Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

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 OM_{MSBrC}, 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.

$$f_{MSBrC} = \frac{OM_{MSBrC}}{TM}; f_{MIBrC} = \frac{OM_{MIBrC}}{TM}; f_{EC} = \frac{EC}{TM}$$

$$\sigma_{f_{MSBrC}}^{2} = \sigma_{OM_{MSBrC}}^{2}\left({}^{1}/_{TM}\right)^{2} + \sigma_{TM}^{2}\left({}^{OM_{MSBrC}}/_{TM^{2}}\right)^{2}$$

$$\sigma_{f_{MIBrC}}^{2} = \sigma_{OM_{MIBrC}}^{2}\left({}^{1}/_{TM}\right)^{2} + \sigma_{TM}^{2}\left({}^{OM_{MIBrC}}/_{TM^{2}}\right)^{2}$$

$$\sigma_{f_{EC}}^{2} = \sigma_{EC}^{2}\left({}^{1}/_{TM}\right)^{2} + \sigma_{TM}^{2}\left({}^{EC}/_{TM^{2}}\right)^{2}$$

S1.4. Uncertainty in k_{MSBrC}

$$k_{MSBrC,\ \lambda} = \frac{A(\lambda)}{C_{MSBrC}} \times \frac{ln10\rho\lambda}{4\pi L}$$

$$\sigma_{k_{MSBrC,\ \lambda}}^{2} = \left(\frac{ln10\rho\lambda}{4\pi L}\right)^{2} \times \left(\sigma_{A(\lambda)}^{2}\left({}^{1}/_{C_{MSBrC}}\right)^{2} + \sigma_{C_{MSBrC}}^{2}\left({}^{A(\lambda)}/_{C_{MSBrC}^{2}}\right)^{2}\right)$$

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*

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

$$\sigma_{w}^{2} = \left(\frac{1}{ln(^{532}/_{422})}\right)^{2} \times \left(\sigma_{k_{422}}^{2}\left({}^{1}/_{k_{422}}\right)^{2} + \sigma_{k_{532}}^{2}\left({}^{1}/_{k_{532}}\right)^{2}\right)$$

In the cases where the equation above corresponds to aerosol measurements, $\sigma_{k_\lambda}$is the standard deviation of the k_λ values obtained from Mie theory calculations over the period of sampling, with one average k_λ 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}

$$k_{550} = k_{532}\left({}^{550}/_{532}\right)^{-w}$$

$$\sigma_{k_{550}}^{2} = \sigma_{k_{532}}^{2}\left({}^{550}/_{532}\right)^{-w} + \sigma_{w}^{2}\left(k_{532} \times ln\left({}^{550}/_{532}\right) \times \left({}^{550}/_{532}\right)^{-w}\right)^{2}$$

S1.7. Uncertainty in k_{MIBrC}

$$k_{MIBrC,\lambda} = \left(k_{BrC,aerosol,\lambda} - k_{MSBrC,\lambda}\frac{f_{MSBrC}}{f_{MSBrC}+f_{MIBrC}}\right)\frac{f_{MSBrC}+f_{MIBrC}}{f_{MIBrC}}$$

$$\sigma_{k_{MIBrC,\lambda}}^{2} = \sigma_{BrC,aerosol,\lambda}^{2}\left(\frac{f_{MSBrC}+f_{MIBrC}}{f_{MIBrC}}\right)^{2} + \sigma_{k_{MSBrC,\lambda}}^{2}\left(\frac{f_{MSBrC}}{f_{MIBrC}}\right)^{2} + \sigma_{f_{MSBrC}}^{2}\left(\frac{k_{BrC,aerosol,\lambda} - k_{MS\ldots}}{f_{MIBrC}}\right.$$
$$\left(\frac{k_{BrC,aerosol,\lambda}\times f_{MSBrC} - k_{MSBrC,\lambda}\times f_{MSBrC}}{f_{MIBrC}^{2}}\right)^{2}$$

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

S1.8. Uncertainty in $X_{abs,\,EC}$, the fraction of absorption attributed to EC.

$$X_{abs,\,EC} = \frac{b_{abs,EC}}{b_{abs}}$$

$$\sigma_{X_{abs,\,EC}}^{2} = \sigma_{b_{abs,EC}}^{2}\left({}^{1}\!/_{b_{abs}}\right)^{2} + \sigma_{b_{abs}}^{2}\left({}^{b_{abs,EC}}\!/_{b_{abs}^{2}}\right)^{2}$$

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

S1.9. Uncertainty in $X_{abs,\,MSBrC}$, the fraction of absorption attributed to MSBrC.

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

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

S1.10. Uncertainty in $X_{abs,\,MIBrC}$, the fraction of absorption attributed to MIBrC.

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

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

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[1]. 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} x f_{EC}) by the mass of a single spherule, assuming an EC (black carbon) density of 1.8 g/cm^3 [2].

We used RDG to estimate $X_{abs,\,EC}$ and then retrieve k_{MIBrC}, as in the main text. The results of k_{MIBrC} 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[3-5].

