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[Abstract]

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LABOR FÜR ATMOSPHÄREN-CHEMIE

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

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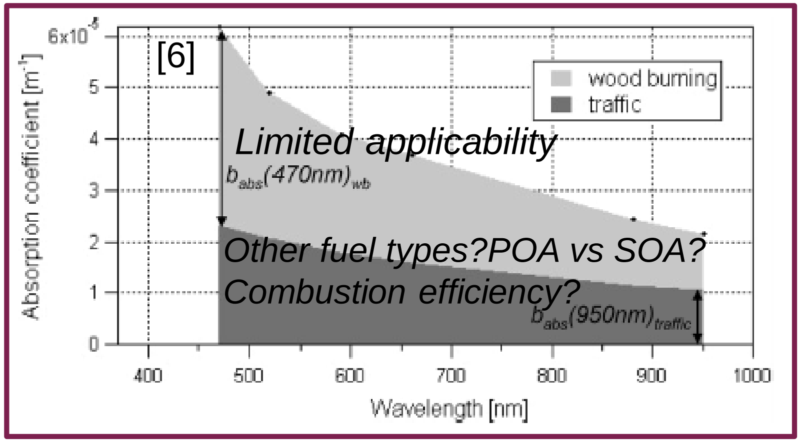
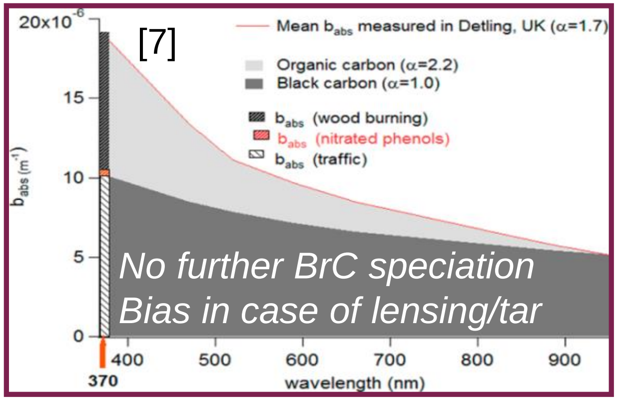
UNIVERSITY OF HELSINKI

INAR

Absorbing atmospheric carbonaceous aerosols

- 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], *α* method[7]



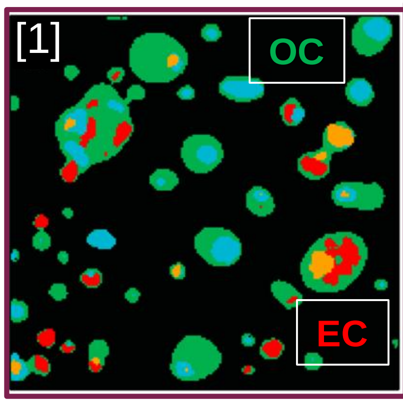


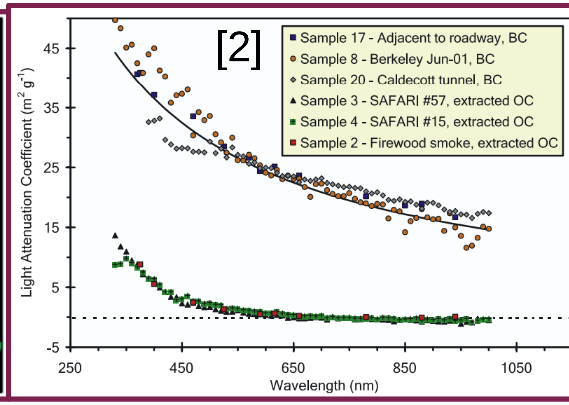
1. IPCC (2013) 2. Zhang (2017) *Nat. Geosci.* 3. Laskin (2015) *Chem. Rev.* 4. Feng (2013) *ACP*
5. Lanz (2008) *ES&T* 6. Sandradewi (2008) *ES&T* 7. Mohr (2013) *ES&T*

