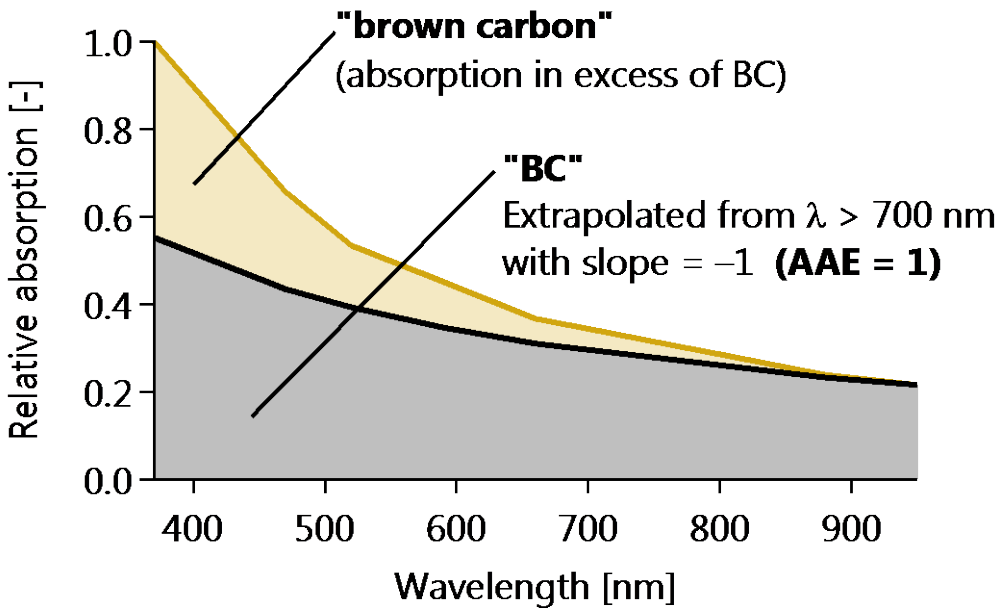


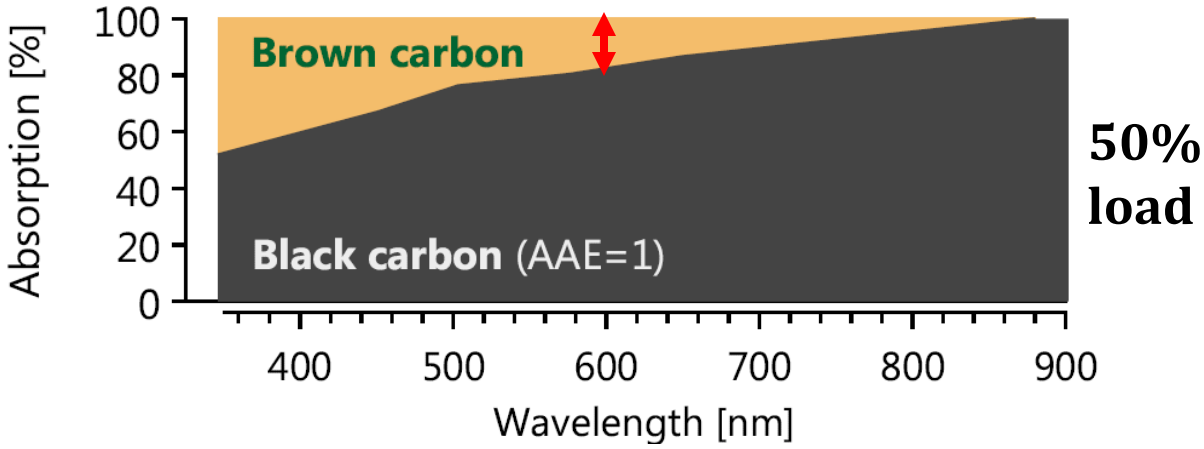


[1] Lack, 2016
Map--ICCT, 2017
Pie chart--Corbin et al., Env Sci Tech 2018

Traditional "brown carbon" (brC) in HFO PM

- **"Apparent brC"** typically defined as "excess absorption" →
  - brC typically absorbs only at λ < **500nm** [1]
- We observed anomalous HFO-PM "brC" absorption:
  - 20% of 600-nm total at 50% load [2]





