

Advanced TC-BC(λ) Method

Aerosol Magee Scientific, R&D

Matic Ivančič, Ph.D.



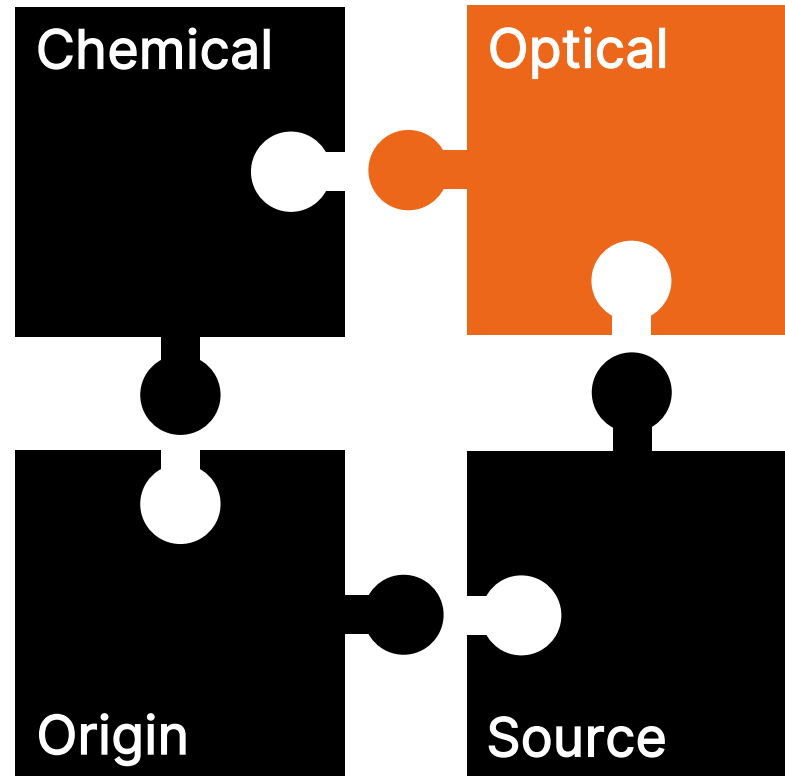
Research Reinforcing in the [Western Balkans](#) in
[Offline](#) and [Online](#) Monitoring and Source
Identification of Atmospheric [Particles](#)

WeBaSOOP training

Ljubljana, 28 May 2024

Carbonaceous aerosols

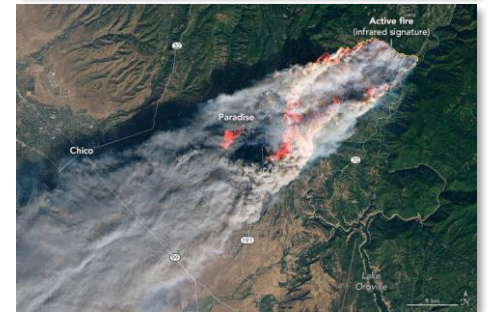
Elemental /
organic



Absorbing /
non-absorbing

Primary /
secondary

Natural /
anthropogenic



TC-BC(λ) method

Measurements

CASS



TCA08
+
AE33

TCA08:

- Simplified thermal protocol for TC
- Two chambers - continuous data
- 20 min – 24 h time resolution

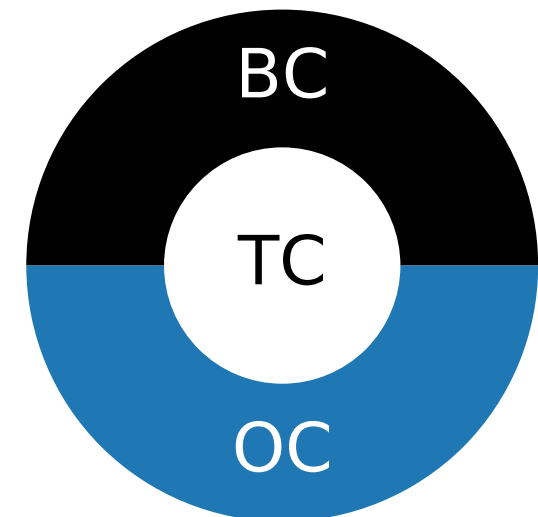
AE33:

- Optical method - 7 λ optical absorption
- BC ~ EC

$$BC = \frac{b_{ATN}}{C \cdot MAC}$$

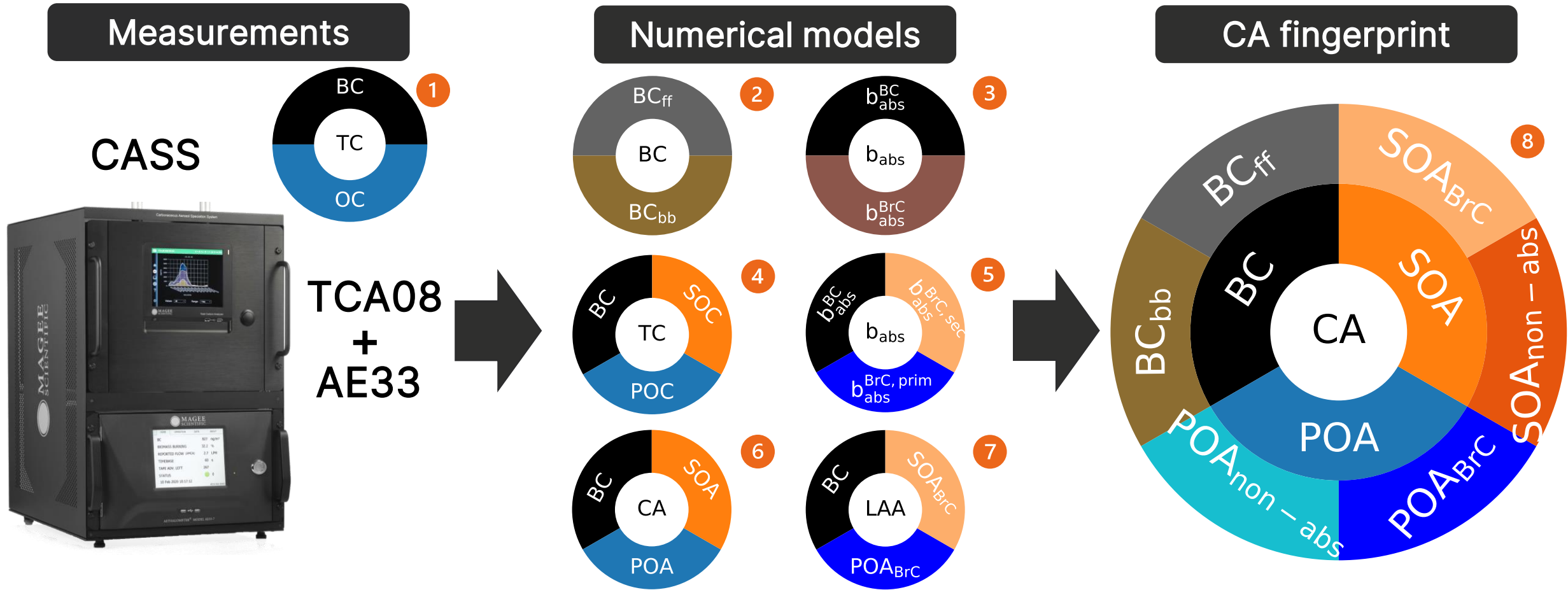
CASS:

$$OC(t) = TC(t) - BC(t)$$



(Rigler et al., AMT, 2020)

Advanced TC-BC(λ) method



(Ivančič et al., STOTEN, 2022)



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Two-year-long high-time-resolution apportionment of primary and secondary carbonaceous aerosols in the Los Angeles Basin using an advanced total carbon–black carbon (TC-BC(λ)) method



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^a Aerosol d.o.o., Research & Development Department, Kamniška 39a, SI-1000 Ljubljana, Slovenia

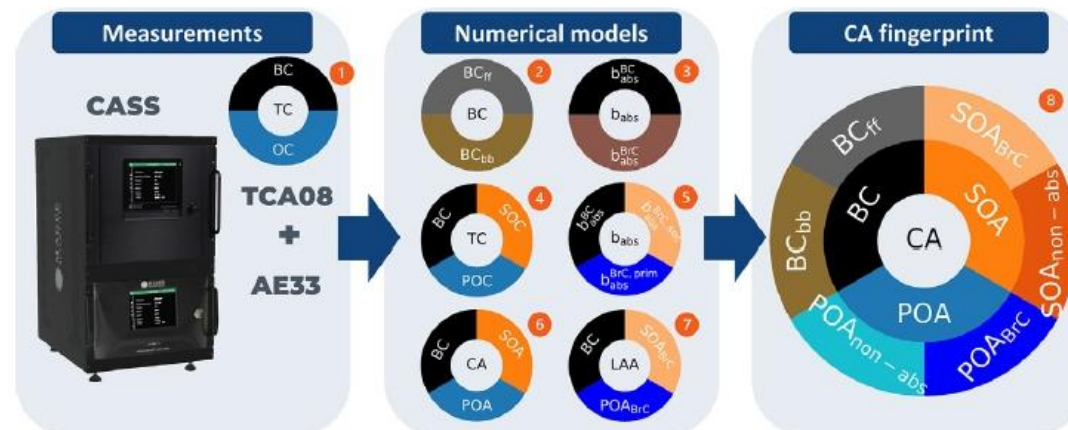
^b Centre for Atmospheric Research, University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia

^c South Coast Air Quality Management District, 21865 Copley Dr, Diamond Bar, CA 91765, USA

HIGHLIGHTS

- A new method for carbonaceous aerosol apportionment into six components
- Focus on the primary or secondary origin and light absorption properties
- Long-term (2 years) measurement campaign in two locations in the Los Angeles Basin
- High-time-resolution apportionment allows studying diurnal profiles.
- Comparable results on both sites with similar seasonal patterns

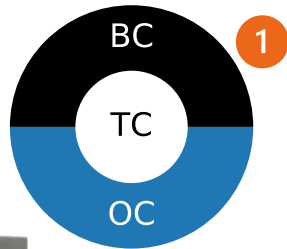
GRAPHICAL ABSTRACT



Advanced TC-BC(λ) method

Measurements

CASS



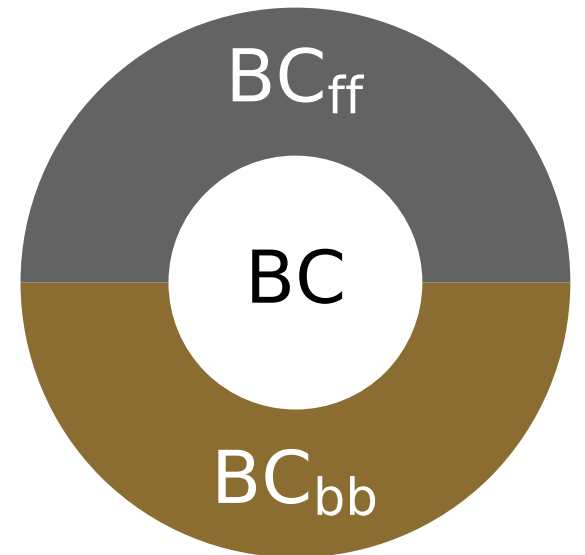
TCA08
+
AE33



Numerical models

2 Aethalometer model

(Sandradewi et al.,
Environ.Sci.Technol., 2008)