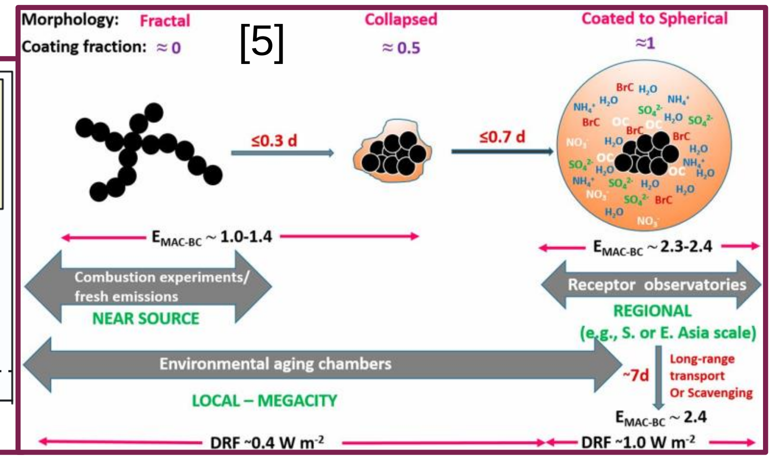
Motivation & Research questions

- 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



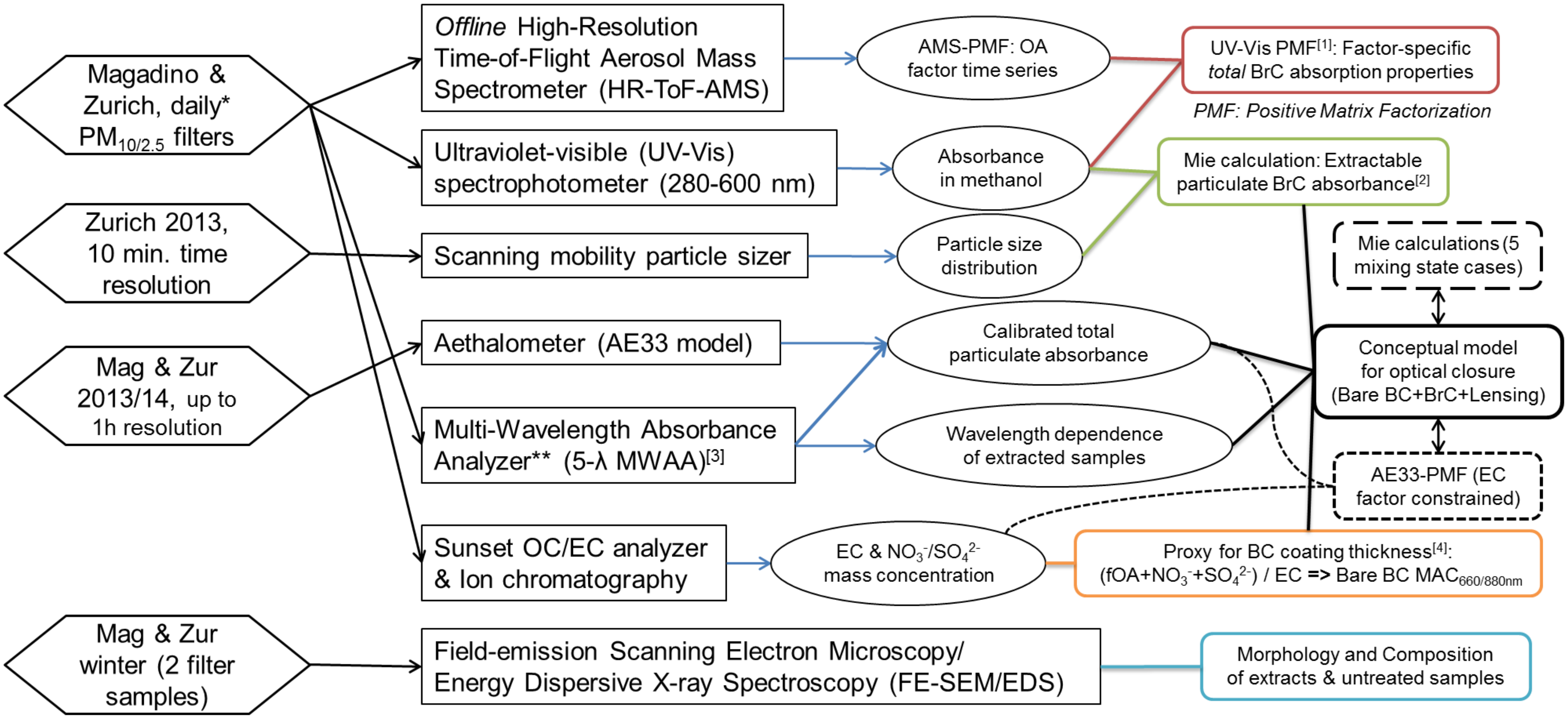




1. **What are the <u>sources</u> of atmospheric BrC and their absorption properties?**
2. **Species-specific λ-dependent absorption <u>closure</u> by *filter-based* methods?**

1. Moffet (2010) *Anal. Chem.*