[1] Laskin et al., Chem Rev 2015 [2] Corbin et al., J. Geophys. Res. 2018

Outline

1. Light-absorbing carbon (LAC)
2. “brown carbon” (brC) in HFO-PM
3. **Identity of “brC” in HFO-PM**
4. Optical properties of brC in HFO-PM

This study: engine details

- 4-stroke research diesel engine
- Single-cylinder, 80 kW
- 1500 rpm
- 150 mm bore
- 180 mm stroke

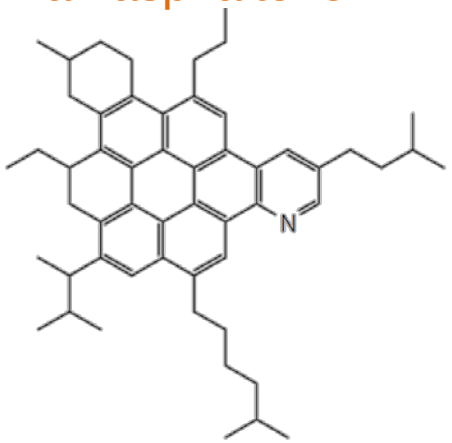
<u>Results from this study:</u>
Corbin et al., J. Geophys. Res. 2018
Corbin et al., Environ. Sci. Tech. 2018

Hypothesis 1:
Is the unique "brC" in HFO-PM due to asphaltenes?

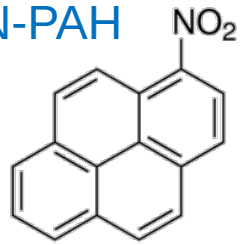
HFO fuel & HFO-PM:

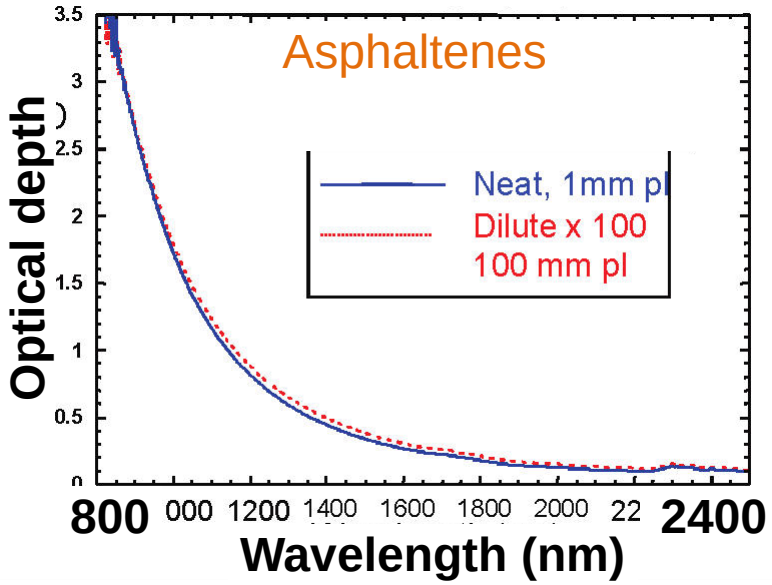
- **Asphaltenes** (**hexane-insoluble, toluene-soluble** molecules) are known to absorb near-infrared light [1]
- Hypothesized because methanol extracts of **HFO-PM and HFO fuel** are both high in **O-** and **N-PAHs** [2,3]