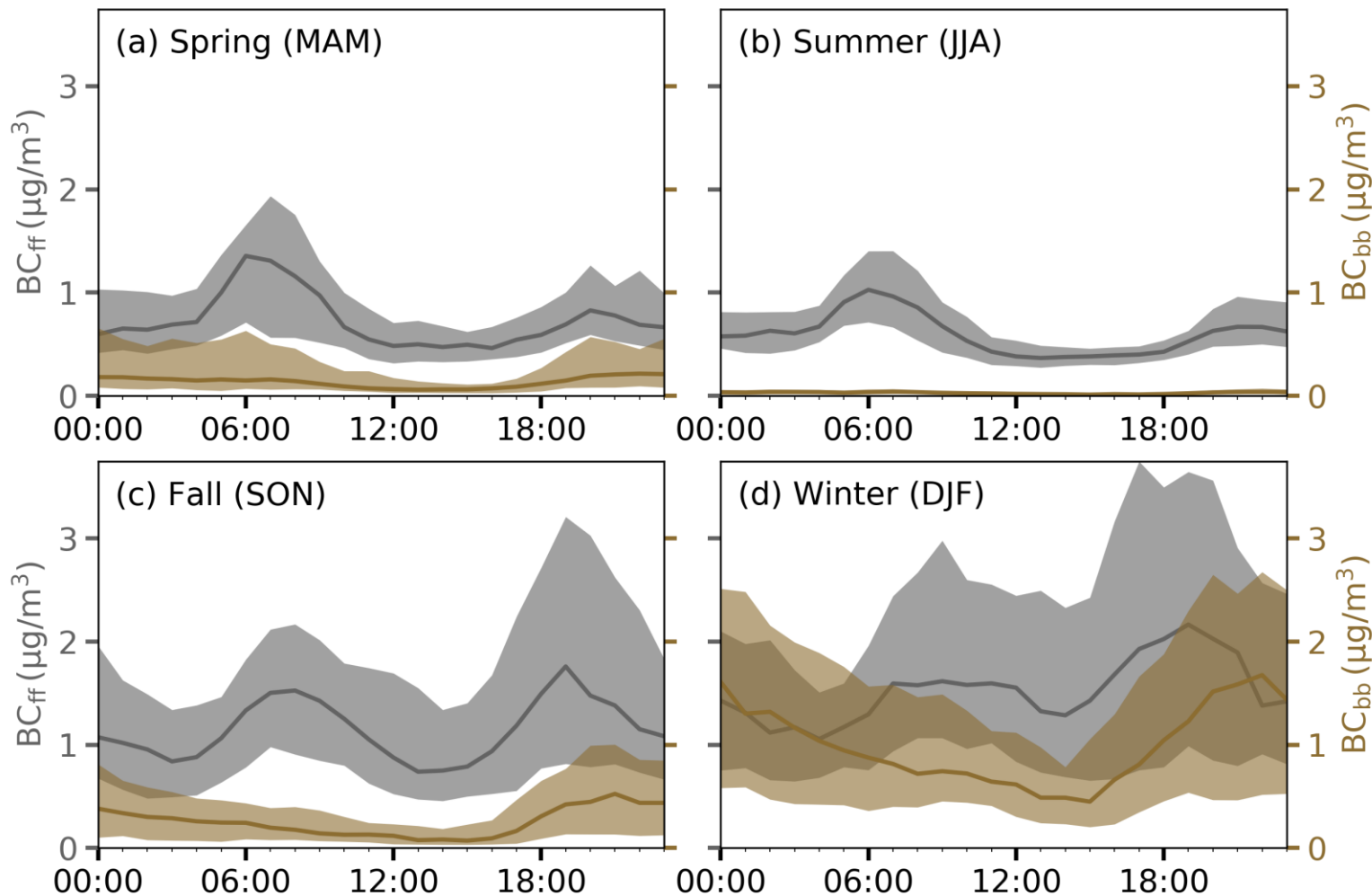
AAE_{ff}, AAE_{bb}

(Fuller et al.,

Atmos.Environ., 2008)

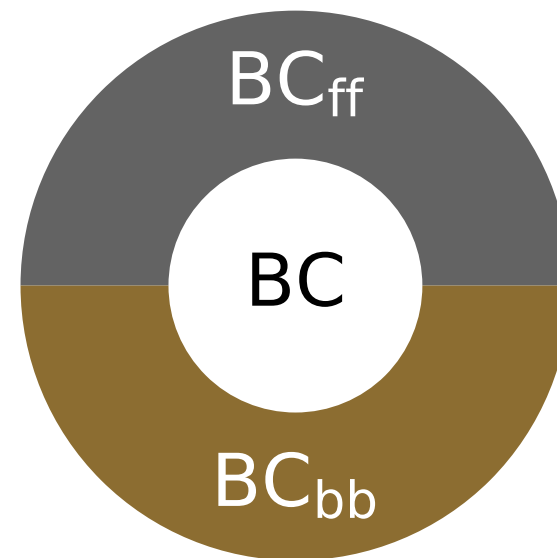
(Ivančić et al., STOTEN, 2022)

Advanced TC-BC(λ) method



2 Aethalometer model

(Sandradewi et al.,
Environ.Sci.Technol., 2008)



$\text{AAE}_{\text{ff}}, \text{AAE}_{\text{bb}}$
(Fuller et al.,
Atmos.Environ., 2008)

Advanced TC-BC(λ) method

A.1 Aethalometer model

The optical absorption can be apportioned into two source components – the absorption on aerosols coming from traffic ($b_{\text{abs}}^{\text{ff}}$ - fossil fuel component) and the contribution from biomass burning ($b_{\text{abs}}^{\text{bb}}$):

$$b_{\text{abs}}(\lambda, t) = b_{\text{abs}}^{\text{ff}}(\lambda, t) + b_{\text{abs}}^{\text{bb}}(\lambda, t), \quad (\text{A.1})$$

where both components have typical absorption wavelength dependence, characterized by different Ångström exponents AAE_{ff} and AAE_{bb} :

$$b_{\text{abs}}^{\text{ff}}(\lambda, t) = b_{\text{abs}}^{\text{ff}}(\lambda_0, t) \cdot \left(\frac{\lambda}{\lambda_0}\right)^{-\text{AAE}_{\text{ff}}}, \quad (\text{A.2})$$

$$b_{\text{abs}}^{\text{bb}}(\lambda, t) = b_{\text{abs}}^{\text{bb}}(\lambda_0, t) \cdot \left(\frac{\lambda}{\lambda_0}\right)^{-\text{AAE}_{\text{bb}}}, \quad (\text{A.3})$$

where λ_0 is baseline wavelength. If we assume both AAE_{ff} and AAE_{bb} are constant with time, the apportionment could be solved analytically (Sandradewi et al., 2008; Zotter et al., 2017):

$$b_{\text{abs}}^{\text{ff}}(\lambda, t) = \frac{b_{\text{abs}}(\lambda_0, t) - b_{\text{abs}}(\lambda, t) \cdot \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{bb}}}}{\left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{ff}}} - \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{bb}}}}, \quad (\text{A.4})$$

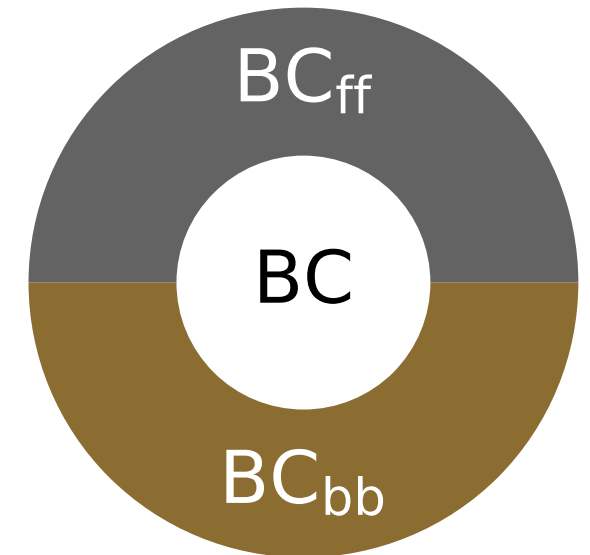
$$b_{\text{abs}}^{\text{bb}}(\lambda, t) = \frac{b_{\text{abs}}(\lambda_0, t) - b_{\text{abs}}(\lambda, t) \cdot \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{ff}}}}{\left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{ff}}} - \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{bb}}}}. \quad (\text{A.5})$$

The contribution of black carbon from fossil fuel sources (BC_{ff}) is then estimated as:

$$\left(\frac{\text{BC}_{\text{ff}}}{\text{BC}}\right)(t) = \frac{1}{1 - \frac{\text{MAC}_{\text{ff}}}{\text{MAC}_{\text{bb}}} \cdot \frac{1 - \frac{b_{\text{abs}}(\lambda, t)}{b_{\text{abs}}(\lambda_0, t)} \cdot \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{ff}}}}{1 - \frac{b_{\text{abs}}(\lambda, t)}{b_{\text{abs}}(\lambda_0, t)} \cdot \left(\frac{\lambda_0}{\lambda}\right)^{-\text{AAE}_{\text{bb}}}}}} \quad (\text{A.6})$$

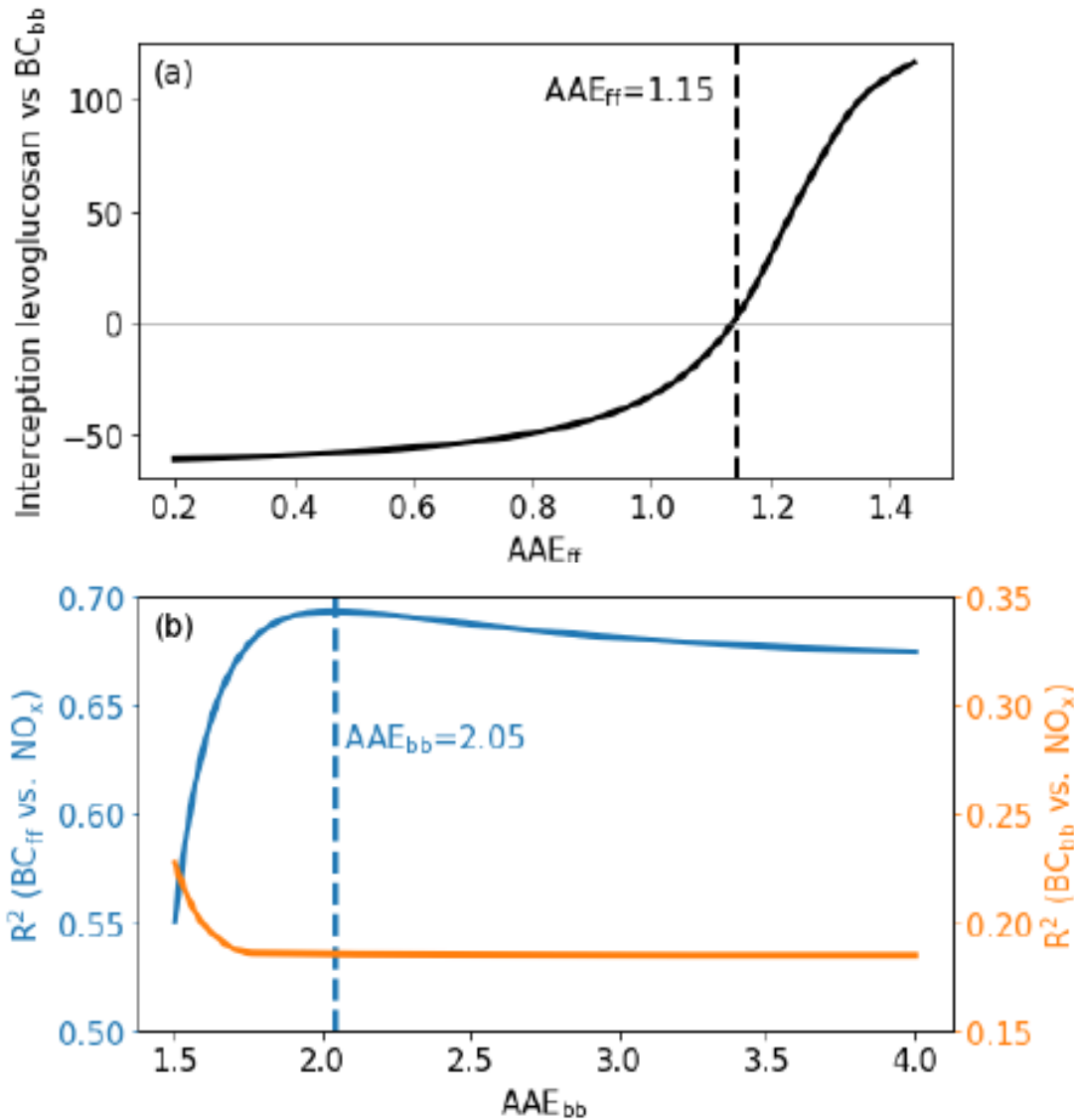
2 Aethalometer model

(Sandradewi et al., Environ.Sci.Technol., 2008)



