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

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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*

<table>
<thead>
<tr>
<th></th>
<th>Soot BC</th>
<th>Char BC</th>
<th>&quot;Tar&quot;</th>
<th>Brown carbon (brC)</th>
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<td><strong>Solubility</strong></td>
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<td><strong>Substantial solar absorption at</strong> $\lambda =$</td>
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<td><strong>Chemical state</strong></td>
<td>Contorted graphene layers (sp2 bonding)</td>
<td><strong>Amorphous solid</strong> (sp3 and sp2 bonding)</td>
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<td><strong>Vapourization at</strong></td>
<td>$\sim 4000$ K</td>
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<td><strong>Produced by</strong></td>
<td>Flame synthesis</td>
<td>Fuel-droplet pyrolysis</td>
<td>Partial pyrolysis</td>
<td>Oxidation, partial pyrolysis, ...</td>
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**Notes:**
- Char: Chen, Shah et al., *Energy Fuels* 2005
- brC: Laskin et al., *Chem Rev.* 2015

**Legend:**
- "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]:

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.

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 $\lambda < 500\text{nm}$ [1]
- We observed anomalous HFO-PM “brC” absorption:
  - 20% of 600-nm total at 50% load [2]

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

Results from this study:
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]

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

Corbin et al., in prep. 2018

- **AAE = 1.7 before and after** \(\rightarrow\) Toluene-insoluble “brC” \(\rightarrow\) 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
Hypothesis 2: is HFO-PM ‘brC’ due to char-BC?
Scanning electron microscopy

- Hypothesis: Char BC
  \((BC \text{ with diameters } \sim 1\mu m)\)
  may show anomalous optical properties.
  
  - SEM showed no char in our samples.

- **SEM identified tar spheres**
  \((\text{involatile, amorphous carbon “tar” spheres, stable in electron beam})\)
  in HFO-PM.

Corbin et al., in prep. 2018
Hypothesis 3: tar is the ‘brC’ species in HFO-PM

- **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**

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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

\[ b_{\text{abn},780} = MAC_{780} \times C_{rBC} - (0.5 \pm 2.3) \times 10^3 \]

MAC_{780} = 7.8 \pm 1.8

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