an asphaltene



N-PAH

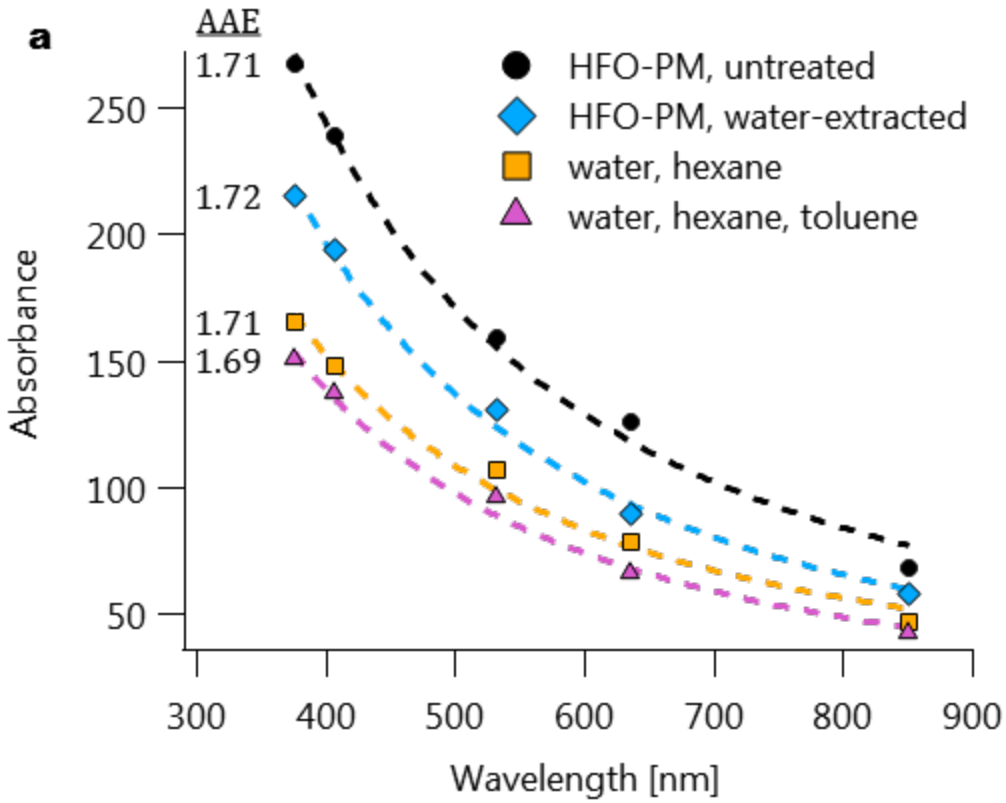


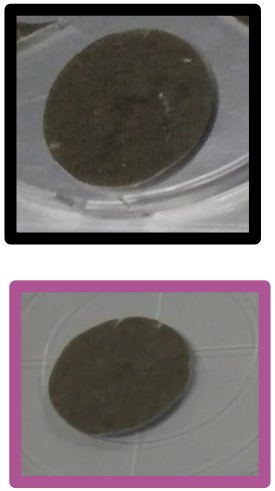


[1] Mullins, Energy & Fuels, 2010
[2] Sippula et al. Environ. Sci. Tech. 2009
[3] Streibel et al., Environ. Sci. Poll. 2017

Hypothesis 1: **Is HFO-PM 'brC' due to asphaltenes?**

Corbin et al., in prep. 2018





- **AAE = 1.7 before and after → Toluene-insoluble "brC" → not asphaltenes**
- First observation of insoluble "brC"

Hypothesis 2: is HFO-PM 'brC' due to char-BC?
Scanning electron microscopy

- Hypothesis: Char BC (BC with diameters ~1μm) may show anomalous optical properties.
  - SEM showed no char in our samples.

Corbin et al., in prep. 2018

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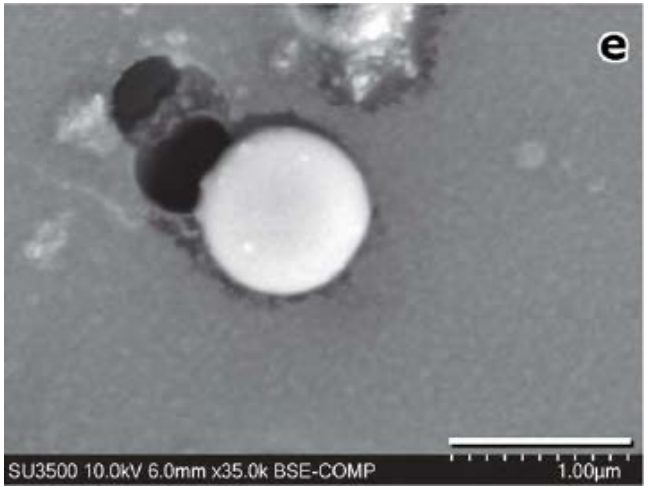
Scanning electron microscopy