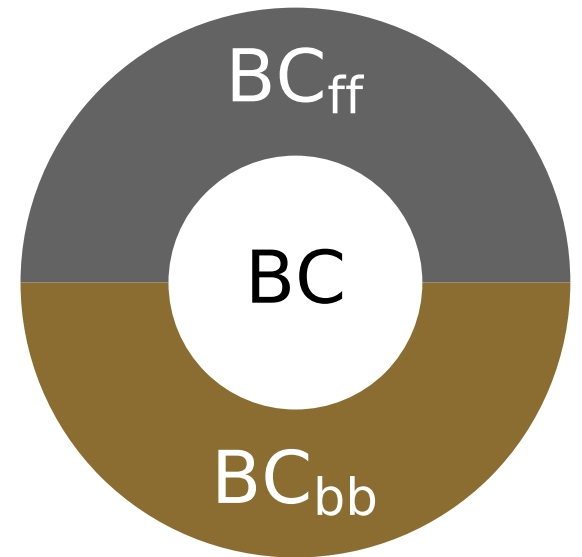
$\text{AAE}_{\text{ff}}, \text{AAE}_{\text{bb}}$
(Fuller et al., Atmos.Environ., 2008)

Advanced TC-BC(λ) method



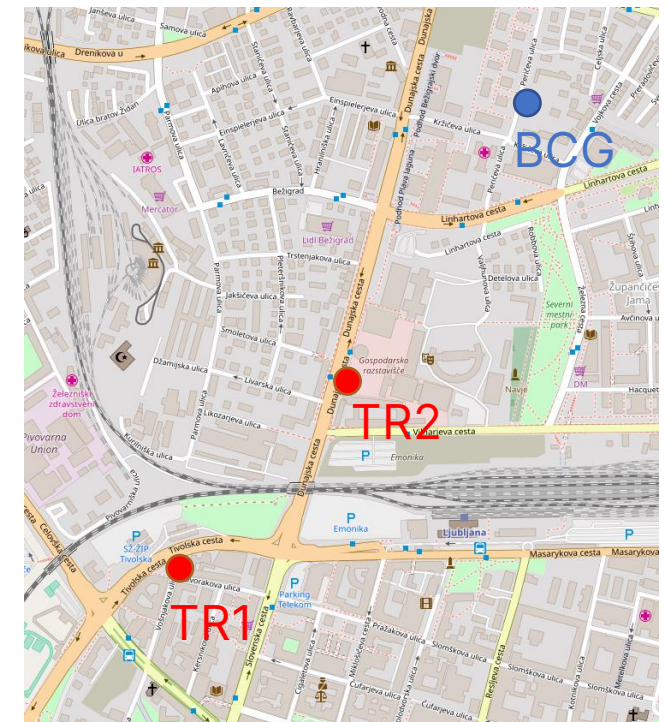
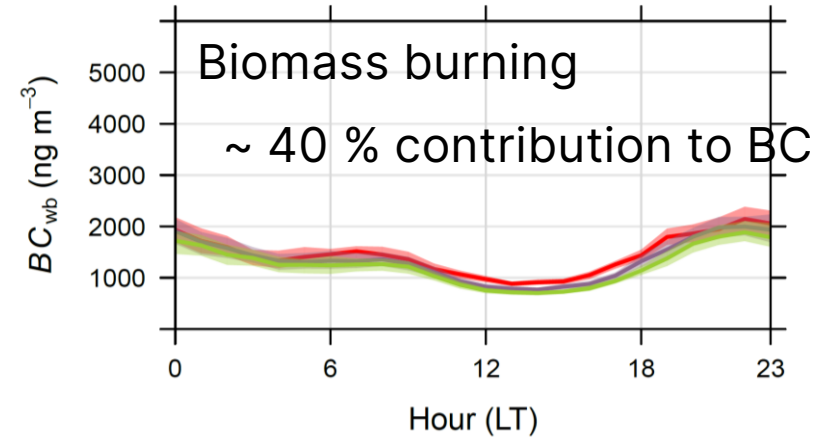
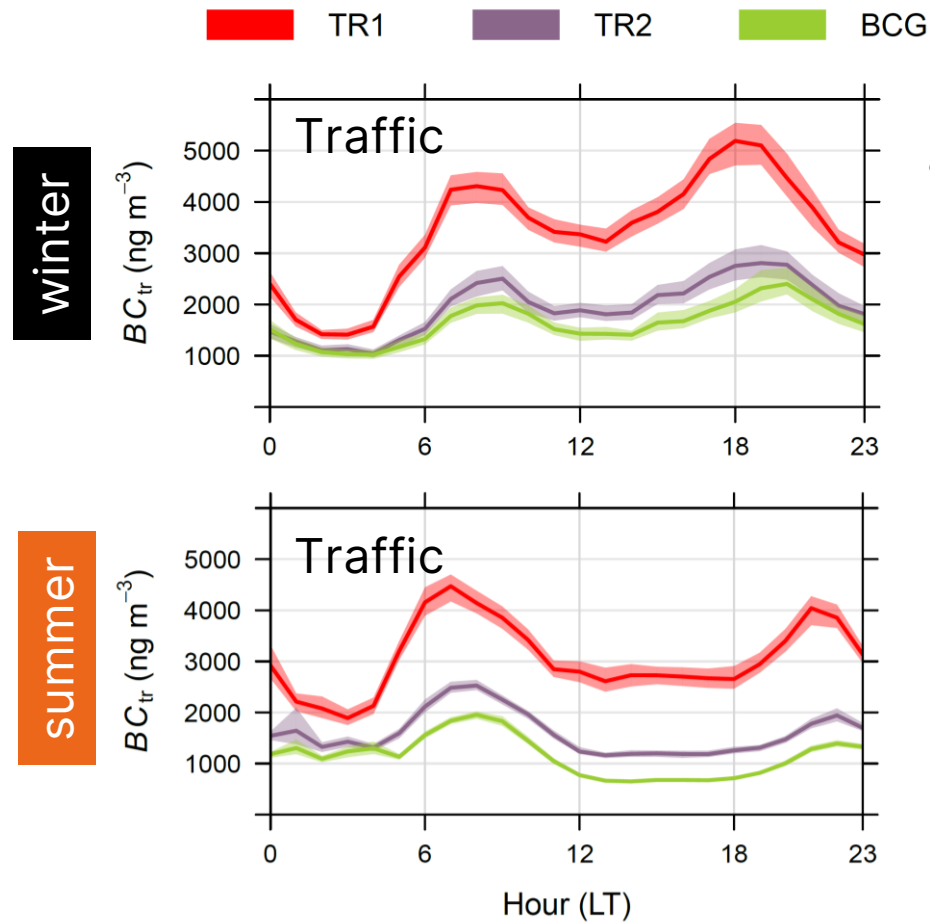
2 Aethalometer model

(Sandradewi et al., Environ.Sci.Technol., 2008)



AAE_{ff} , AAE_{bb}
(Fuller et al., Atmos.Environ., 2008)

Optimal AAE



Understanding BC distribution and sources

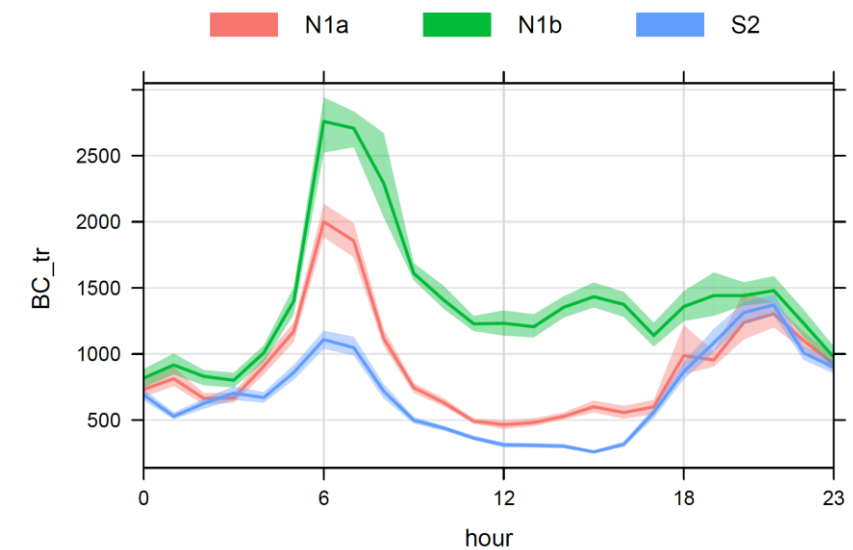
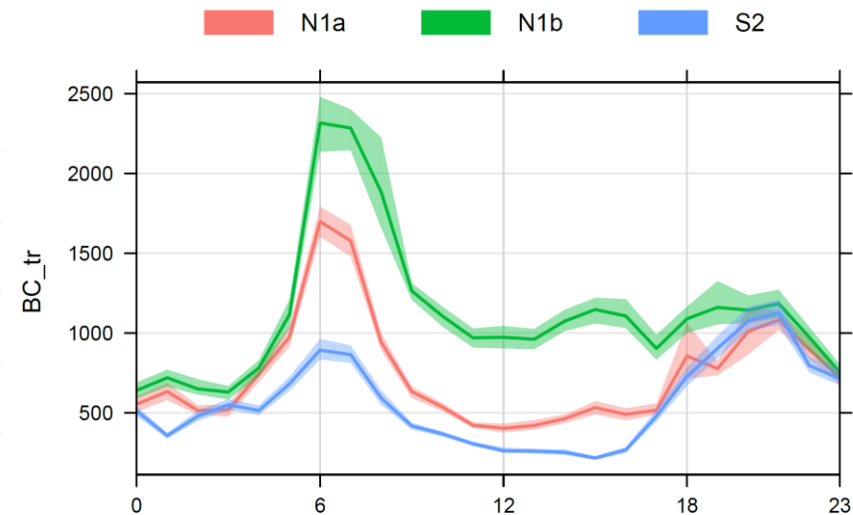
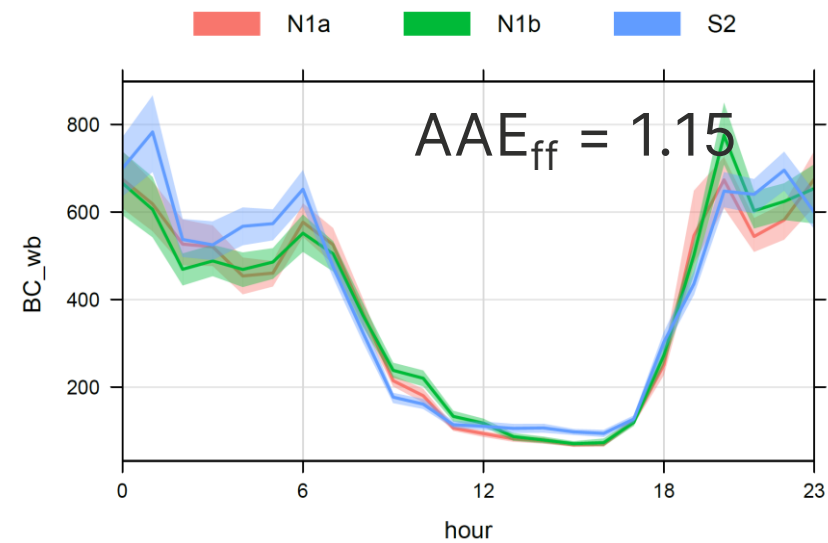
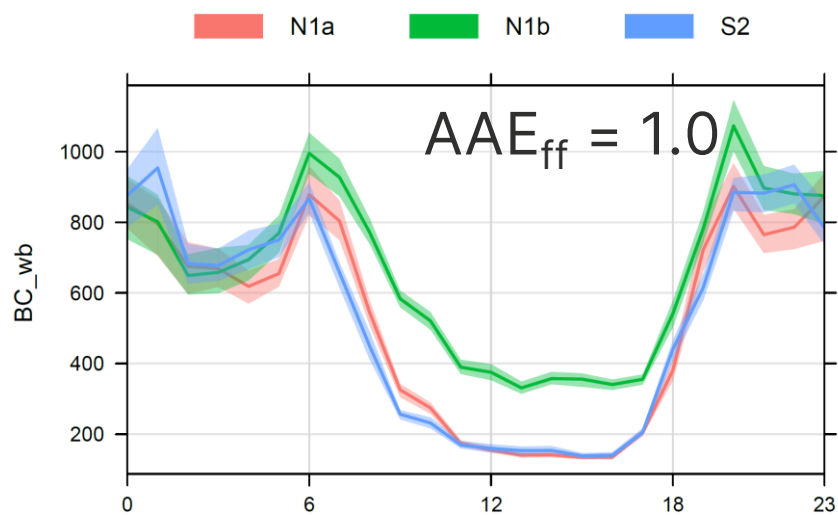
Traffic: **heterogeneous** spatial distribution