2. Kirchstetter (2004) *JGR Atmos.*
3. Peng (2016) *PNAS*
4. Liu (2017) *Nat. Geosci.*
5. Gustafsson (2018) *PNAS*

Instrumentation & Methods flowsheet

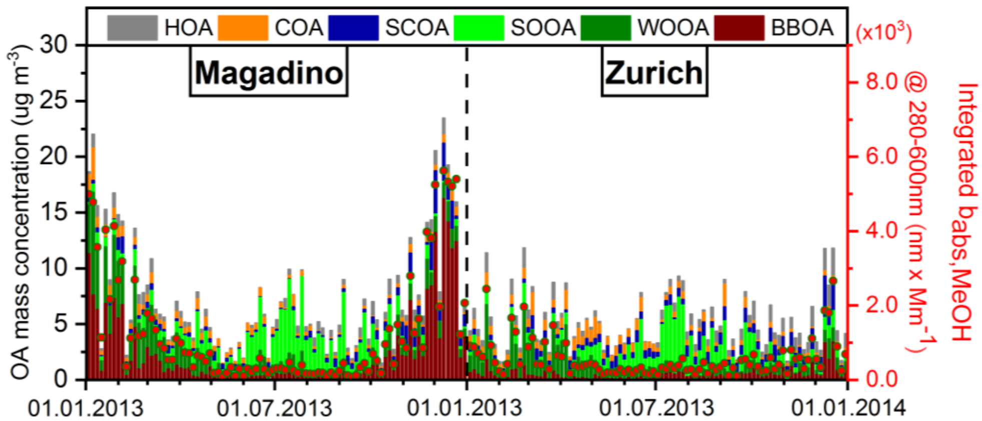


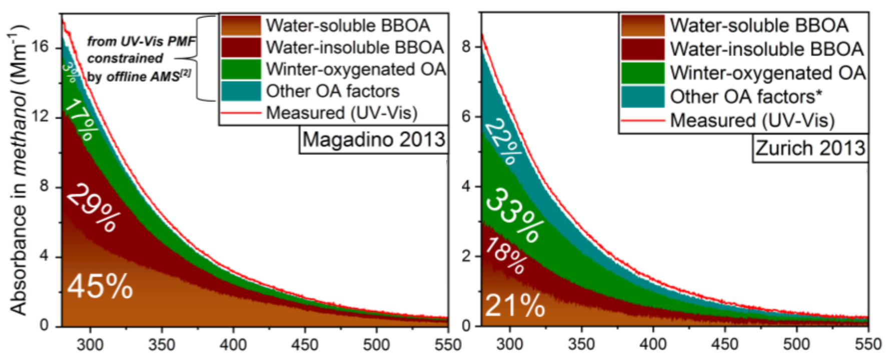
*Every 4th day: Magadino Jan '13 – Sep '14 & Zurich Jan – Dec '13 (247 PM_{10} filters) & Magadino Jan – Sep '14 (65 $PM_{2.5}$ filters)