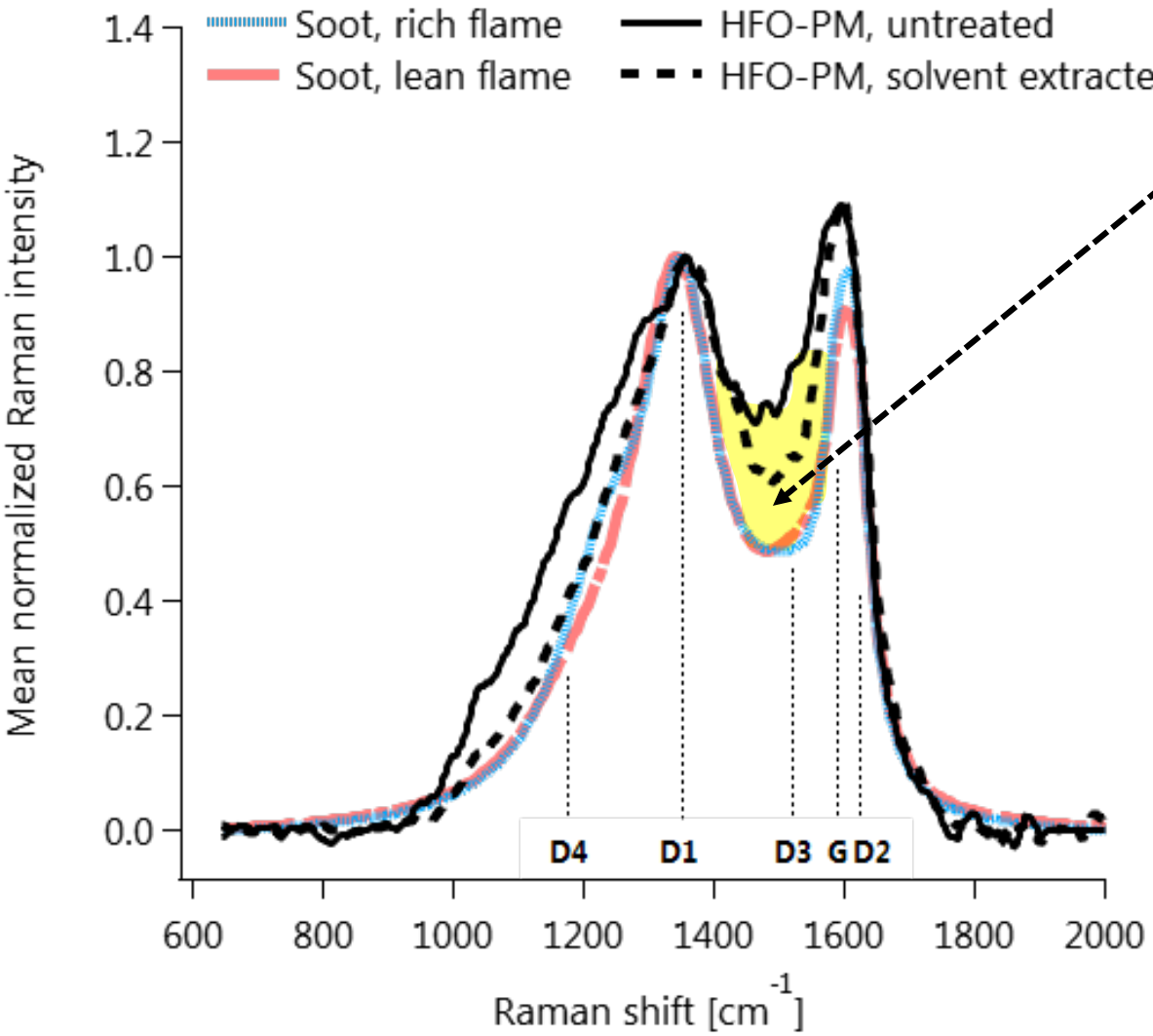
- Hypothesis: Char BC *(BC with diameters ~1µm)* may show anomalous optical properties.
  - SEM showed no char in our samples.
- **SEM identified tar spheres** *(involatile, amorphous carbon "**tar**" spheres, stable in electron beam)* in HFO-PM.