Biomass burning: **homogenous** spatial distribution

AAE_{ff} > 1 Ljubljana



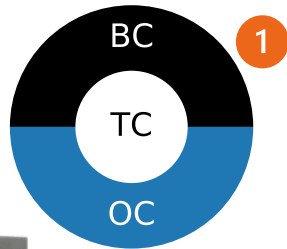
12



Advanced TC-BC(λ) method

Measurements

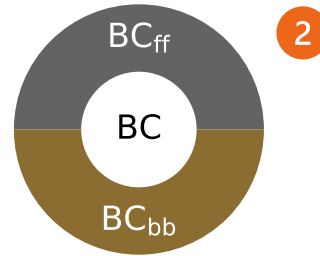
CASS



TCA08
+
AE33

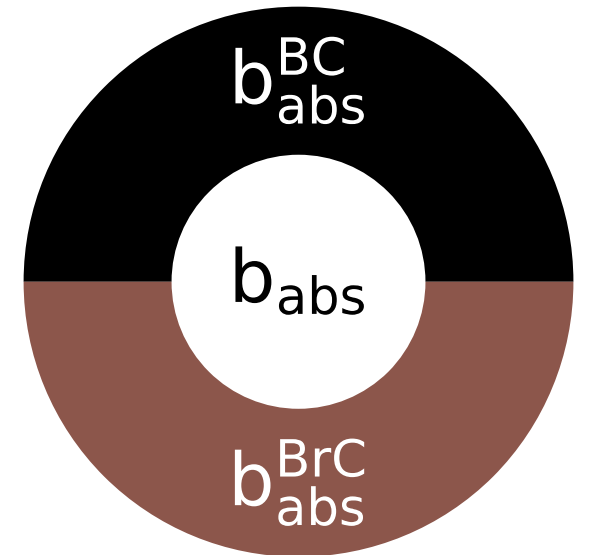


Numerical models



3 BrC model

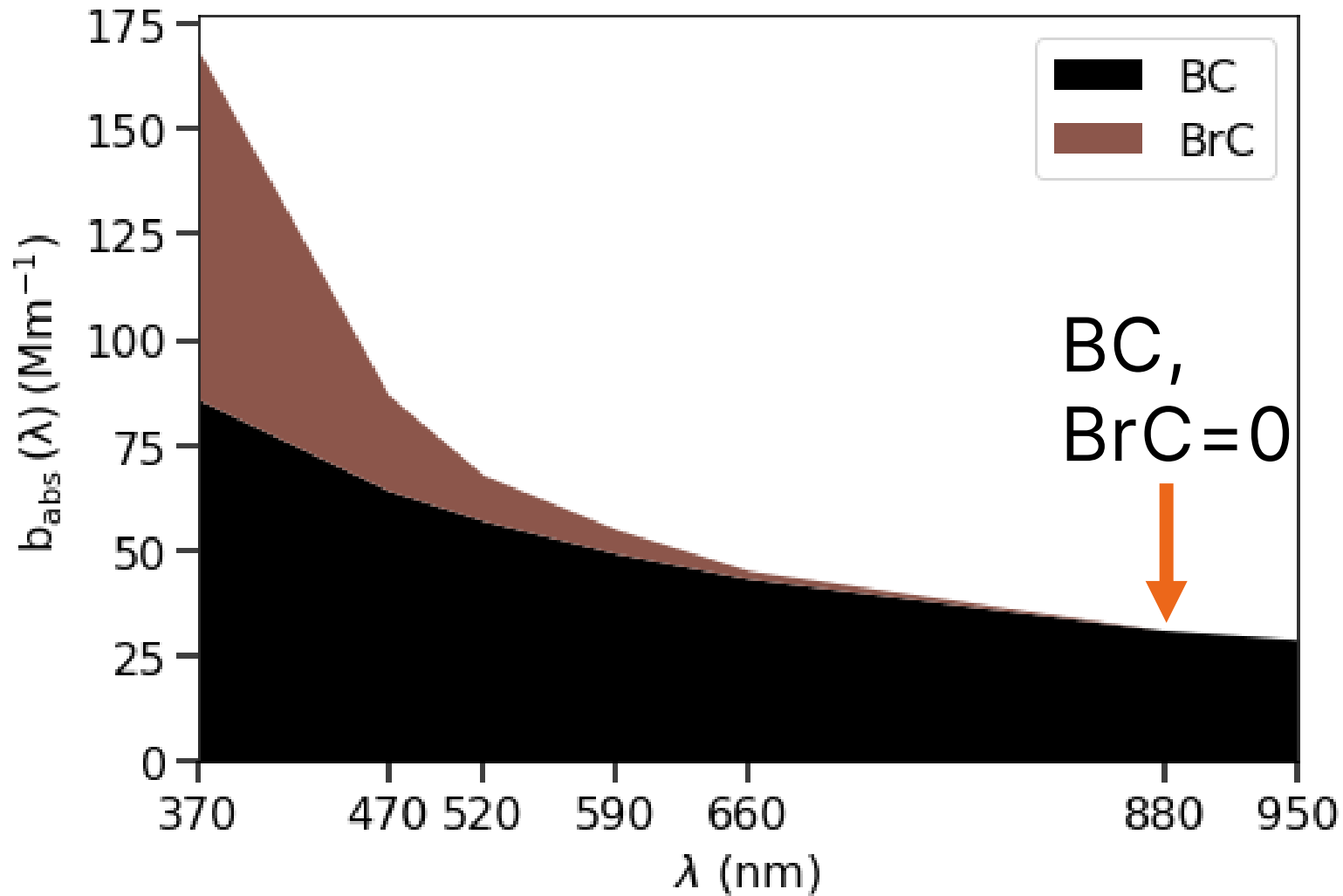
(Zhang et al., STOTEN, 2020)



AAE_{BC}

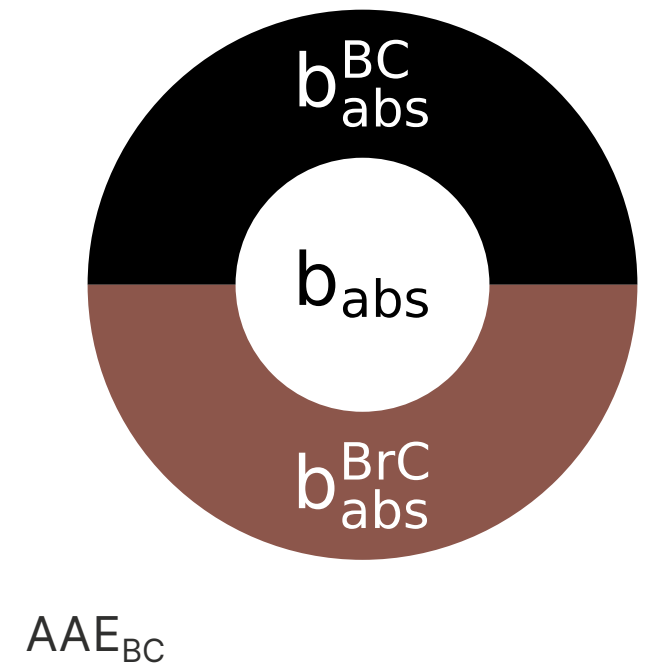
(Ivančić et al., STOTEN, 2022)

Advanced TC-BC(λ) method



3 BrC model

(Zhang et al., STOTEN, 2020)



Advanced TC-BC(λ) method

A.2 Brown carbon

The wavelength-dependent optical absorption of carbonaceous aerosol can be apportioned into two components, $b_{\text{abs}}^{\text{BC}}$ and $b_{\text{abs}}^{\text{BrC}}$:

$$b_{\text{abs}}(\lambda, t) = b_{\text{abs}}^{\text{BC}}(\lambda, t) + b_{\text{abs}}^{\text{BrC}}(\lambda, t), \quad (\text{A.9})$$

where the wavelength dependence of each component can be described with AAE_{BC} and $\text{AAE}_{\text{BrC}}(t)$, the absorption Ångström exponent of pure BC and BrC, respectively:

$$b_{\text{abs}}^{\text{BC}}(\lambda, t) = b_{\text{abs}}^{\text{BC}}(\lambda_0, t) \cdot \left(\frac{\lambda}{\lambda_0}\right)^{-\text{AAE}_{\text{BC}}}, \quad (\text{A.10})$$

$$b_{\text{abs}}^{\text{BrC}}(\lambda, t) = b_{\text{abs}}^{\text{BrC}}(\lambda_0, t) \cdot \left(\frac{\lambda}{\lambda_0}\right)^{-\text{AAE}_{\text{BrC}}(t)}. \quad (\text{A.11})$$

Because $\text{AAE}_{\text{BrC}}(t)$ is allowed to vary with time, the apportionment set of Eq. (A.10) and (A.11) cannot be solved analytically. The numerically robust model for optical apportionment of absorption assumes that the BC is the only light-absorbing carbonaceous component at 880 nm (Gilardoni et al., 2020; Qin et al., 2018; Tian et al., 2019; Wang et al., 2020, 2016; Wu et al., 2021; Zhang et al., 2020):

$$b_{\text{abs}}(880 \text{ nm}, t) = b_{\text{abs}}^{\text{BC}}(880 \text{ nm}, t); \quad b_{\text{abs}}^{\text{BrC}}(880 \text{ nm}, t) = 0 \quad (\text{A.12})$$

