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Experimental evidence of the lensing effect suppression for atmospheric black carbon containing brown coatings

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ᵃnow at: Institute for Atmospheric and Earth System Research, Univ. Helsinki, Helsinki, FI-00014, Finland
• Short-lived climate forcers produced by anthropogenic activities (e.g., residential wood burning)\[1\]
• Organic carbon (OC) vs elemental carbon (EC): Abundance/absorptivity/vertical distribution\[2,3\]
• Wavelength- and source-dependent absorption by light-absorbing organic (brown) carbon (BrC)\[3\]
• BrC contributes up to 7-19% of the solar radiation absorption by anthropogenic aerosols\[4\]
• Carbonaceous aerosol sources: Mass spectrometry/\(^{14}\)C\[5\], Aethalometer model\[6\], \(\alpha\) method\[7\]
Motivation & Research questions

- EC absorption enhancement (lensing) by non-refractory coatings: BrC/Lensing decoupling?
- BrC isolation by lab optical analysis of liquid filter extracts[^2], no mixing state assumptions
- Biomass burning/aged (unlike fresh traffic) BC is largely internally mixed, with high OC:EC[^3,4]

Heterogeneous, internally-mixed atmospheric particle ensembles

1. What are the sources of atmospheric BrC and their absorption properties?
2. Species-specific \( \lambda \)-dependent absorption closure by *filter-based* methods?

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[^1]: Motivation & Research questions
[^2]: No mixing state assumptions
[^3]: Biomass burning/aged BC
[^4]: Unlike fresh traffic
[^5]: Internal mixing fraction
Instrumentation & Methods flowsheet

- **Magadino & Zurich, daily** PM\(_{10/2.5}\) filters
  - **UV-VIS**: Ultraviolet-visible spectrophotometer (280-600 nm)
  - **Scanning Mobility Particle Sizer**
  - **Aethalometer (AE33 model)**
  - **Multi-Wavelength Absorbance Analyzer** (5-wavelength MWAA)
  - **Sunset OC/EC analyzer** & Ion chromatography
- **Zurich 2013**, 10 min. time resolution
- **Mag & Zur 2013/14**, up to 1h resolution
- **Mag & Zur winter (2 filter samples)**

**Offline High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)**

- **AMS-PMF**: OA factor time series
- **Ultraviolet-Visible (UV-Vis) Absorbance in methanol**
- **Particle size distribution**
- **Calibrated total particulate BrC absorbance**
- **Wavelength dependence of extracted samples**
- **EC & NO\(_3^-/SO_4^{2-}\) mass concentration**
- **Mie calculations (5 mixing state cases)**

**Conceptual model for optical closure (Bare BC+BrC+Lensing)**

**Proxy for BC coating thickness**: (IOA+NO\(_3^-)+SO_4^{2-}\) / EC => Bare BC MAC\(_{060/880nm}\)

**Mie calculations (EC factor constrained)**

**Field-emission Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (FE-SEM/EDS)**

**Morphology and Composition of extracts & untreated samples**

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2. Liu (2013) *ACP*

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*Every 4th day: Magadino Jan ‘13 – Sep ‘14 & Zurich Jan – Dec ‘13 (247 PM\(_{10}\) filters)
& Magadino Jan – Sep ‘14 (65 PM\(_{2.5}\) filters)

**Selection of 27 filters (Mag PM\(_{10/2.5}\) & Zur PM\(_{2.5}\)), wavelengths: 375, 407, 532, 635, 850 nm, exponential curve fitting (R\(^2\) > 0.97) to correct & compare with AE-33 b\(_{ATN}\)**
UV-vis PMF for methanol extracts

Primary factors: HOA: hydrocarbon-like, COA: cooking-related, SCOA: sulfur-containing, BBOA: biomass burning

Secondary factors: WOOA: winter-oxygenated, SOOA: summer-oxygenated [1,3]

1. Daellenbach (2017) ACP

Anthropogenic (non-fossil[3]) BBOA & WOOA are the predominant BrC sources

Non-negligible WOOA contribution to mass & integrated absorbance (also during summer)

- $\text{MAE}_{\text{WINS-BBOA}} \geq \text{MAE}_{\text{BBOA}} > \text{MAE}_{\text{WOOA}}$
- Sensitivity on solvent, spatial/temporal coverage and resolution, and AMS factor solution (regional vs site-specific)
FE-SEM/EDS analyses

- Carbon assemblies accumulate onto deeper, thinner & rougher fibers and their intersections
- No tar balls\(^1\) identified
- Pseudo-spherical carbon particles not observed after water washing

Zurich winter

Magadino winter

Less volatile\(^2\)/viscous\(^3\) (BB)OA (coating)?