Corbin et al., in prep. 2018



Hypothesis 3: tar is the 'brC' species in HFO-PM

Raman spectroscopy



- **sp3/sp2 ratio** in HFO-PM substantially higher than BC.
  - Related to AAE of 1.8
- HFO-PM **tar is molecularly distinct** from BC and brC.
  - HFO-PM **tar is a new type of LAC** (light-absorbing carbon).

Corbin et al., in prep. 2018

Summary of tar properties

Thank you.
Questions?

Corbin et al., in prep. 2018

	Soot BC	Char BC	"Tar"	Brown carbon (brC)
Solubility	Insoluble in any common solvent			Soluble
Substantial solar absorption at λ =	300–1000 nm (black)			300–500 nm (yellow/brown)
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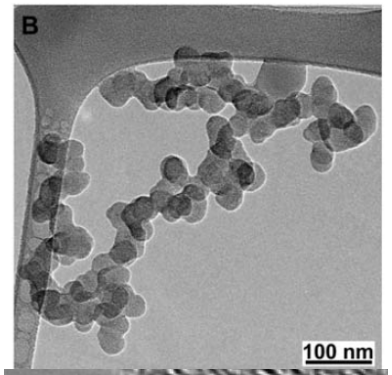
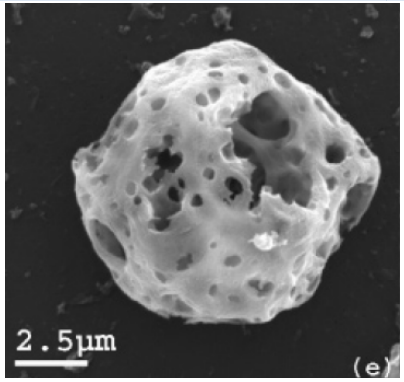
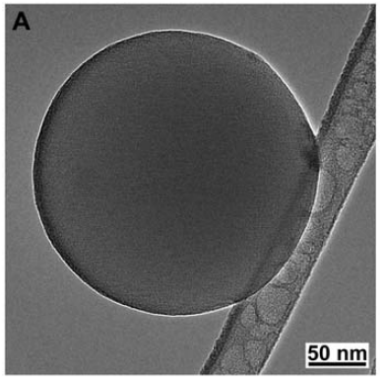
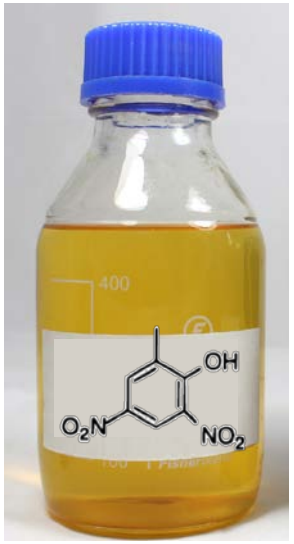
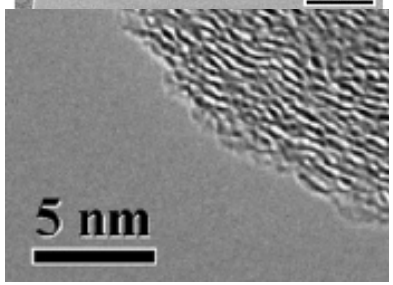
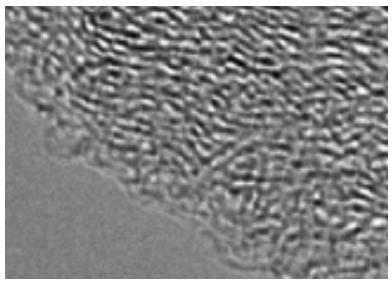