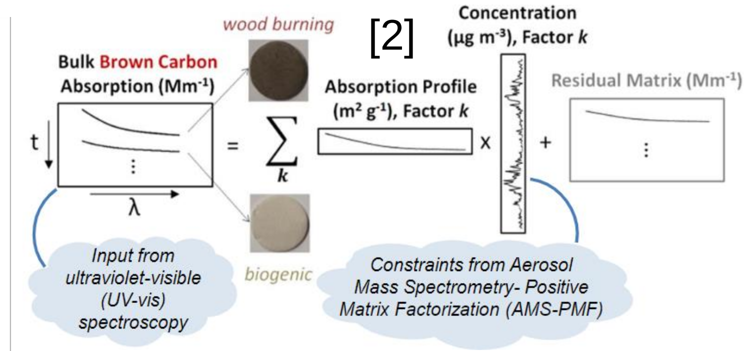
**Selection of 27 filters (Mag $PM_{10/2.5}$ & Zur $PM_{2.5}$), wavelengths: 375, 407, 532, 635, 850 nm, exponential curve fitting ($R^2 > 0.97$) to correct & compare with AE-33 b_{ATN}

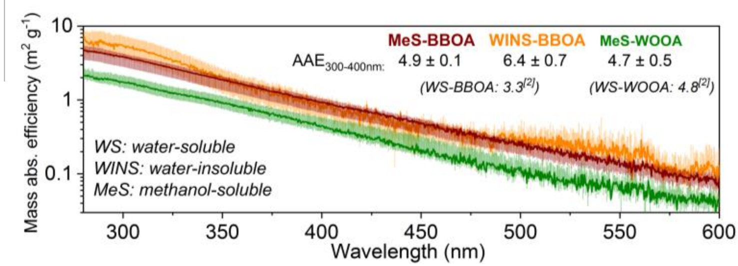
1. Moschos (2018) *ES&T Lett.* 2. Liu (2013) *ACP* 3. Massabò (2013) *J. Aerosol Sci.* 4. Cappa (2012) *Science*

UV-vis PMF for methanol extracts









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

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

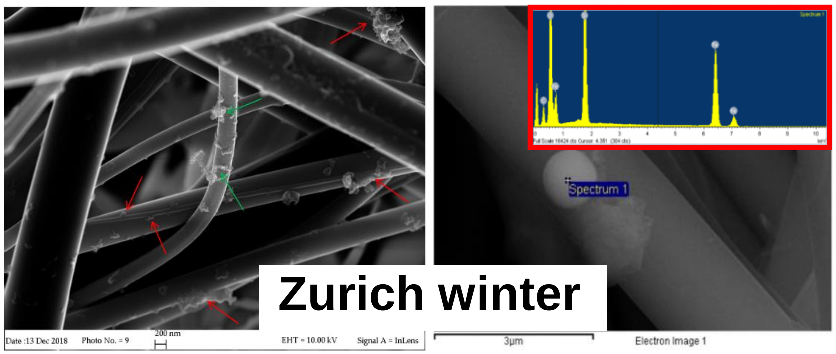
Secondary factors: WOOA: winter-oxygenated, SOOA: summer-oxygenated [1,3]

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

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

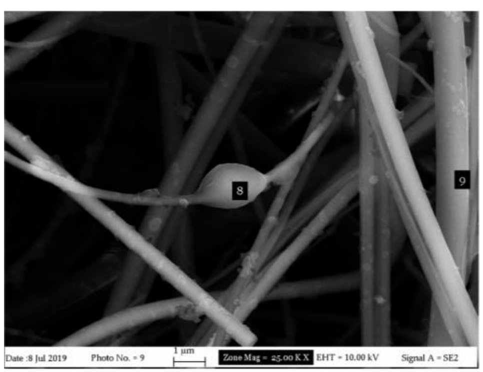
1. Daellenbach (2017) *ACP* 2. Moschos (2018) *ES&T Lett.* 3. Vlachou (2018) *ACP*

