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

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Outline

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

CAM5 adjusted BC direct forcing (W m\(^{-2}\))

anthropogenic CO2 absorption by soot "black carbon"

Black carbon (BC):

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

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


# Defining and measuring BC Light-Absorbing Carbon

<table>
<thead>
<tr>
<th>Property</th>
<th>Soot BC</th>
<th>Tar brC</th>
</tr>
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<tbody>
<tr>
<td>Solubility&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Negligible solubility in common solvents</td>
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<td>Light absorption</td>
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<td>Contorted graphene layers</td>
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<td>Carbon bonding</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt; dominated</td>
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<td>Vapourization at&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>Produced by</td>
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<td><img src="image1.png" alt="Image" /></td>
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<td>Diameter&lt;sup&gt;c&lt;/sup&gt; [μm]</td>
<td>0.02–0.2</td>
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<sup>a</sup> Solubility refers to the ability of the BC to dissolve in various solvents.

<sup>b</sup> Vapourization temperature indicates the threshold at which the BC starts to evaporate or volatilize.

<sup>c</sup> Diameter refers to the size range of the BC particles.
# Defining and measuring Light-Absorbing Carbon

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<sup>a</sup> New categorization of light-absorbing carbon (LAC) in the atmosphere.
Defining and measuring Light-Absorbing Carbon

Corbin et al., Nature npj Clim Atmos Sci 2019

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<td>0.2–1.2</td>
<td>2.7–9.9</td>
<td>≪0.1–6.0</td>
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<td>MAE (550 nm)&lt;sup&gt;d&lt;/sup&gt; [m&lt;sup&gt;2&lt;/sup&gt;/g]</td>
<td>7.5 ± 1.2</td>
<td>0.2–1.3</td>
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⇒ New categorization of light-absorbing carbon (LAC) in the atmosphere.
Tar $\gg$ 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.
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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
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Experiment Overview

- **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 tar
Evaporating, non-incandescing tar [1/2]

578 of $2.5 \times 10^5$ 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 tar
Incandescing tar identified in combination with light-scattering analysis

[Graphs showing aerosol particle distributions]

a) soot-BC case

b) tar-rich case
Conclusions

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.
Acknowledgements

Prem Lobo, NRC
Martin Gysel, NRC
BLACARAT EU Grant
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Corbin et al., Nature npj Clim Atmos Sci 2019

Proxies for

\(\Rightarrow\) ‘EC’: Refractory carbon at 900-1200 K
slow heating in helium
optical absorption correction for org. pyrolysis

\(\Rightarrow\) ‘eBC’: Light absorption equivalent
based on literature
mass absorption efficiency (MAE)

\(\Rightarrow\) ‘rBC’: Refractory carbon at \(\sim 3500\) K
rapid laser heating,
measure incandescence (UI)
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

- "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]

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

- rBC GSD ~ 2.1

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