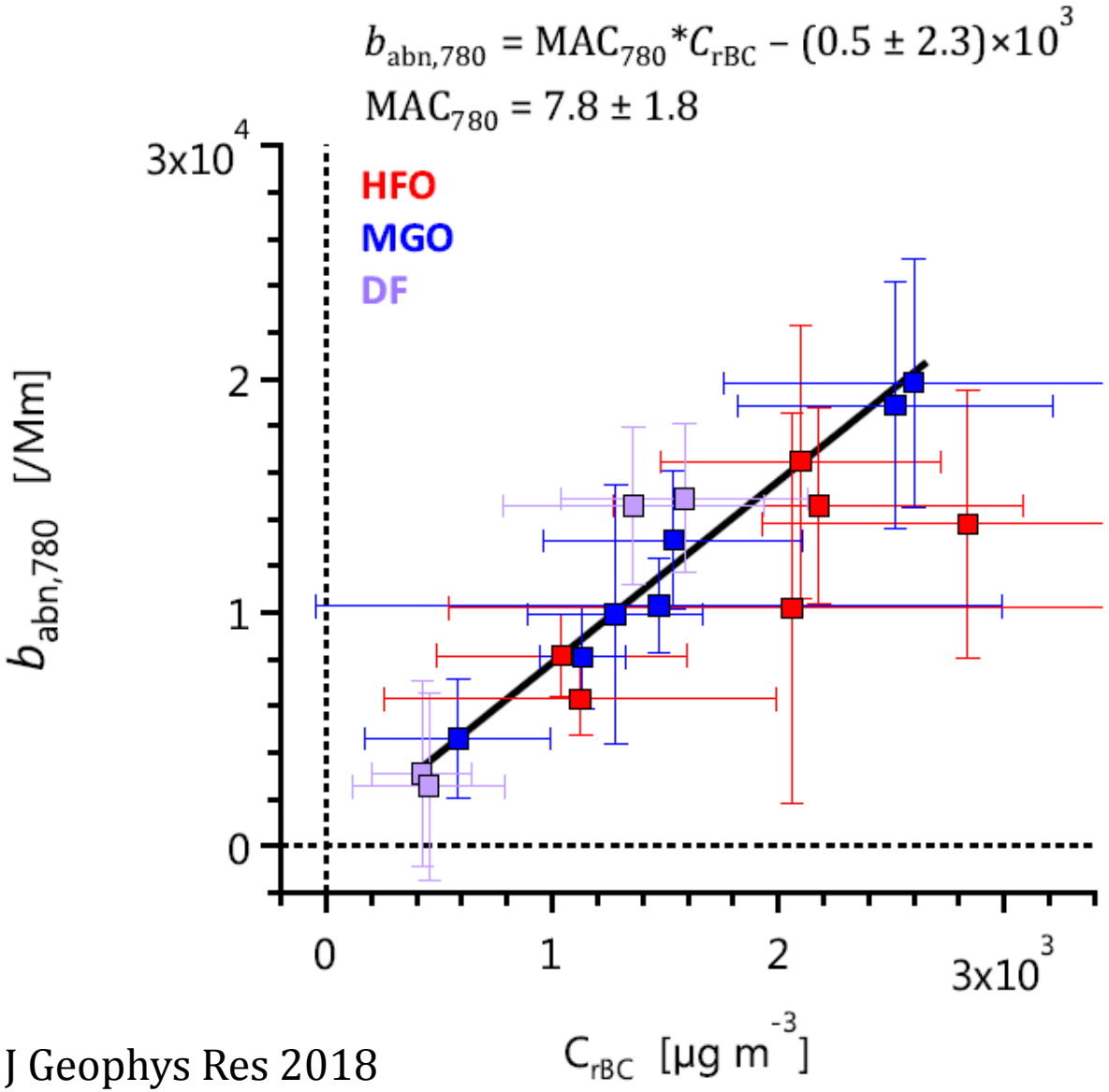




Tar identified as dominant light absorber in HFO-PM emissions, at low loads.

Thank you

MAC (MAE) of BC from this study's engine



[1] Corbin et al., J Geophys Res 2018