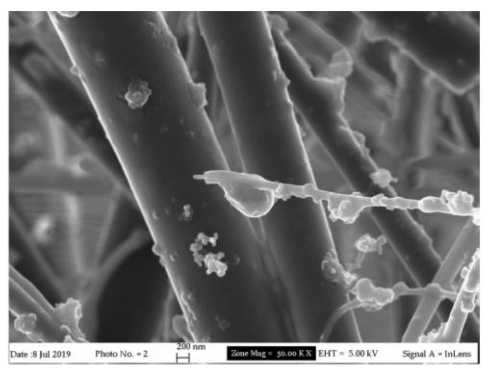
FE-SEM/EDS analyses

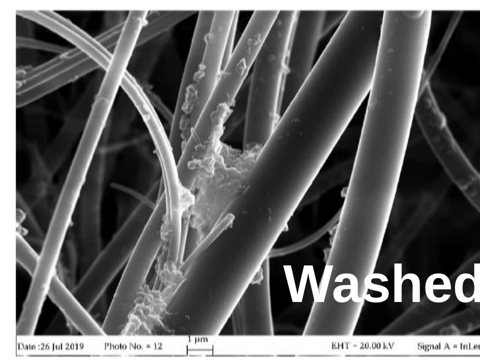


- Carbon assemblies accumulate onto deeper, thinner & rougher fibers and their intersections
- No tar balls[1] identified
- Pseudo-spherical carbon particles not observed after water washing

Less volatile[2]/viscous[3] (BB)OA (coating)?

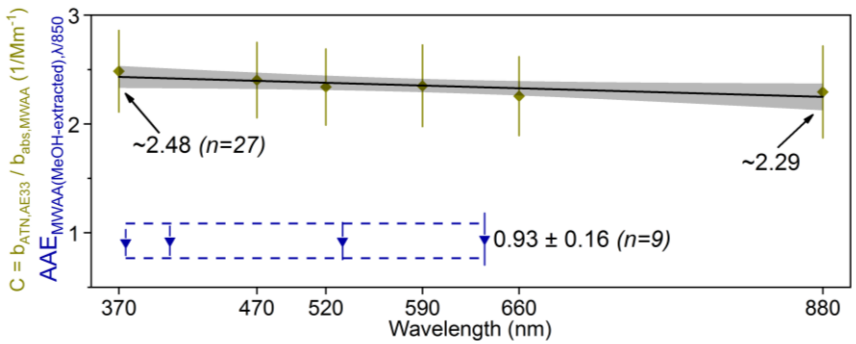






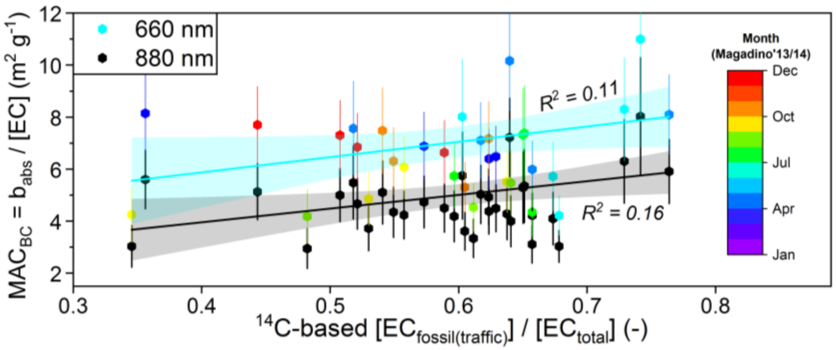
1. Corbin (2019) *npj CAS* 2. Pirjola (2017) *Atmos Environ* 3. Sharma (2018) *GRL*