The wavelength-dependent optical absorption of BC is determined as

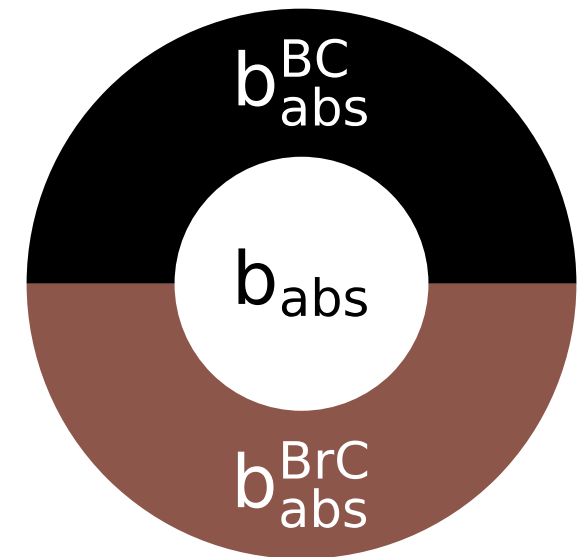
$$b_{\text{abs}}^{\text{BC}}(\lambda, t) = b_{\text{abs}}^{\text{BC}}(880 \text{ nm}, t) \cdot \left(\frac{\lambda}{880 \text{ nm}}\right)^{-\text{AAE}_{\text{BC}}}, \quad (\text{A.13})$$

and finally, the wavelength-dependent optical absorption of BrC as

$$b_{\text{abs}}^{\text{BrC}}(\lambda, t) = b_{\text{abs}}(\lambda, t) - b_{\text{abs}}^{\text{BC}}(\lambda, t). \quad (\text{A.14})$$

3 BrC model

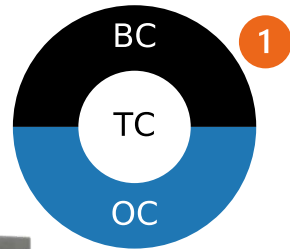
(Zhang et al., STOTEN, 2020)



Advanced TC-BC(λ) method

Measurements

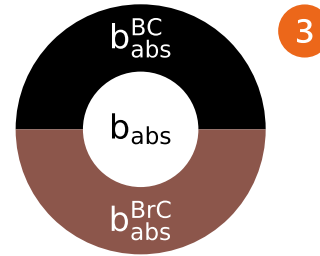
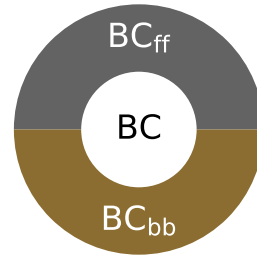
CASS



TCA08
+
AE33

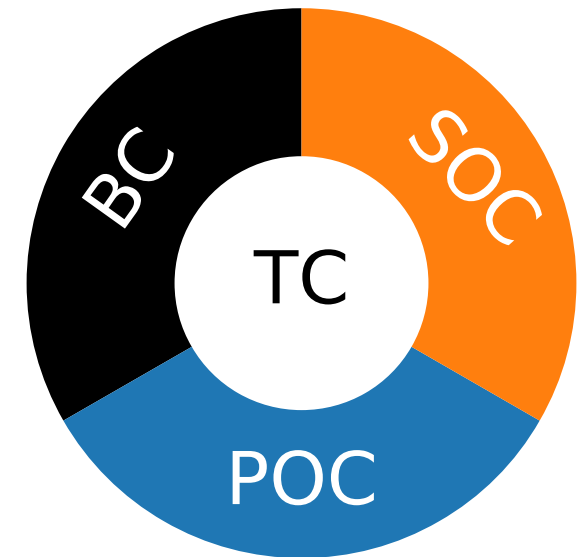


Numerical models



4 EC (BC) tracer

(Turpin & Hunticker,
Atmos. Environ., 1995)



(OC/BC)_{prim} from MRS
(Wu&Yu,
Atmos.Chem.Phys., 2016)

(Ivančić et al., STOTEN, 2022)

Advanced TC-BC(λ) method

A.3 Primary and secondary OC

The OC is a complex mixture of many chemical species with primary or secondary origins. The EC tracer method to distinguish between POC and SOC was introduced by (Turpin and Huntzicker, 1995). The main assumption of this method is that the EC and POC are emitted from the same source and they should be well correlated, while the correlation between the EC and SOC should be low due to different formation paths. In this paper, we are using the BC as the optically determined EC. Therefore, the BC tracer will be used as the method name here and after. If the primary OC from non-combustion sources is neglected, the POC can be estimated as:

$$\text{POC}(t) = \left(\frac{\text{OC}}{\text{BC}}\right)_{\text{prim}} \cdot \text{BC}(t) \quad (\text{A.15})$$

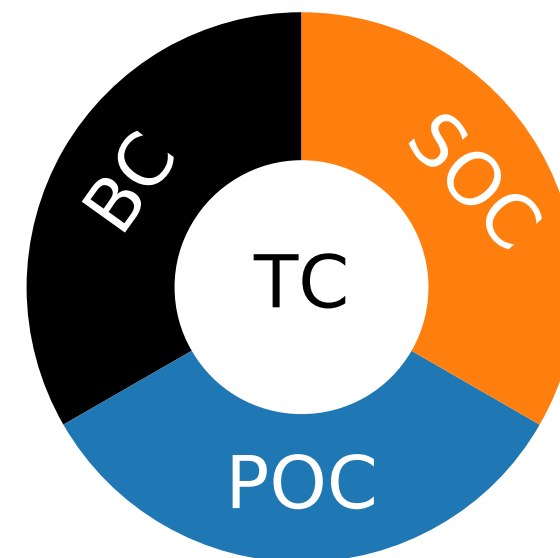
The SOC is then calculated as:

$$\text{SOC}(t) = \text{OC}(t) - \text{POC}(t) = \text{OC}(t) - \left(\frac{\text{OC}}{\text{BC}}\right)_{\text{prim}} \cdot \text{BC}(t). \quad (\text{A.16})$$

The $(\text{OC}/\text{BC})_{\text{prim}}$ ratio is expected to be site (source) and season-dependent. In our work, we used the minimum R-squared method (Hu et al., 2012; Millet et al., 2005; Wu and Yu, 2016) for $(\text{OC}/\text{BC})_{\text{prim}}$ determination. Briefly, the hypothetical SOC(t) within each season is firstly calculated for a wide range of hypothetical $(\text{OC}/\text{BC})_{\text{prim}}$ ratios (for ratios 0.1 to 10 in 0.1 steps). Then the R-squared value between SOC and BC is calculated for every hypothetical $(\text{OC}/\text{BC})_{\text{prim}}$ ratio, and the optimal $(\text{OC}/\text{BC})_{\text{prim}}$ ratio is chosen where the R-squared is minimal.

4 EC (BC) tracer

(Turpin & Huntzicker,
Atmos.Environ., 1995)



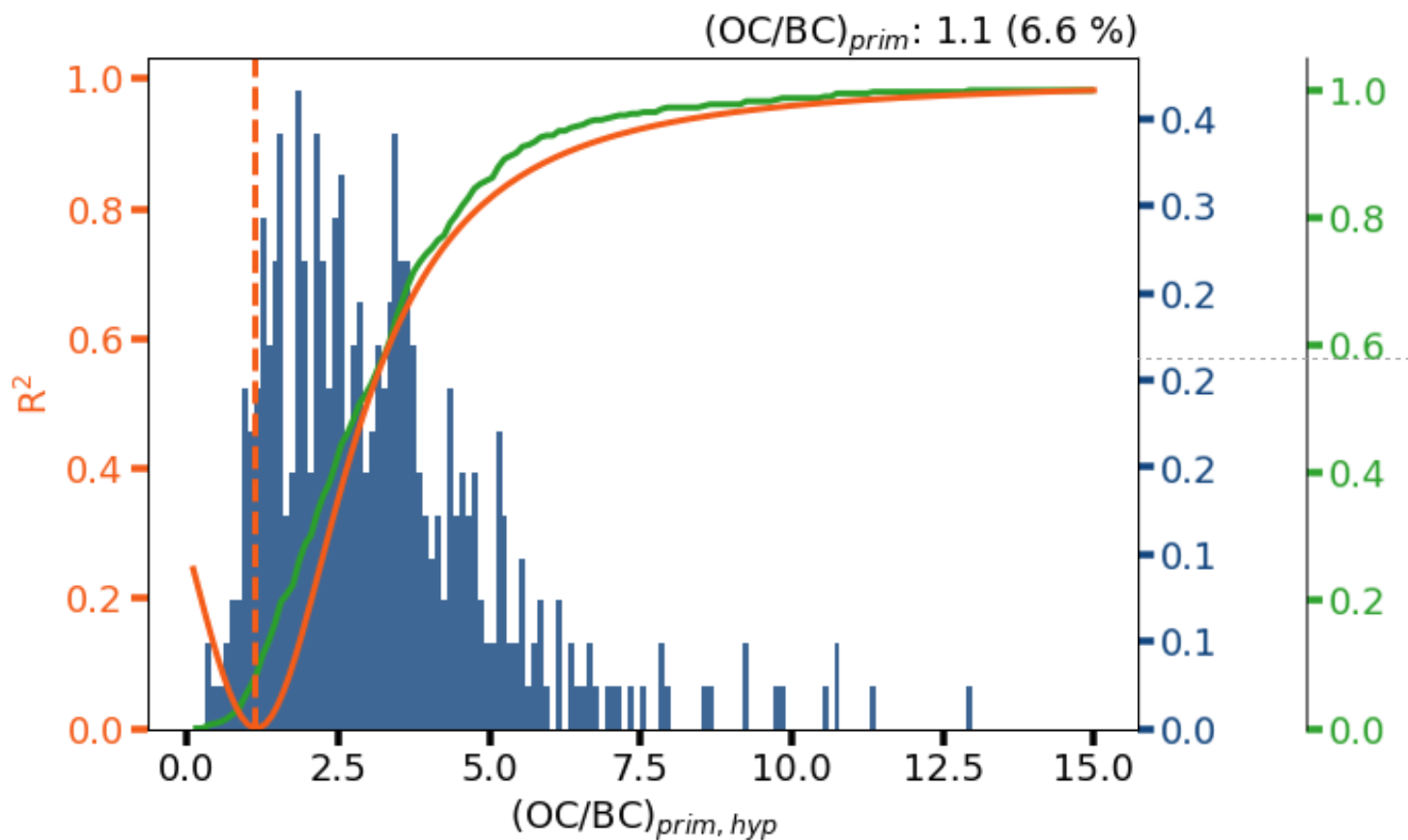
$(\text{OC}/\text{BC})_{\text{prim}}$ from MRS

(Wu&Yu,

Atmos.Chem.Phys., 2016)

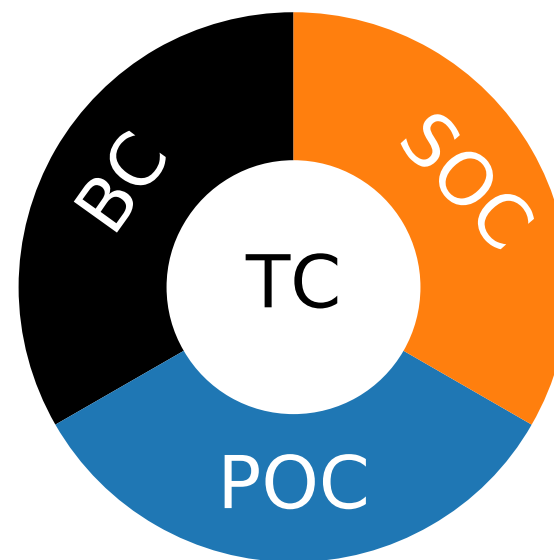
Advanced TC-BC(λ) method

- $R^2(\text{SOC}_{hyp}$ vs. BC)
- OC/BC probability distribution
- OC/BC cumulative distribution



4 EC (BC) tracer

(Turpin & Hunticker,
Atmos. Environ., 1995)



