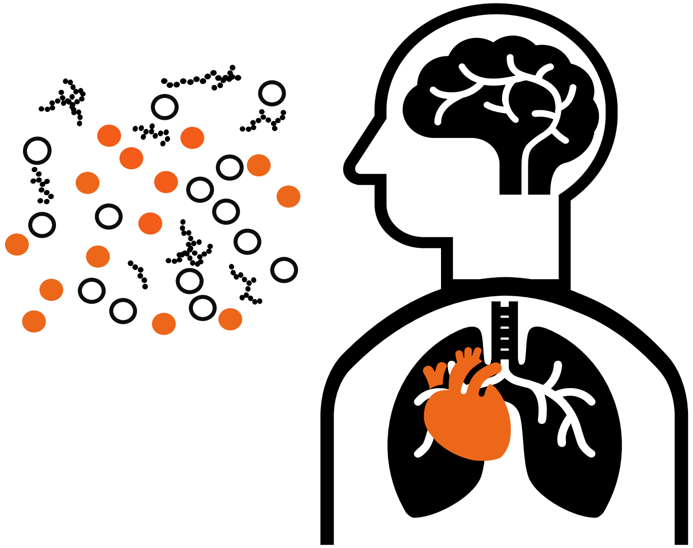
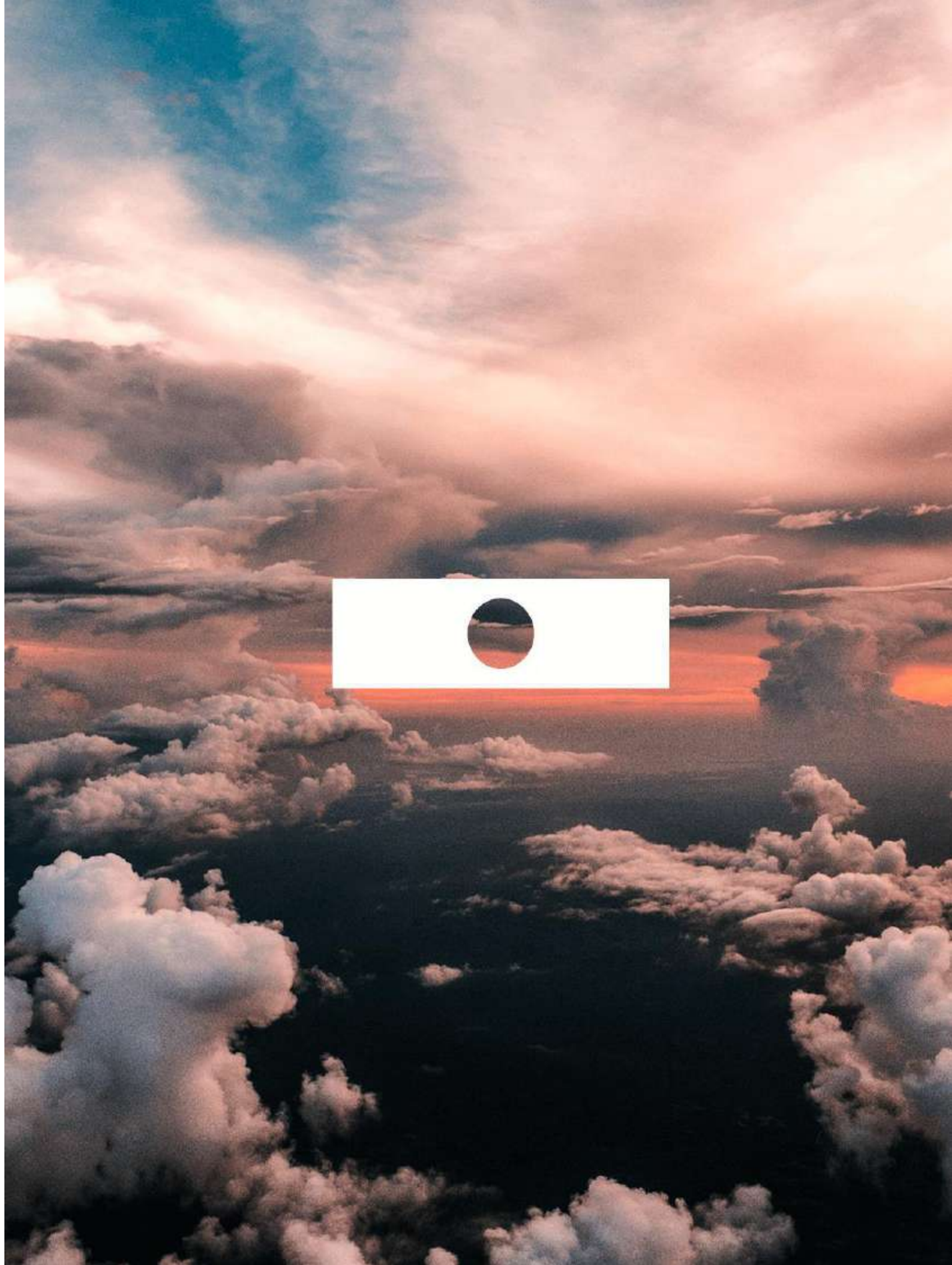
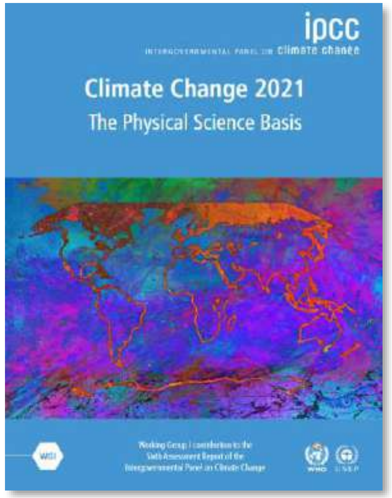
Outline