BC spectral absorption properties

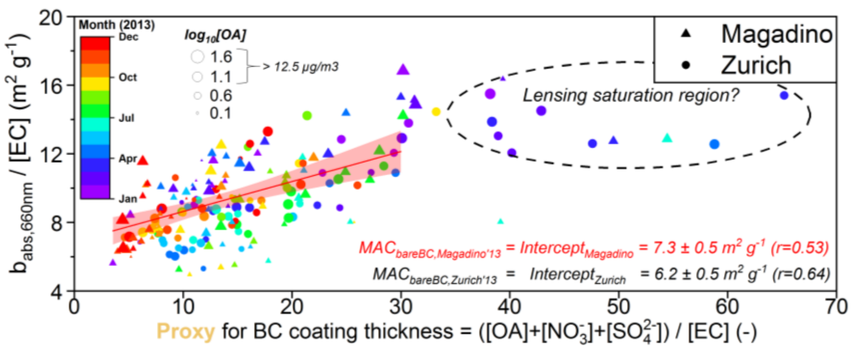


AE33 calibration constant (C_λ) based on Multi-Wavelength Absorbance Analyzer (MWAA)

AAE of bare BC from MWAA upon methanol extraction (removal of coatings/BrC influence)



Assessment of possible source-related MAC_{BC} variability, relevant also for the application of the Aethalometer model

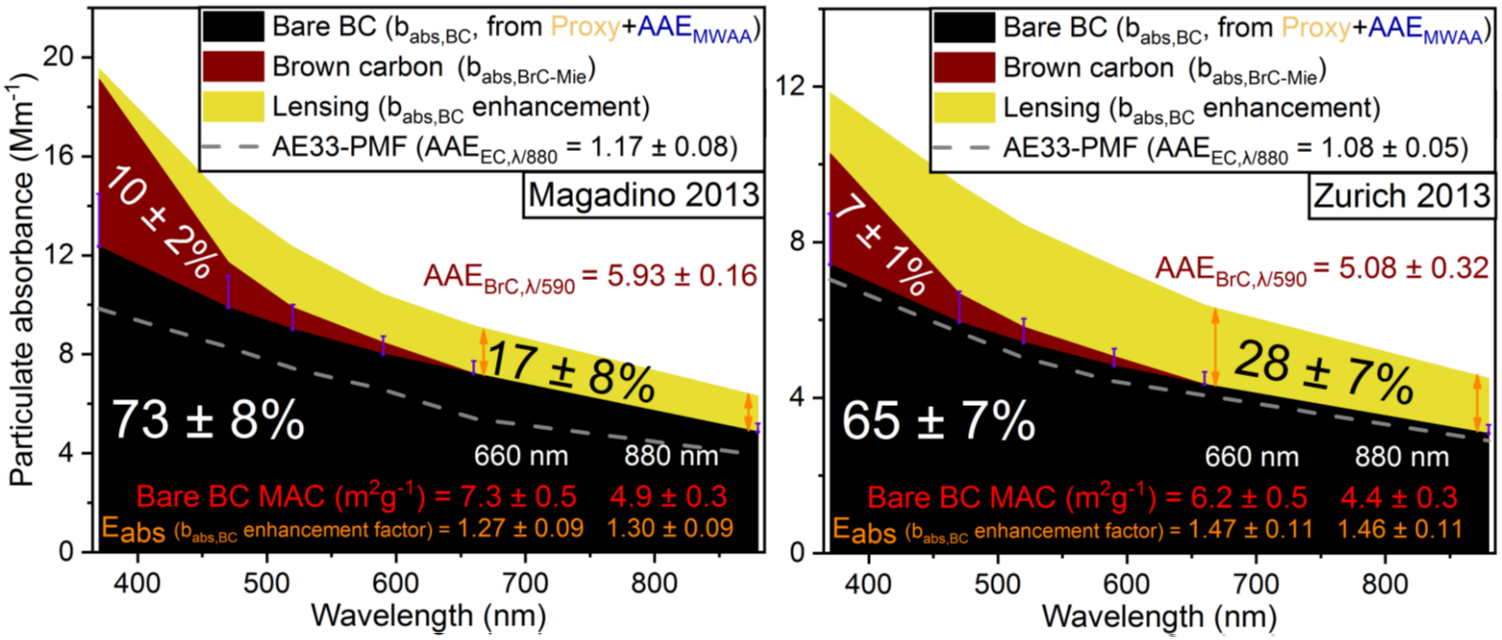


Reduced data scattering with **refined** proxy:
([**OOA+HOA+BBOA**]+[Nitrate]+[Sulfate]):[EC]
Mag'13: r = 0.74, Zur'13: r = 0.70
Calculated intercept within same range

