Tar Balls: An Important Class of BrC

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**Type of Spherical Carbonaceous Solids**

### Tar Balls (TBs)

- Spherical shape
- Particle diameter between 200 - 500 nm
- High viscosity
- Lack of crystallinity and absence of graphitic fine structure
- Composed primarily of carbon and oxygen
- Low volatility
- Recognized only through transmission electron microscopy (TEM)
Hand et al., JGR 2005

Yosemite Aerosol Characterization Study observed several wildfires that contained > 70% TBs.

Hoffer et al., (2016) reported that TBs absorb from visible to the near-IR.

Figure 2. Absorption Ångström exponent of tar balls prepared from the liquid distillate of black locust and Norway spruce.

Radiative forcing impact of TBs could be significant:
- BB events produce a lot of these particles
- TBs appear to possess a wide absorption spectrum

Evidence for 2 Flavors of TBs.

Evidence for TB aggregates

Li et al., ACP 2019
How are Tar Balls Formed?

- TB formation involving secondary gas-to-particle polymerization
- Followed by dehydration.

\[ \text{Gas-to-particle formation} \rightarrow \text{Polymerization and dehydration} \]

- Upon initial plant burning a liquid tar droplet is released from the pores of plants
- Transformation of tar droplet to tar balls occurs upon rapid heating (600 C)

\[ \text{Tar-water emulsion} + \text{fire} = \text{Tar ball} \]

BBOP demonstrated that TBs are a processed primary particles (Sedlacek ACP et al., 2018)

Pósfai et al., 2004
Toth et al., (2014)
Compositional and Microphysical Changes Support Indirect Mechanism

Adachi et al., (under review)

Changes in particle shape and element distributions

- Particles become spherical and the TB number fraction increases.
- C, O, N, and Cl occur in all particles.
- K is a conserved tracer.

STXM analysis
Retention of spherical shape upon impact on the substrate indicates particles possess higher viscosity and surface tension.

Particle shape becomes more spherical with age.

Increase in O and N associated with increased sphericity.
Previous reported values of Tar Ball refractive index:

- $m = 1.67 - 0.27i$ (Alexander et al., 2008)
- $m = 1.84 - 0.21i$ (Hoffer et al., 2015)
- $m = 1.56 - 0.02i$ (Hand et al., 2005)
- $m = 1.80 - 0.007i$ (Chakrabarty et al., 2010)
- $m = 1.75 - 0.002i$ (Chakrabarty et al., 2010)

100x range in imaginary component

$m = 1.56 - 0.02i$, based on SSA consistency between calculations and BBOP field measurements. (Sedlacek et al., 2018)
Evolution of Brown Carbon (BrC) Absorption

AAE

<table>
<thead>
<tr>
<th>Wavelength pair</th>
<th>Near source</th>
<th>Downwind</th>
<th>%Δ</th>
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<tbody>
<tr>
<td>355/532 nm</td>
<td>2.6</td>
<td>3.5</td>
<td>36</td>
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<tr>
<td>464/522 nm</td>
<td>2.2</td>
<td>2.7</td>
<td>23</td>
</tr>
<tr>
<td>522/648 nm</td>
<td>1.9</td>
<td>2.3</td>
<td>13</td>
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Absorption apportionment

<table>
<thead>
<tr>
<th>532 nm</th>
<th>45</th>
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<tbody>
<tr>
<td>$B_{abs-BrC}/B_{abs-total}$</td>
<td>19%</td>
</tr>
<tr>
<td>355 nm</td>
<td>-25</td>
</tr>
<tr>
<td>$B_{abs-BC}/B_{abs-total}$</td>
<td>40%</td>
</tr>
</tbody>
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Use $B_{BC}^{532nm}$ to estimate $B_{BC}^{355nm}$

$B_{BrC}^{355nm} = B_{expt}^{355nm} - B_{BC}^{355nm}$

OA loading from SP-AMS

$\lambda = 355 \text{ nm}$

MAC$_{BrC}$: 1.3 m$^2$/g
**MAC\textsubscript{BrC} (1.3 m\textsuperscript{2}/g @ 355 nm) compares very favorable with MAC\textsubscript{TB} = 1.1 m\textsuperscript{2}/g reported by Li et al., (2019)**

Core assumption: all ORG contributes to BrC absorption
**Microphysical Properties of Tar Balls**

Volume changes upon heating of aerosol particles from biomass burning using transmission electron microscopy

Kouji Adachi, Arthur J. Sedlack 3, Lawrence Kleinman, Duli Chand, John M. Hubbe, and Peter R. Buseck

- Chemical analysis reveals that K and Na remain in the residues, whereas S and O were lost.
- Some organic particles exhibit significant thermal stability.
- Results suggest caution assuming complete loss of organic material with thermal denuders.

- Single-particle results imply that many individual organic particles consist of multiple types of organic matter having different thermal stabilities.
- Potentially under report measurements of carbonaceous particles using thermal/optical carbon analyzers.
Evidence for Charring of Tar Balls

In 2016, Aerodyne and Brookhaven pyrolyzing pine twigs to generate TBs and found these TBs to contain hydrocarbons and rBC. The latter a very puzzling result.

Pyrolysis of pine twigs

Lab-generated TBs similar

Hoffer et al., (2016) that SP2 can induce charring and rBC production in those materials possessing a near-IR absorption

It is estimated that ~10% of the TBs generated underwent SP2 laser-induced charring.
Sedlacek et al., 2018 demonstrates that rBC production via laser-induced charring of near-IR light absorbing OA

- TBs possess requisite near-IR (NIR) light absorption: ~ 10% charring efficiency.
- Potentially technique to provide particle-resolved measurement of NIR light absorbing BrC.
Observation of Coagulated and Uncoagulated Tar Balls

Aircraft-based measurements see little evidence for coagulated TBs
Ground-based measurements report presence for coagulated TBs

One explanation to reconcile these two observations

- Smoldering conditions are lower temperature translating to lower injection height of emissions.
- Resulting concentration gradient would favor high concentrations lower to the ground.
- Higher concentrations favor coagulation.
Summary

Tar balls are an important class of aerosol that can (should) be treated as uniquely as soot is treated in models of wildfire plumes.

- Detected by several groups throughout the world representing several different fire source.
- These aerosols can represent a sizable contribution to BB aerosol mass.
- Light absorption spans the entire spectral range from UV to near-IR.
- Refractive index is closer to that of BrC ($i \sim 0.02$) and not $i \sim 0.2$.
- Primary processed particles (low-viscosity OA $\rightarrow$ high-viscosity, spherical particle).
- Evidence that TBs can be uniquely detected via online techniques (SP-LD-REMPI; AMS; SP2).

Outstanding questions

- How representative are laboratory-generated TBs to those measured in the field.
- What are the hygroscopic properties of these particles.