(OC/BC)_{prim} from MRS

(Wu&Yu,

Atmos. Chem. Phys., 2016)

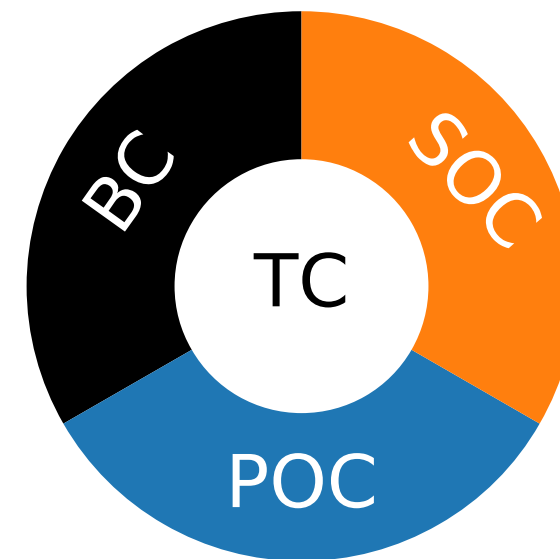
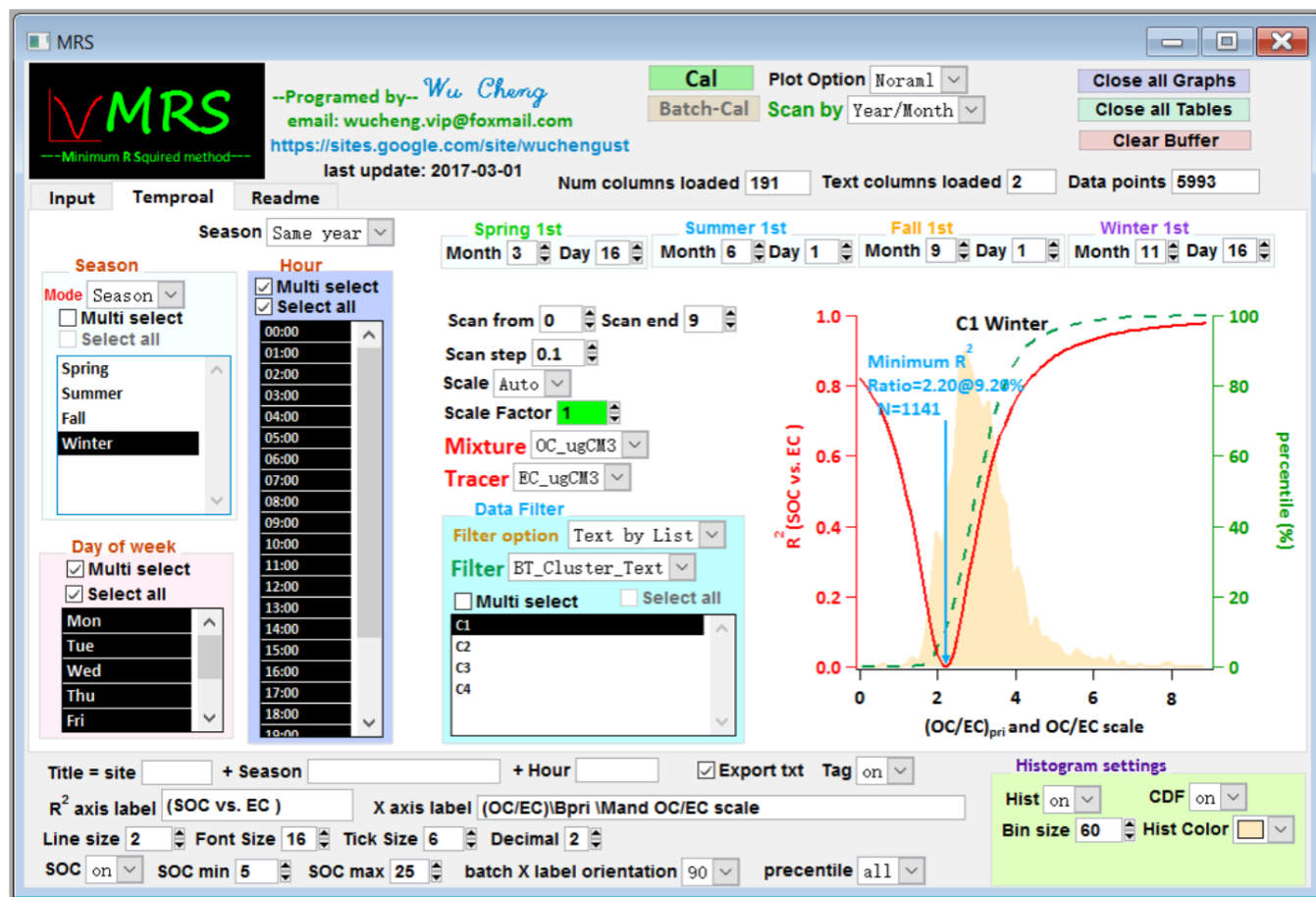
Advanced TC-BC(λ) method

Wu&Yu, Atmos.Chem.Phys., 2016

<https://sites.google.com/site/wuchengust>

4 EC (BC) tracer

(Turpin & Hunticker,
Atmos.Environ., 1995)



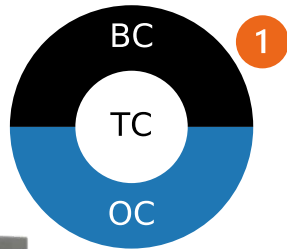
$(OC/BC)_{prim}$ from MRS

(Wu&Yu,
Atmos.Chem.Phys., 2016)

Advanced TC-BC(λ) method

Measurements

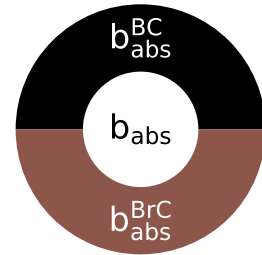
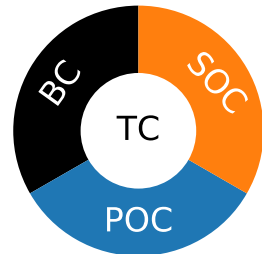
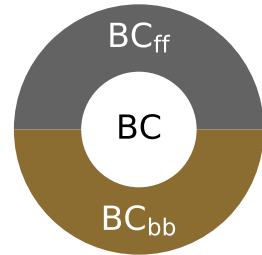
CASS



TCA08
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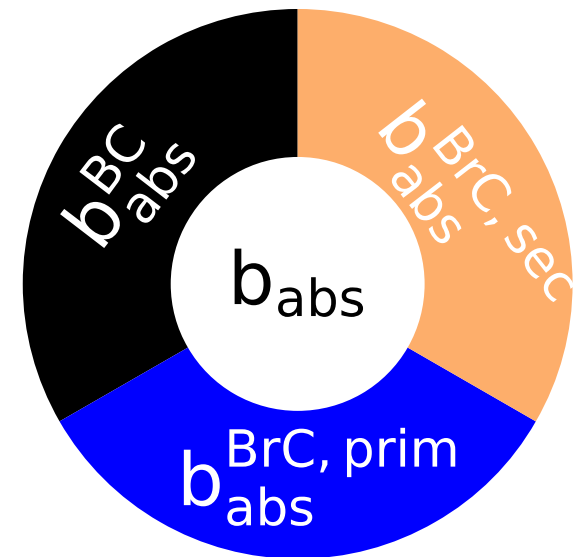


Numerical models



5 BC tracer for BrC

(Wang et al.,
Geophys.Res.Lett., 2019)



MRS method

(Ivančić et al., STOTEN, 2022)

Advanced TC-BC(λ) method

A.4 Primary and secondary BrC

BC tracer method was also used to differentiate between the light absorption on primary and secondary BrC (Liakakou et al., 2020; Wang et al., 2020, 2019b, 2019a). All studies used the minimum R-squared method to determine the optimal $(b_{\text{abs}}(\lambda)/\text{BC})_{\text{prim}}$ ratio. In our study, we modified the approach slightly. Because the BC is recognized as the only absorber at 880 nm, we used the light absorption at $\lambda_0=880$ nm instead of BC concentration, and the required ratio becomes dimensional-less. Because the only light-absorbing material formed secondarily is BrC, the light absorption of secondary BrC can be calculated with the modified BC tracer method:

$$b_{\text{abs}}^{\text{BrC,sec}}(\lambda, t) = b_{\text{abs}}(\lambda, t) - \left(\frac{b_{\text{abs}}(\lambda)}{b_{\text{abs}}(\lambda_0)} \right)_{\text{prim}} \cdot b_{\text{abs}}(\lambda_0, t). \quad (\text{A.17})$$

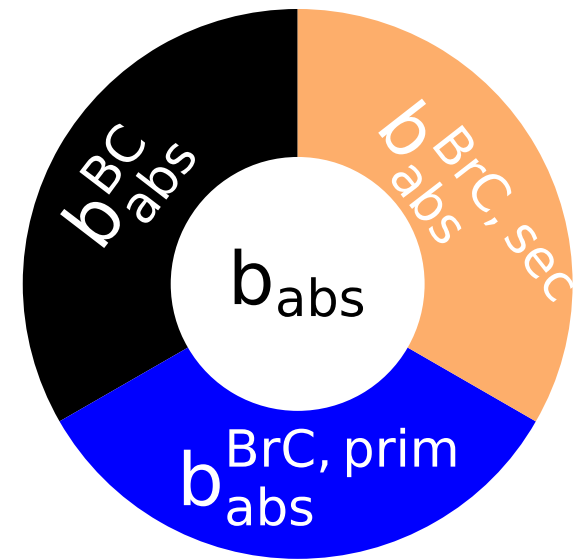
To find optimal $(b_{\text{abs}}(\lambda)/b_{\text{abs}}(\lambda_0))_{\text{prim}}$ ratio, we varied the hypothetical $(b_{\text{abs}}(\lambda)/b_{\text{abs}}(\lambda_0))_{\text{prim,hyp}}$ ratio from 0 to 6 with step 0.1. For every hypothetical $(b_{\text{abs}}(\lambda)/b_{\text{abs}}(\lambda_0))_{\text{prim,hyp}}$ ratio, the hypothetical $b_{\text{abs,sec,hyp}}^{\text{BrC}}(\lambda, t)$ was calculated, and then the optimal $(b_{\text{abs}}(\lambda)/b_{\text{abs}}(\lambda_0))_{\text{prim}}$ ratio was determined where the correlation between $b_{\text{abs,sec,hyp}}^{\text{BrC}}(\lambda, t)$ and $b_{\text{abs}}(\lambda_0, t)$ has its minimum.

