Supplementary information for:

A dominant contribution to light absorption by methanol-insoluble brown carbon produced in the combustion of biomass fuels typically consumed in wildland fires in the United States

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S1. Uncertainty Analysis:

Here we present uncertainty propagation for variables in the main text, which was used to produce the error bars in the figures. The uncertainty in values measured online (using SMPS and MultiPAS-III) are the standard deviation from a number of measurements, while the uncertainty in values measured offline (UV-vis and OCEC analyzer) are obtained from values reported by the instrument manufacturer. Uncertainties for calculated values are determined using propagation of error, as detailed below. For each value, we show the equation used to calculate it in the main text followed by the uncertainty calculation.

S1.1. Uncertainty in TM, the mass of organic and elemental particulate carbon on the quartz filter.

\[ TM = TM_{Q,unextracted} - TM_{QBT} \]
\[ \sigma_{TM}^2 = \sigma_{TM_{Q,unextracted}}^2 + \sigma_{TM_{QBT}}^2 \]

S1.2. Uncertainty in OMMSbrC, the mass of organic particulate carbon on the quartz filter.

\[ OM_{MSbrC} = (TM_{Q,unextracted} - TM_{QBT}) - TM_{extracted} \]
\[ \sigma_{OM_{MSbrC}}^2 = \sigma_{TM_{Q,unextracted}}^2 + \sigma_{TM_{QBT}}^2 + \sigma_{TM_{extracted}}^2 \]

Where \( \sigma_{TM_{Q,unextracted}}, \sigma_{TM_{QBT}}, \) and \( \sigma_{TM_{extracted}} \) are reported by the OCEC analyzer.

S1.3. Uncertainties in the mass fractions of MSBrC, MIBrC, and EC.
\[ f_{MSBrC} = \frac{OM_{MSBrC}}{TM}, f_{MIBrC} = \frac{OM_{MIBrC}}{TM}, f_{EC} = \frac{EC}{TM} \]

\[ \sigma_{f_{MSBrC}}^2 = \sigma_{OM_{MSBrC}}^2 \left( \frac{1}{TM} \right)^2 + \sigma_{TM}^2 \left( \frac{OM_{MSBrC}}{TM^2} \right)^2 \]

\[ \sigma_{f_{MIBrC}}^2 = \sigma_{OM_{MIBrC}}^2 \left( \frac{1}{TM} \right)^2 + \sigma_{TM}^2 \left( \frac{OM_{MIBrC}}{TM^2} \right)^2 \]

\[ \sigma_{f_{EC}}^2 = \sigma_{EC}^2 \left( \frac{1}{TM} \right)^2 + \sigma_{TM}^2 \left( \frac{EC}{TM^2} \right)^2 \]

**S1.4. Uncertainty in \( k_{MSBrC} \)**

\[ k_{MSBrC, \lambda} = \frac{A(\lambda)}{C_{MSBrC}} \times \frac{\ln 10 \rho \lambda}{4\pi L} \]

\[ \sigma_{k_{MSBrC, \lambda}}^2 = \left( \frac{\ln 10 \rho \lambda}{4\pi L} \right)^2 \times \left( \sigma_{A(\lambda)}^2 \left( \frac{1}{C_{MSBrC}} \right)^2 + \sigma_{C_{MSBrC}}^2 \left( \frac{A(\lambda)}{C_{MSBrC}} \right)^2 \right) \]

Where \( C_{MSBrC} \) is the concentration of the MSBrC solution and \( \sigma_{C_{MSBrC}} \) is retrieved from the OCEC analyzer. \( \sigma_{A(\lambda)} \) is 1% of \( A(\lambda) \), per manufacturer’s specifications.

**S1.5. Uncertainty in \( w \)**

\[ w = \frac{\log (k_{422}/k_{532})}{\log (532/422)} \]

\[ \sigma_w^2 = \left( \frac{1}{\ln(532/422)} \right)^2 \times \left( \sigma_{k_{422}}^2 \left( \frac{1}{k_{422}} \right)^2 + \sigma_{k_{532}}^2 \left( \frac{1}{k_{532}} \right)^2 \right) \]

In the cases where the equation above corresponds to aerosol measurements, \( \sigma_{k_{\lambda}} \) is the standard deviation of the \( k_{\lambda} \) values obtained from Mie theory calculations over the period of sampling, with one average \( k_{\lambda} \) calculated for every 90 s of measurement, the length of an SMPS scan. For MSBrC and MIBrC, \( \sigma_{k_{\lambda}} \) is calculated as described in S1.4 and S1.7, respectively.