Example calculation of $MAC_{bareBC,660nm}$ at 95% confidence level

No consistent correlation of MAC_{BC} with *OA*, OA:EC, OOA:EC or OOA:OA

Species-specific optical closure



Relative contribution of particulate species to total absorption

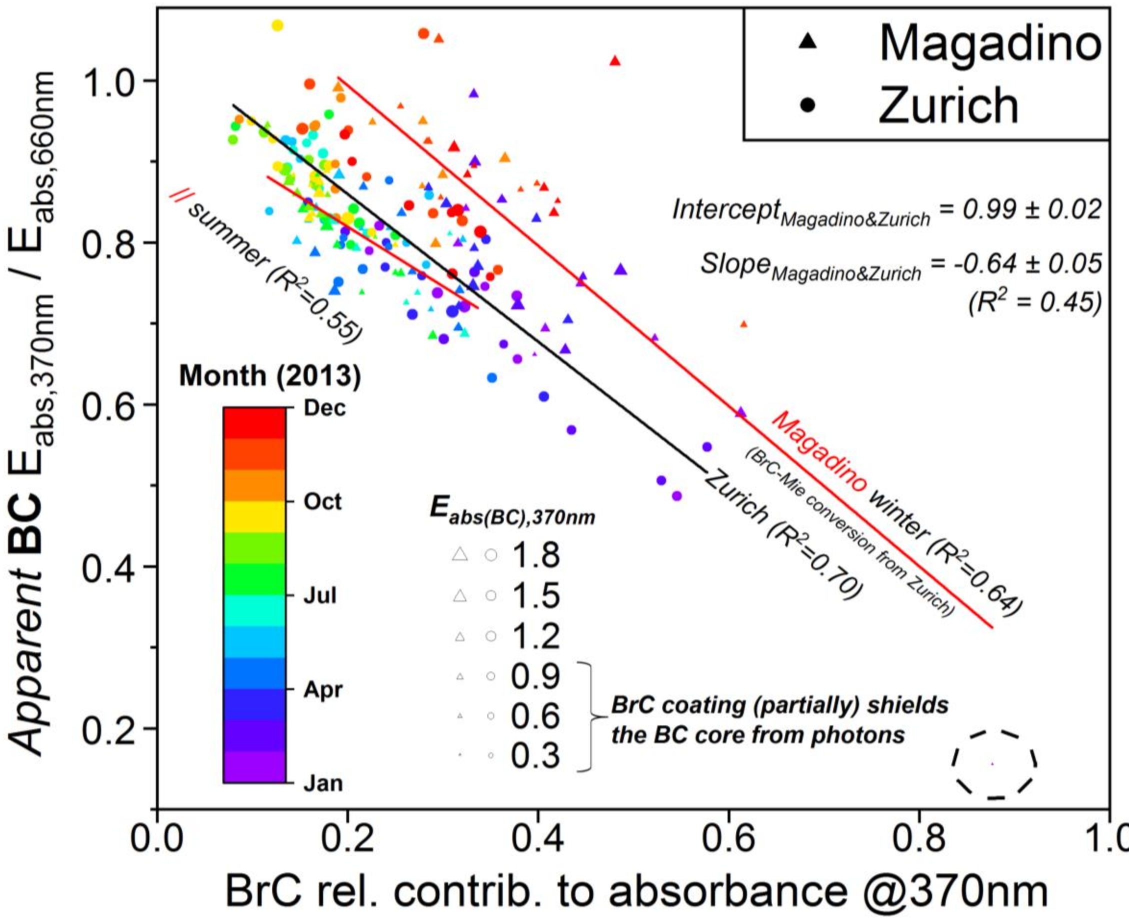
Agreement of $E_{abs,660/880}$ with other filter-based results & global modeling[1]