Figures

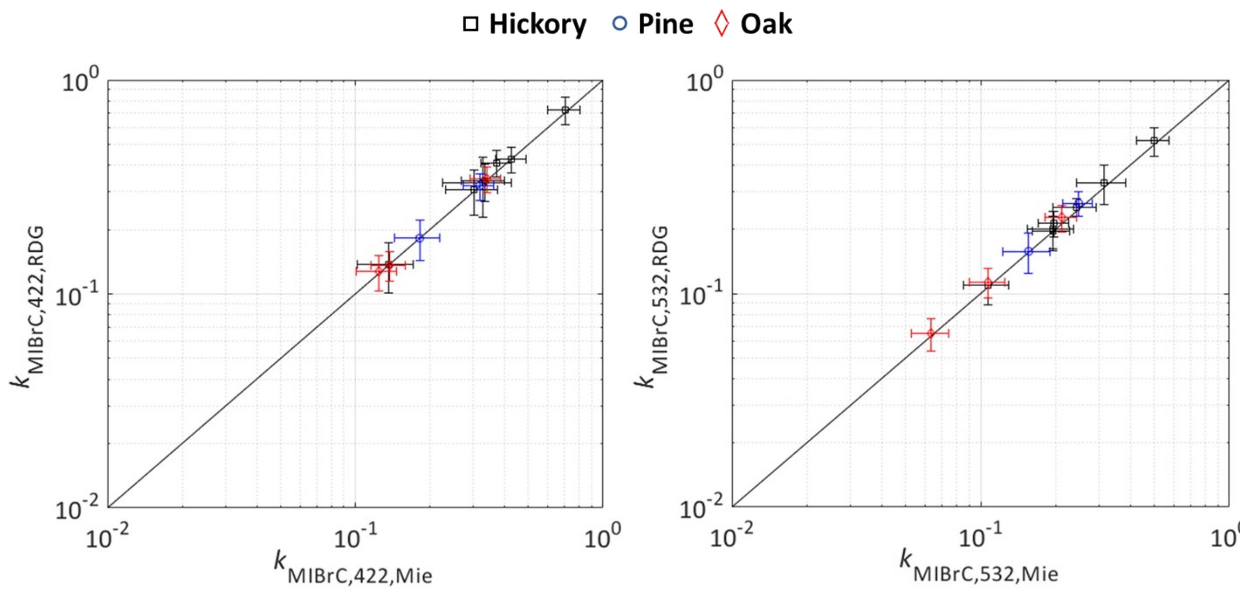

Figure S1 Comparison between the imaginary component of the refractive index of MIBrC retrieved using Mie calculations and RDG calculations to represent light absorption by EC. Each data point corresponds to a different experiment. The solid black line is the 1:1 line.

Tables

Table S1 NIOSH-870 protocol[6]

Carrier gas	Temperature (°C)	Residence time (s)	Carbon Fraction
Helium	310	80	OC1
	475	60	OC2
	615	60	OC3
	870	90	OC4
Oxygen (2%) in helium	550	45	EC1
	625	45	EC2
	700	45	EC3
	775	45	EC4
	850	45	EC5
	870	45	EC6

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

	aerosol		OM/OC = 1.8				OM/OC = 1.5				OM/OC = 2.0			
			MSBrC		MIBrC		MSBrC		MIBrC		MSBrC		MIBrC	
	k_{422}	k_{532}	k_{422}	k_{532}	k_{422}	k_{532}	k_{422}	k_{532}	k_{422}	k_{532}	k_{422}	k_{532}	k_{422}	k_{532}
Hickory	0.058	0.030	0.019	0.002	0.759	0.504	0.022	0.003	0.690	0.496	0.017	0.002	0.793	0.508
Hickory	0.058	0.028	0.012	0.003	0.391	0.202	0.015	0.004	0.370	0.197	0.011	0.003	0.402	0.205
Hickory	0.043	0.021	0.016	0.004	0.367	0.204	0.019	0.005	0.327	0.192	0.014	0.004	0.387	0.209
Hickory	0.043	0.028	0.018	0.005	0.373	0.326	0.021	0.006	0.317	0.310	0.016	0.005	0.401	0.334
Hickory	0.045	0.017	0.015	0.004	0.465	0.204	0.018	0.005	0.421	0.193	0.014	0.003	0.487	0.210
Hickory	0.069	0.049	0.016	0.004	0.315	0.247	0.020	0.005	0.301	0.244	0.015	0.004	0.322	0.248
Hickory	0.023	0.011	0.013	0.003	0.167	0.115	0.015	0.004	0.129	0.106	0.011	0.003	0.186	0.119
Oak	0.044	0.027	0.012	0.004	0.358	0.219	0.014	0.005	0.334	0.210	0.011	0.004	0.370	0.224
Oak	0.022	0.013	0.009	0.001	0.138	0.109	0.011	0.001	0.121	0.107	0.008	0.001	0.147	0.110
Oak	0.027	0.011	0.009	0.001	0.148	0.065	0.011	0.002	0.135	0.063	0.008	0.001	0.154	0.066
Pine	0.036	0.026	0.011	0.004	0.339	0.257	0.013	0.005	0.313	0.246	0.009	0.004	0.352	0.262
Pine	0.048	0.034	0.011	0.003	0.189	0.158	0.013	0.003	0.181	0.156	0.010	0.002	0.193	0.158

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