**S1.6. Uncertainty in \( k_{550} \)**

\[ k_{550} = k_{532} \left( \frac{550}{532} \right)^{-w} \]

\[ \sigma_{k_{550}}^2 = \sigma_{k_{532}}^2 \left( \frac{550}{532} \right)^{-2w} + \sigma_w^2 \left( k_{532} \times \ln \left( \frac{550}{532} \right) \times \left( \frac{550}{532} \right)^{-w} \right)^2 \]

**S1.7. Uncertainty in \( k_{MIBrC} \)**
\[ k_{\text{MBrC}} = \left( k_{\text{BrC, aerosol}} - f_{\text{MSBrC}} \right) \frac{f_{\text{MSBrC}} + f_{\text{MBrC}}}{f_{\text{MBrC}}} \]

\[ \sigma_{k_{\text{MBrC}}}^2 = \sigma_{\text{BrC, aerosol}}^2 \left( \frac{f_{\text{MSBrC}} + f_{\text{MBrC}}}{f_{\text{MBrC}}} \right)^2 + \sigma_{f_{\text{MBrC}}}^2 \left( \frac{f_{\text{MBrC}}}{f_{\text{MSBrC}} + f_{\text{MBrC}}} \right)^2 + \sigma_{f_{\text{MBrC}}}^2 \left( \frac{k_{\text{BrC, aerosol}} - k_{\text{MBrC}}}{f_{\text{MBrC}}} \right)^2 \]

Where \( \sigma_{\text{BrC, aerosol}} \) is the standard deviation of the \( k_{\lambda} \) values calculated from Mie theory calculations, as in S1.4.

**S1.8. Uncertainty in \( X_{\text{abs, EC}} \), the fraction of absorption attributed to EC.**

\[ X_{\text{abs, EC}} = \frac{b_{\text{abs, EC}}}{b_{\text{abs}}} \]

\[ \sigma_{X_{\text{abs, EC}}}^2 = \sigma_{b_{\text{abs, EC}}}^2 \left( \frac{1}{b_{\text{abs}}} \right)^2 + \sigma_{b_{\text{abs}}}^2 \left( \frac{b_{\text{abs, EC}}}{b_{\text{abs}}} \right)^2 \]

Where \( \sigma_{b_{\text{abs}}} \) is the standard deviation of the absorption measured from Multi-PAS III, with one average \( \sigma_{b_{\text{abs}}} \) calculated for every 90 s of measurement, the length of an SMPS scan. \( \sigma_{b_{\text{abs, EC}}} \) is the standard deviation of the absorption attributed to EC and is calculated in the same fashion.

**S1.9. Uncertainty in \( X_{\text{abs, MSBrC}} \), the fraction of absorption attributed to MSBrC.**

\[ X_{\text{abs, MSBrC}} = (1 - X_{\text{abs, EC}}) \frac{k_{\text{MSBrC}} \times f_{\text{MSBrC}}}{f_{\text{MBrC}}} \]

\[ \sigma_{X_{\text{abs, MSBrC}}}^2 = \sigma_{X_{\text{abs, EC}}}^2 \left( \frac{k_{\text{MSBrC}} \times f_{\text{MSBrC}}}{f_{\text{MBrC}}} \right)^2 + \sigma_{f_{\text{MBrC}}}^2 \left( \frac{f_{\text{MBrC}}}{f_{\text{MSBrC}} + f_{\text{MBrC}}} \right)^2 + \sigma_{f_{\text{MSBrC}}}^2 \left( \frac{k_{\text{BrC, aerosol}} \times f_{\text{MSBrC}}}{f_{\text{MBrC}}} \right)^2 + \sigma_{k_{\text{BrC, aerosol}}}^2 \left( \frac{k_{\text{BrC, aerosol}} \times f_{\text{MSBrC}}}{f_{\text{MBrC}}} \right)^2 \]
S1.10. Uncertainty in $X_{abs, MIBrC}$, the fraction of absorption attributed to MIBrC.

$$X_{abs, MIBrC} = (1 - X_{abs, EC}) \frac{k_{MIBrC} \times f_{MIBrC}}{k_{BrC, aerosol}} \left(\frac{f_{MSBrC} + f_{MIBrC}}{k_{BrC, aerosol}}\right)$$

$$\sigma_{X_{abs, MIBrC}}^2 = \sigma_{X_{abs, EC}}^2 \left(\frac{k_{MIBrC,\lambda} \times f_{MIBrC}}{k_{BrC, aerosol}}\right)^2 + \sigma_{k_{MIBrC,\lambda}}^2 \left(1 - X_{abs, EC,\lambda}\right)$$

$$+ \sigma_{f_{MIBrC}}^2 \left(1 - X_{abs, EC}\right) \frac{k_{MIBrC} \times f_{MIBrC}}{k_{BrC, aerosol}} \left(\frac{f_{MSBrC} + f_{MIBrC}}{k_{BrC, aerosol}}\right)^2 + \sigma_{f_{MSBrC}}^2$$

$$+ \sigma_{k_{BrC, aerosol}}^2 \left(1 - X_{abs, EC}\right) \frac{k_{MIBrC} \times f_{MIBrC}}{k_{BrC, aerosol}} \left(\frac{f_{MSBrC} + f_{MIBrC}}{k_{BrC, aerosol}}\right)^2$$