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

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

1. Fierce (2016) *Nat. Commun.*

BrC-induced BC lensing suppression



Indication of lensing suppression for calibrated AE33 data considering accumulation mode BrC

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

<u>Here</u>: Moderately-absorbing BrC[1], EC:OA ~0.06-0.20

<u>Data scattering:</u>

Variable BrC/BC mixing ratio

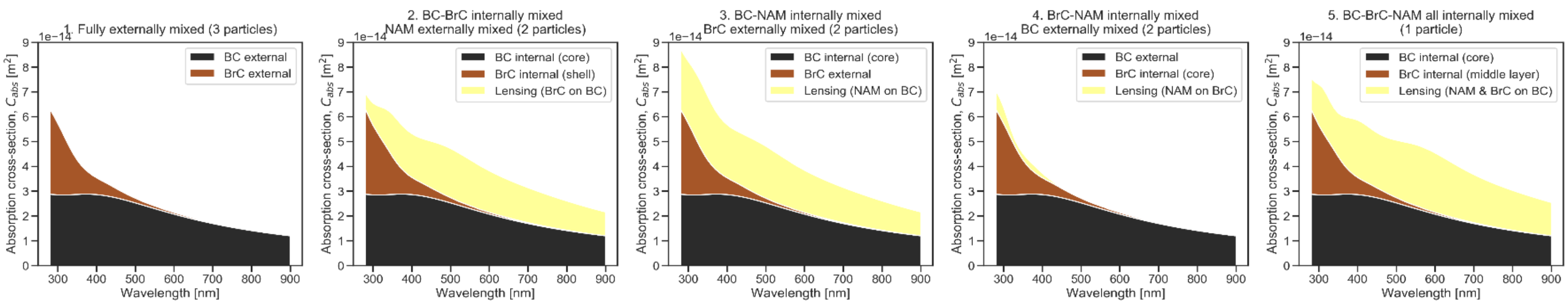
Errors in BrC absorbance, daily C value uncertainty etc.

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

1. Feng (2013) *ACP*

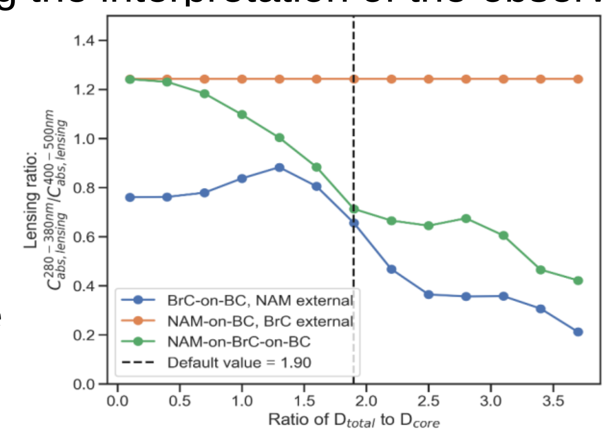
Mie-predicted $E_{abs,BC}$ sensitivity to mixing state

Single-particle core-shell Mie calculations for 5 distinct mixing state configurations
Yearly average EC/OA/NAM mass concentrations from the observational data
$d_{(bare)BC}$ = 150 nm (typical), $d_{BrC/NAM}$ = 270 nm (median SMPS mass mode), fixed BC RI/AAE



1) Brown coatings can suppress the lensing effect at short wavelengths (as seen with the 2nd and 5th 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



Summary & Conclusion

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 $E_{abs,BC}$ 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 $E_{abs,BC,\lambda}$

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

1. Lack (2010) *ACP*   2. Saleh (2015) *JGR Atmos.*   3. Cheng (2017) *STOTEN*   4. Luo (2018) *ACP*

Labor für Atmosphären-Chemie

Questions?

Acknowledgements
Denise Verhoeven
Julia Schmale

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