Washed

1. Corbin (2019) *npj CAS*  
2. Pirjola (2017) *Atmos Environ*  
BC spectral absorption properties

Example calculation of $\text{MAC}_{\text{bareBC,660nm}}$ at 95% confidence level

$\text{AE33 calibration constant} \ (C_\lambda)$ based on Multi-Wavelength Absorbance Analyzer (MWAA)

$\text{AAE of bare BC from MWAA upon methanol extraction (removal of coatings/BrC influence)}$

Assessment of possible source-related $\text{MAC}_{\text{BC}}$ variability, relevant also for the application of the Aethalometer model

Reduced data scattering with refined proxy: $([\text{OOA}+\text{HOA}+\text{BBOA}]+[\text{Nitrate}]+[\text{Sulfate}]):[\text{EC}]$

$\text{Mag’13: } r = 0.74, \text{ Zur’13: } r = 0.70$

Calculated intercept within same range

No consistent correlation of $\text{MAC}_{\text{BC}}$ with OA, OA:EC, OOA:EC or OOA:OA
Species-specific optical closure

Relative contribution of particulate species to total absorption

Agreement of $E_{\text{abs,660/880}}$ with other filter-based results & global modeling\(^1\)

Yearly averaged *apparent* $E_{\text{abs,}\lambda} > 1.0$, but wavelength-dependent:

$\text{AAE}_{\text{BC,370-660nm}} = 0.60 \pm 0.23$ (upon BrC-Mie absorption subtraction)

BrC-induced BC lensing suppression

Relevance for high BrC to BC mass/absorbance ratio (co-emitted species from biomass burning, or aged plumes)

Here: Moderately-absorbing BrC\textsuperscript{[1]}, EC:OA ~0.06-0.20

Data scattering:
Variable BrC/BC mixing ratio

Errors in BrC absorbance, daily C value uncertainty etc.

Magadino fitted line shift:
Selective BBOA/WOOA BrC partitioning in coatings (larger BBOA fraction externally mixed vs WOOA)?

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1. Feng (2013) ACP
Single-particle core-shell Mie calculations for 5 distinct mixing state configurations

Yearly average EC/OA/NAM mass concentrations from the observational data

\[ d_{(\text{bare})\text{BC}} = 150 \text{ nm (typical)}, \quad d_{\text{BrC/NAM}} = 270 \text{ nm (median SMPS mass mode)}, \] fixed BC RI/AAE

1) Brown coatings can suppress the lensing effect at short wavelengths (as seen with the 2\textsuperscript{nd} and 5\textsuperscript{th} mixing state configurations), supporting the interpretation of the observations.

2) For the default inputs, NAM does not need to be present for this suppression to occur.

The degree of lensing effect suppression is driven by the BrC shell size relative to the BC core size.
Comprehensive optical & source/chemical speciation of total BrC in Switzerland

Unique combination of multiple filter-based techniques for long-term, spectrally-resolved, source- & species-specific calibrated absorbance closure

First *experimental* verification of BrC-induced BC lensing suppression\(^{[1-4]}\) <470 nm:

*Long-term* \(E_{\text{abs},BC}\) reduction 18 ± 2 % @370 nm (unknown coated particle morphology)

Core-shell models predict a reduction of up to 50 % @400 nm\(^{[1]}\)

>25 % reduction observed here in ~20 % of the filter samples

10 ± 3 % integrated lensing reduction vs clear coatings with assumed constant \(E_{\text{abs},BC,\lambda}\)

Long-term integrated BrC (regardless of mixing state) absorption (> 7 %) overwhelms the reduction in BC lensing (< 3 %)

1. Lack (2010) *ACP*  
3. Cheng (2017) *STOTEN*  
4. Luo (2018) *ACP*
We create knowledge today – for use tomorrow

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Questions?