S2. Light absorption by the EC fraction

We employed alternative methods of estimating the contribution of the EC fraction to light absorption. In the main text, we assumed that the EC fraction was externally mixed with the BrC and constituted a fraction of the number distribution equal to $f_{EC}$. We then used Mie Theory calculations to calculate the absorption by the EC fraction of the distribution.

Here, we use the Rayleigh-Debye-Gans (RDG) approximation to estimate the absorption by the EC fraction. In RDG, we assumed a diameter of 50 nm for the EC spherules, as an intermediate estimate between previously used values. The total number of EC spherules in a distribution can then be estimated by dividing the EC mass concentration in the distribution (i.e., $C_{OA} \times f_{EC}$) by the mass of a single spherule, assuming an EC (black carbon) density of 1.8 g/cm$^3$.

We used RDG to estimate $X_{abs, EC}$ and then retrieve $k_{MIBrC}$, as in the main text. The results of $k_{MSBrC}$ are shown in Figure S1 using the alternative calculation methods. On average, the difference between $k_{MIBrC, Mie}$ and $k_{MIBrC, RDG}$ was around 3%, with a maximum value of 10%.

S3. Uncertainty in OM/OC

To account for the uncertainty in the OM/OC ratios and its implications on the measured and calculated light absorption properties of MSBrC and MIBrC, we recalculated $k_{MSBrC}$ and $k_{MIBrC}$ using OM/OC of 1.5 and OM/OC of 2, accounting for the ranges reported in the literature.
Figure S1 Comparison between the imaginary component of the refractive index of MIBrC retrieved using Mie calculations and RDG calculations to represent light absorption by EC. Each data point corresponds to a different experiment. The solid black line is the 1:1 line.
### Tables

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>Temperature (°C)</th>
<th>Residence time (s)</th>
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<tr>
<td>Helium</td>
<td>310</td>
<td>80</td>
<td>OC1</td>
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<tr>
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<td>475</td>
<td>60</td>
<td>OC2</td>
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<td></td>
<td>615</td>
<td>60</td>
<td>OC3</td>
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<tr>
<td></td>
<td>870</td>
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<td>OC4</td>
</tr>
<tr>
<td>Oxygen (2%) in helium</td>
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<td>45</td>
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</tr>
<tr>
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<td>625</td>
<td>45</td>
<td>EC2</td>
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<tr>
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<td>870</td>
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<td>EC6</td>
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#### Table S1 NIOSH-870 protocol

#### Table S2 Light Absorption Properties of MSBrC and MIBrC calculated using OM/OC = 1.8 (Default), OM/OC = 1.5, and OM/OC = 2.0

<table>
<thead>
<tr>
<th>aerosol</th>
<th>OM/OC = 1.8</th>
<th>OM/OC = 1.5</th>
<th>OM/OC = 2.0</th>
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<td>MSBrC</td>
<td>MIBrC</td>
<td>MSBrC</td>
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<td>Hickory</td>
<td>$k_{422}$ 0.058, $k_{532}$ 0.030</td>
<td>$k_{422}$ 0.019, $k_{532}$ 0.002</td>
<td>$k_{422}$ 0.759, $k_{532}$ 0.504</td>
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<td>Hickory</td>
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<td>Hickory</td>
<td>$k_{422}$ 0.043, $k_{532}$ 0.021</td>
<td>$k_{422}$ 0.016, $k_{532}$ 0.004</td>
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<td>$k_{422}$ 0.043, $k_{532}$ 0.028</td>
<td>$k_{422}$ 0.018, $k_{532}$ 0.005</td>
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<td>$k_{422}$ 0.045, $k_{532}$ 0.017</td>
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<td>$k_{422}$ 0.009, $k_{532}$ 0.001</td>
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<td>Pine</td>
<td>$k_{422}$ 0.048, $k_{532}$ 0.034</td>
<td>$k_{422}$ 0.011, $k_{532}$ 0.003</td>
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#### References