Using the light absorption on BrC from Eq. (A.14), the light absorption on primary BrC is:

$$b_{\text{abs}}^{\text{BrC,prim}}(\lambda, t) = b_{\text{abs}}^{\text{BrC}}(\lambda, t) - b_{\text{abs}}^{\text{BrC,sec}}(\lambda, t). \quad (\text{A.18})$$

5 BC tracer for BrC

(Wang et al.,
Geophys.Res.Lett., 2019)

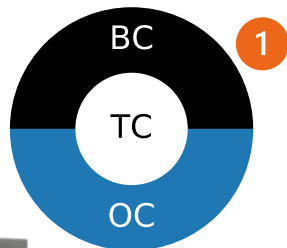


MRS method

Advanced TC-BC(λ) method

Measurements

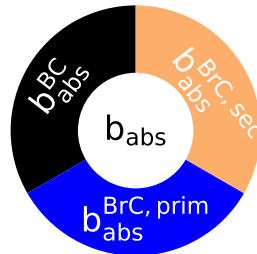
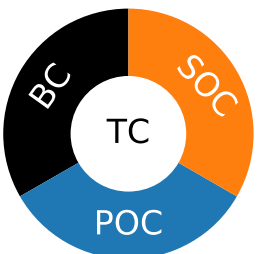
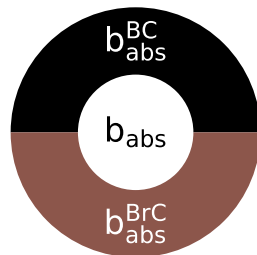
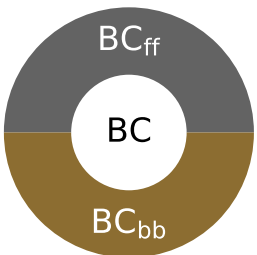
CASS



TCA08
+
AE33

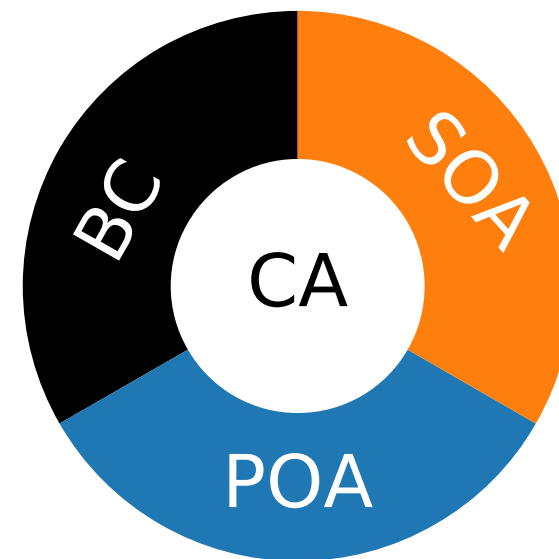


Numerical models



6 OC to OM

(Docherty et al.,
STOTEN, 2008)



(Ivančić et al., STOTEN, 2022)

$$POA(t) = POC(t) \cdot \left(\frac{POA}{POC} \right)$$

$$SOA(t) = SOC(t) \cdot \left(\frac{SOA}{SOC} \right)$$

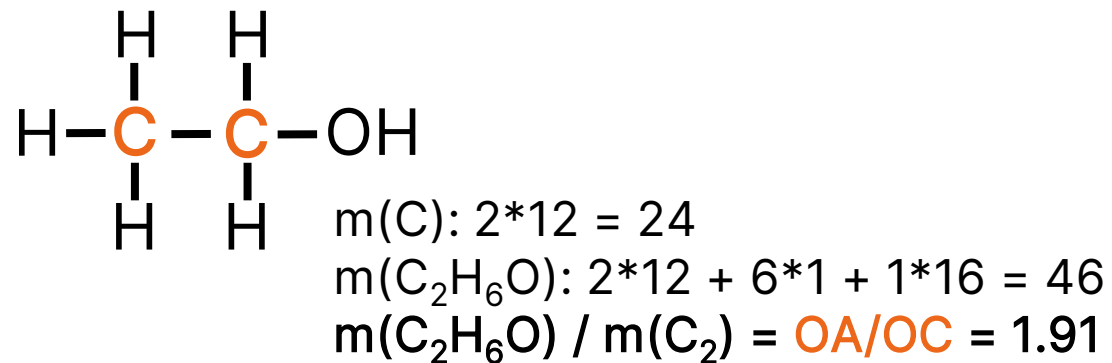
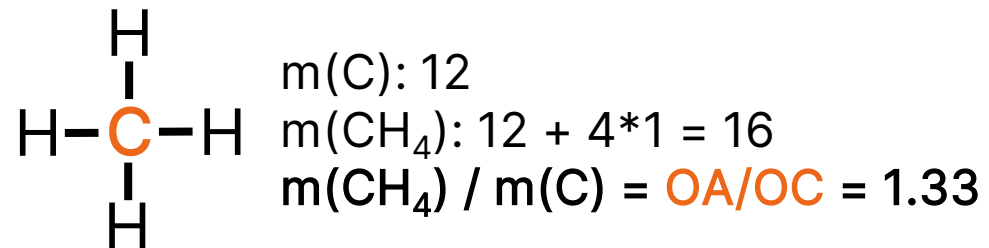
$$POA/POC = 1.2$$

$$SOA/SOC = 1.8$$

Advanced TC-BC(λ) method

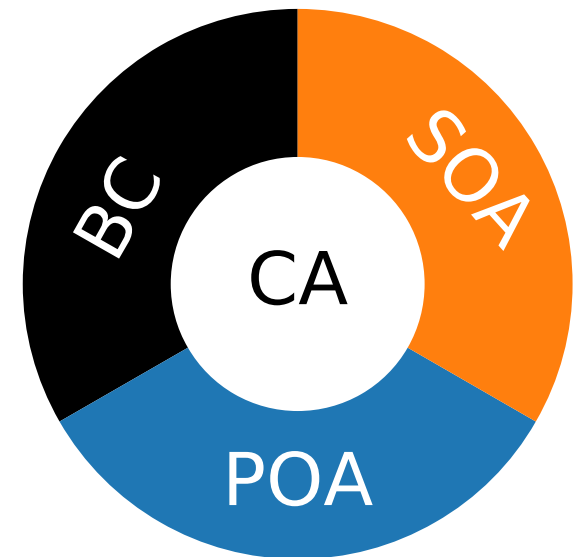
$$CA = BC + OA$$

$$TC = BC + OC$$



6 OC to OM

(Docherty et al.,
STOTEN, 2008)



$$POA/POC = 1.2$$

$$SOA/SOC = 1.8$$

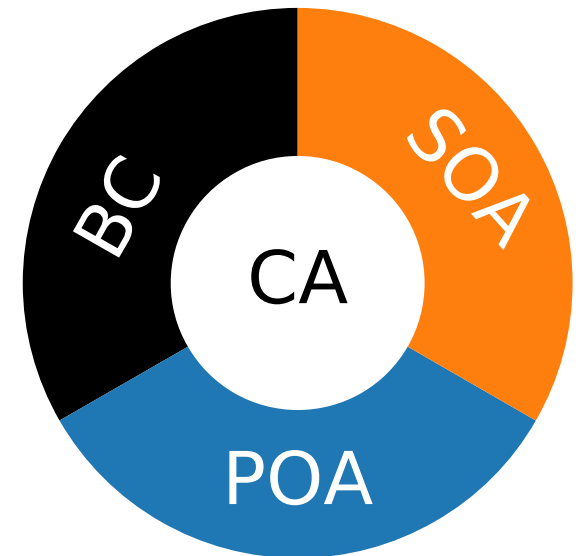
Advanced TC-BC(λ) method

Table A.1: A literature review of organic aerosol vs. organic carbon (OA/OC) conversion factors.

Ratio	Site specification	Reference
POA/POC = 1.2, SOA/SOC = 1.8	Riverside, USA	(Docherty et al., 2008)
OA/OC = 1.6 – 2.1	1.65 (LA downtown), 1.77 (LA Rubidoux), 1.6 (urban sites in general) 2.1 (nonurban sites in general)	(Turpin and Lim, 2001)
POA/POC = 1.3 SOA/SOC = 2.2	Shanghai downtown, China	(Zhang et al., 2018)
OA/OC = 1.4	The Pearl River Delta region, China	(Wu et al., 2019)
OA/OC = 1.82	Fresh emissions from traffic with a regionally homogeneous contribution of biomass burning for household heating (Ljubljana, Slovenia, EU)	(Rigler et al., 2020)
OA/OC = 1.2 – 2.5	Worldwide: max OA/OC=2.5 for aged ambient oxygenated OA	(Aiken et al., 2008)
OA/OC = 1.6 – 2.1	Worldwide: 1.6 for urban sites and 2.1 for rural/remote sites	(Massabò and Prati, 2021)
OA/OC = 1.8	Sanya, China	(Wang et al., 2020)
OA/OC = 1.7 - 1.98	1.7 for fresh and 1.98 for aged aerosols in Back Garden, China	(Hu et al., 2012)
OA/OC = 1.9 - 2.3	1.9 for urban background and 2.3 for regional background in Barcelona, Spain, EU	(Karanasiou et al., 2020)

6 OC to OM

(Docherty et al.,
STOTEN, 2008)



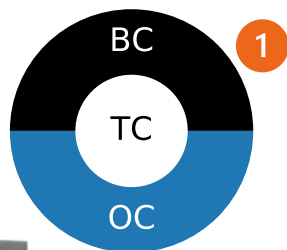
POA/POC = 1.2

SOA/SOC = 1.8

Advanced TC-BC(λ) method

Measurements

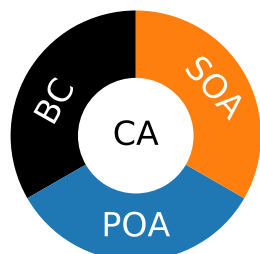
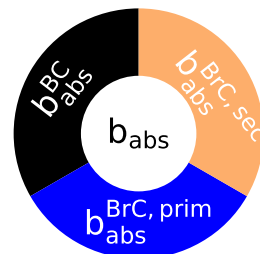
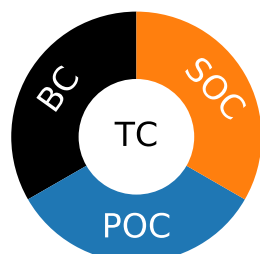
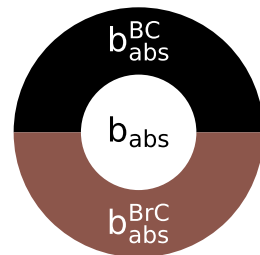
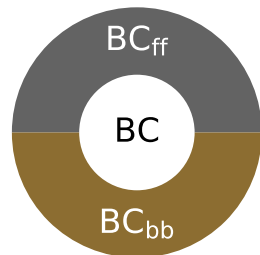
CASS



TCA08
+
AE33

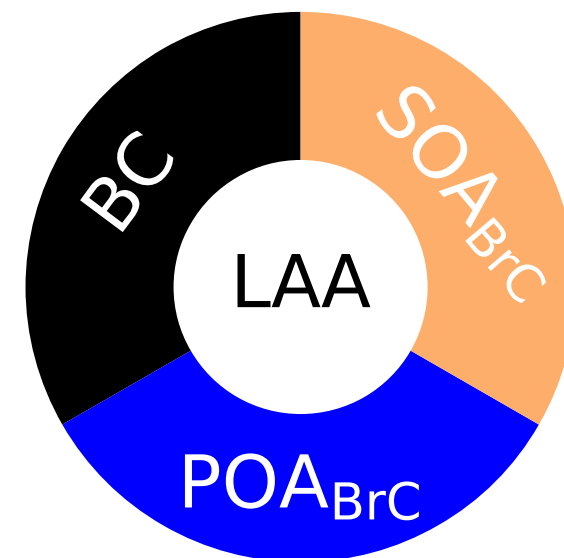


Numerical models



7 MAC

(Kumar et al., ACP, 2018)



(Ivančič et al., STOTEN, 2022)

$$POA_{BrC}(t) = \frac{b_{abs}^{BrC,prim}(\lambda, t)}{MAC_{BrC,prim}(\lambda)}$$

$$SOA_{BrC}(t) = \frac{b_{abs}^{BrC,sec}(\lambda, t)}{MAC_{BrC,sec}(\lambda)}$$

$$MAC_{BC}(880 \text{ nm}) = 7.77 \text{ m}^2/\text{g}$$

$$MAC_{BrC,prim}(370 \text{ nm}) = 5.5 \text{ m}^2/\text{g}$$

$$MAC_{BrC,sec}(370 \text{ nm}) = 2.4 \text{ m}^2/\text{g}$$

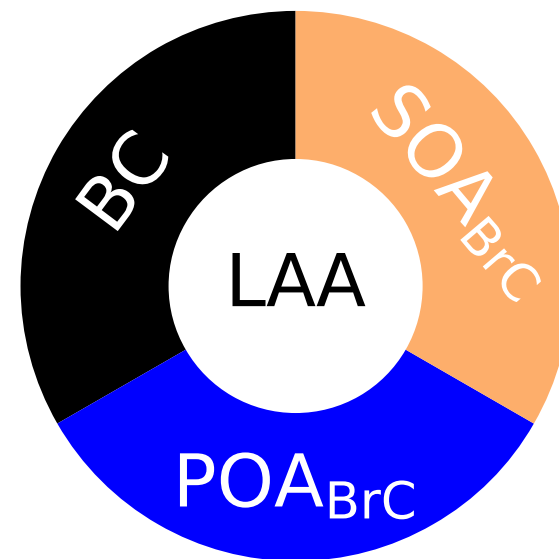
Advanced TC-BC(λ) method

Table A.2: A literature review of published MAC_{BrC} values.

MAC_{BrC} (m^2/g)	λ (nm)	Experiment description	Reference
5.5 (primary BrC) 2.4 (secondary BrC)	370	Chamber experiment.	(Kumar et al., 2018)
0.4-2.3	405	Chamber experiment.	(Cappa et al., 2020)
2.7 (primary BrC) 4.0 (secondary BrC) 3.4 (BBOA)	370	Multiple regression analysis for different OA components in Xianghe, China.	(Wang et al., 2019b)
1.80 – 5.63	370	Laboratory BrC formation with photo-oxidation.	(Vidović et al., 2020)
0.618 – 3.121	365	Oxidation experiments in a continuous flow stirred tank Reactor.	(Mayorga et al., 2021)
0.3 – 1.2	370	Methanol-soluble BrC in Milan, Italy, EU.	(Gilardoni et al., 2020)
4.38-7.44	340	Ambient study in Xi'an, China, with water-soluble BrC.	(Shen et al., 2017)
5.0	350	Outdoor burning of firewood in Bay Area, USA.	(Kirchstetter et al., 2004)
0.61 - 3.4 3.4 (BBOA) 1.7 (LVOOA)	370	Multiple regression analysis for different OA components in Guangzhou, China.	(Qin et al., 2018)
4.85 for LO-BBOA 2.02 for MO-BBOA	370	Multiple linear regression analysis for different OA components in France, EU.	(Zhang et al., 2020)

7 MAC

(Kumar et al., ACP, 2018)

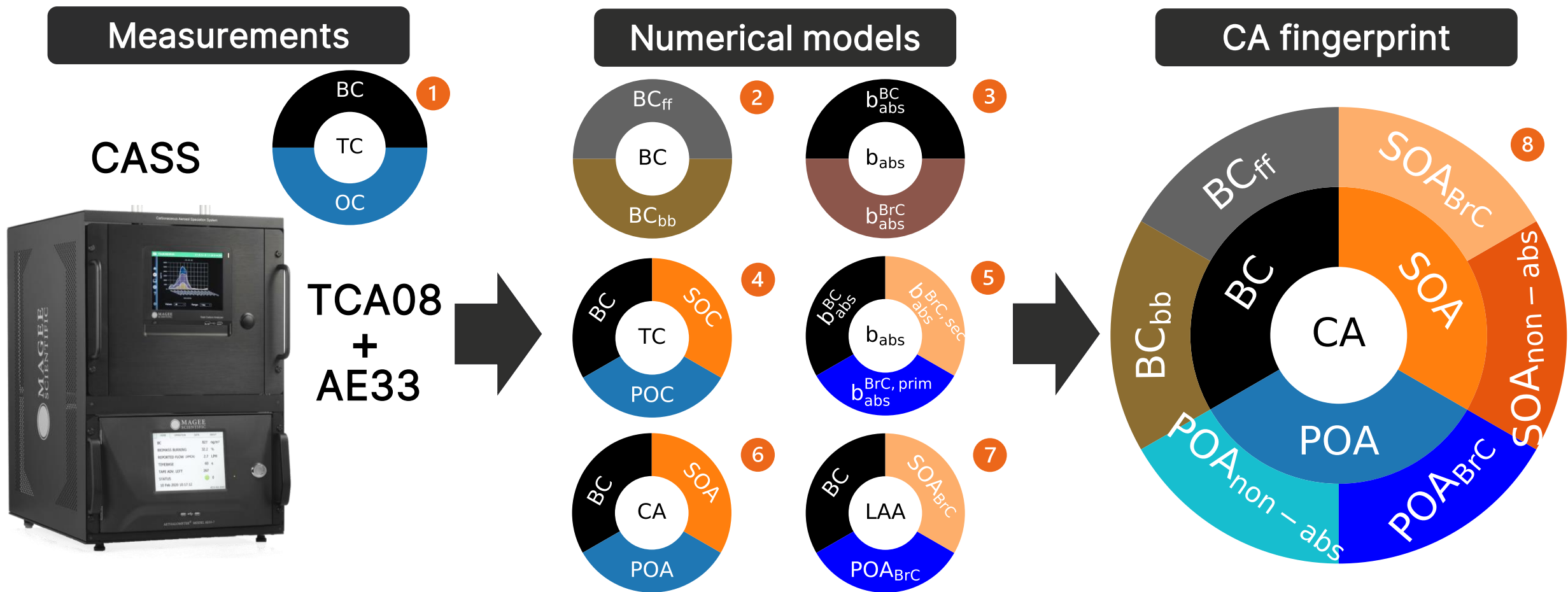


$$MAC_{BC} (880 \text{ nm}) = 7.77 \text{ m}^2/\text{g}$$

$$MAC_{BrC,prim} (370 \text{ nm}) = 5.5 \text{ m}^2/\text{g}$$

$$MAC_{BrC,sec} (370 \text{ nm}) = 2.4 \text{ m}^2/\text{g}$$

Advanced TC-BC(λ) method

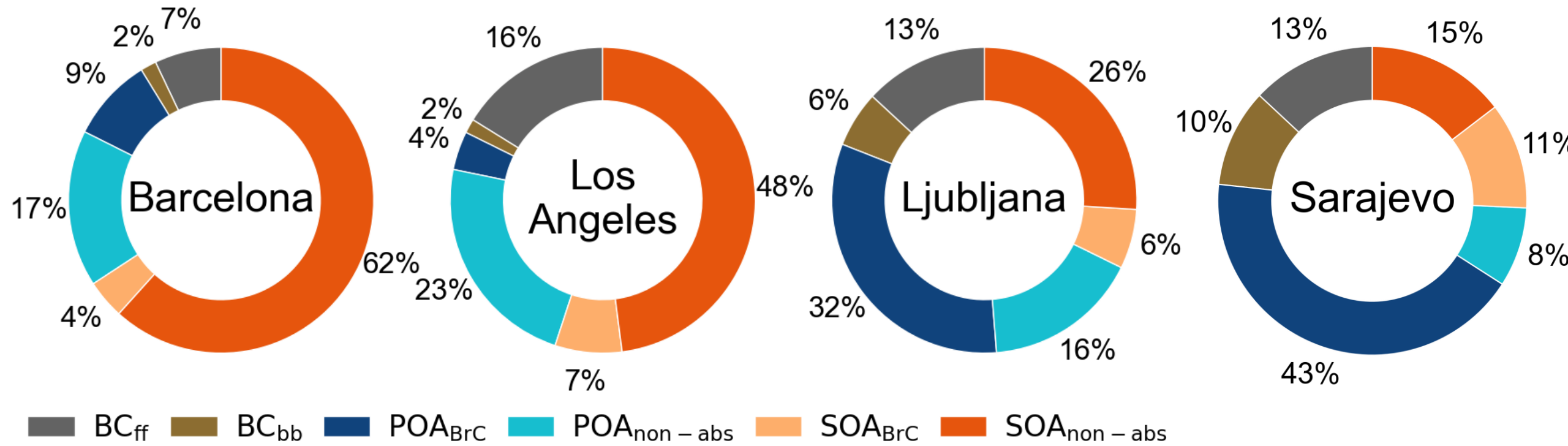


(Ivančič et al., STOTEN, 2022)

$$POA_{\text{non-abs}}(t) = POA(t) - POA_{\text{BrC}}(t)$$

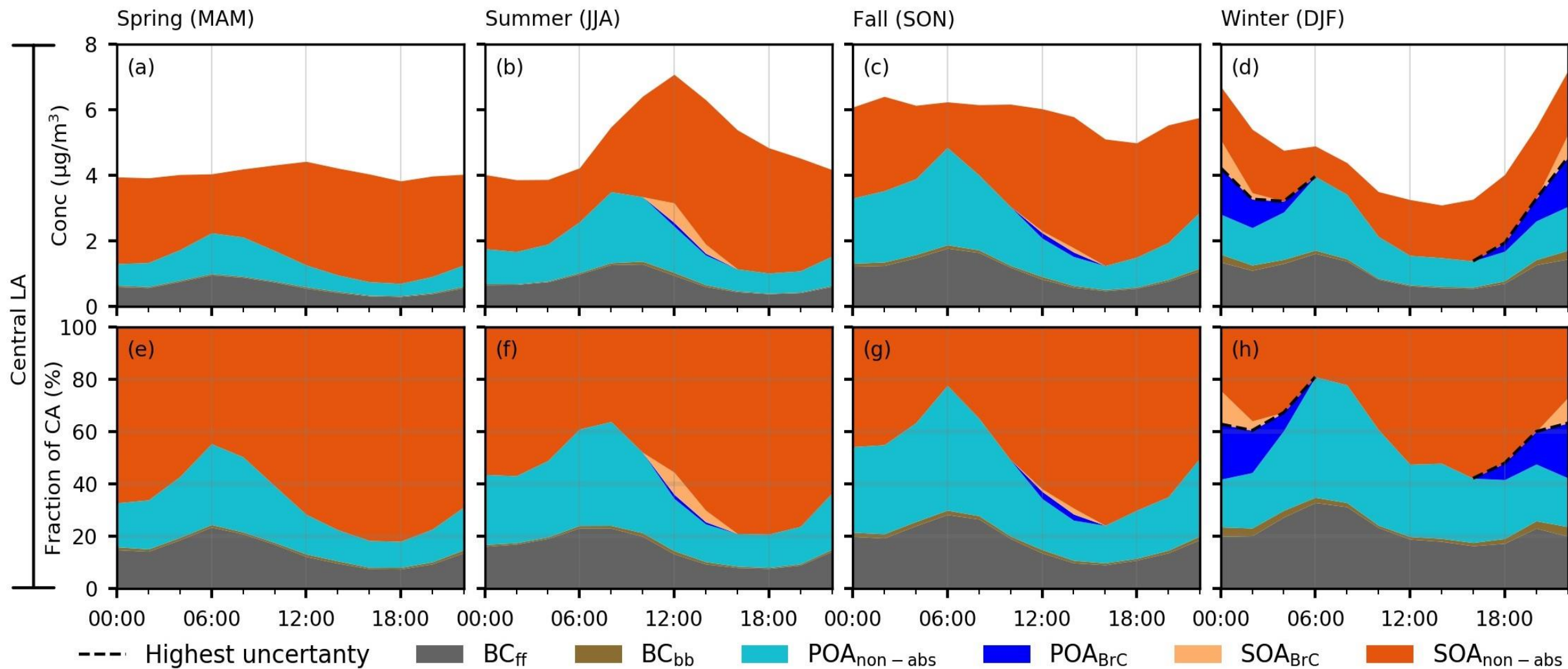
$$SOA_{\text{non-abs}}(t) = SOA(t) - SOA_{\text{BrC}}(t)$$

Results: CA fingerprints



Results: Two-year long campaign in Los Angeles

(Ivančić et al., STOTEN, 2022)





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Thank you for your attention!

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28 May 2024