- Motivation
- Carbonaceous aerosols
- Measurements & models
- Results & on-going research
- Conclusions

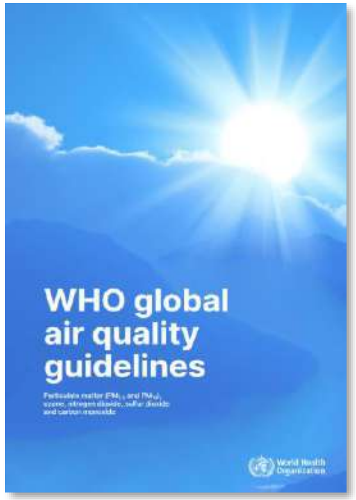




Motivation



IPPC, 2021



WHO, 2021

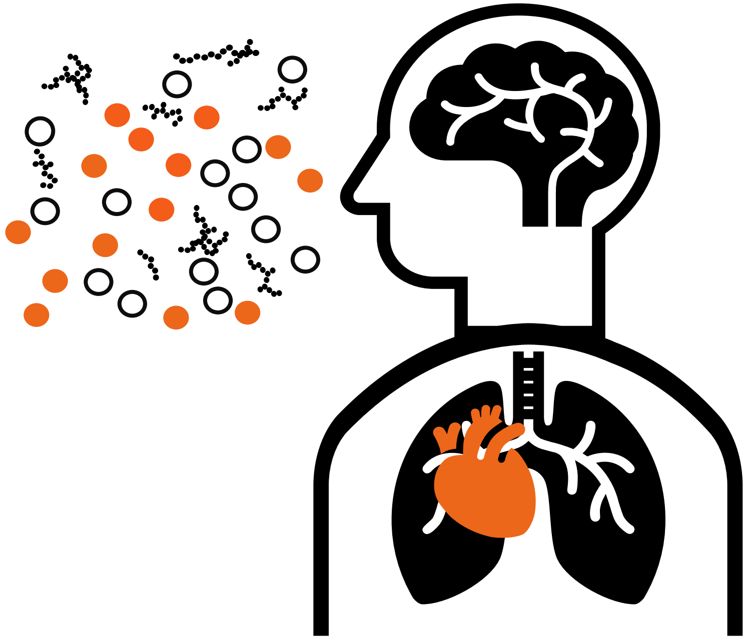
Carbonaceous aerosols are the largest and often dominant fraction of PM2.5

Impact on Earth's radiation balance

- Direct: Light absorption and scattering
  black carbon is the second highest contributor to global warming, after CO_2
- Indirect: cloud nucleation, albedo change (darkening snow and ice)

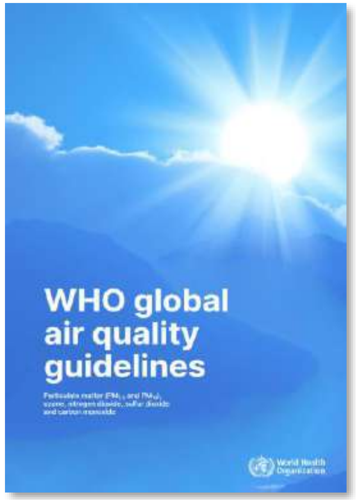
Impact on health

- Carbonaceous aerosols are more hazardous than other PM2.5 compounds
- Deep penetration into tissues
- High potential to inflict oxidative stress



Motivation

- Air pollution is now recognized as the single biggest environmental threat to human health
- New EU directive includes mandatory measurements of Black Carbon, Ultra Fine Particles and Oxidative Potential at supersites



WHO, 2021

Recommended AQ guidelines

Pollutant	Averaging time	AQG level
$PM_{2.5}$, µg/m³	Annual	5
	24-hour[a]	15
PM_{10}, µg/m³	Annual	15
	24-hour[a]	45

new directives

new directives

US EPA (Feb 2024)

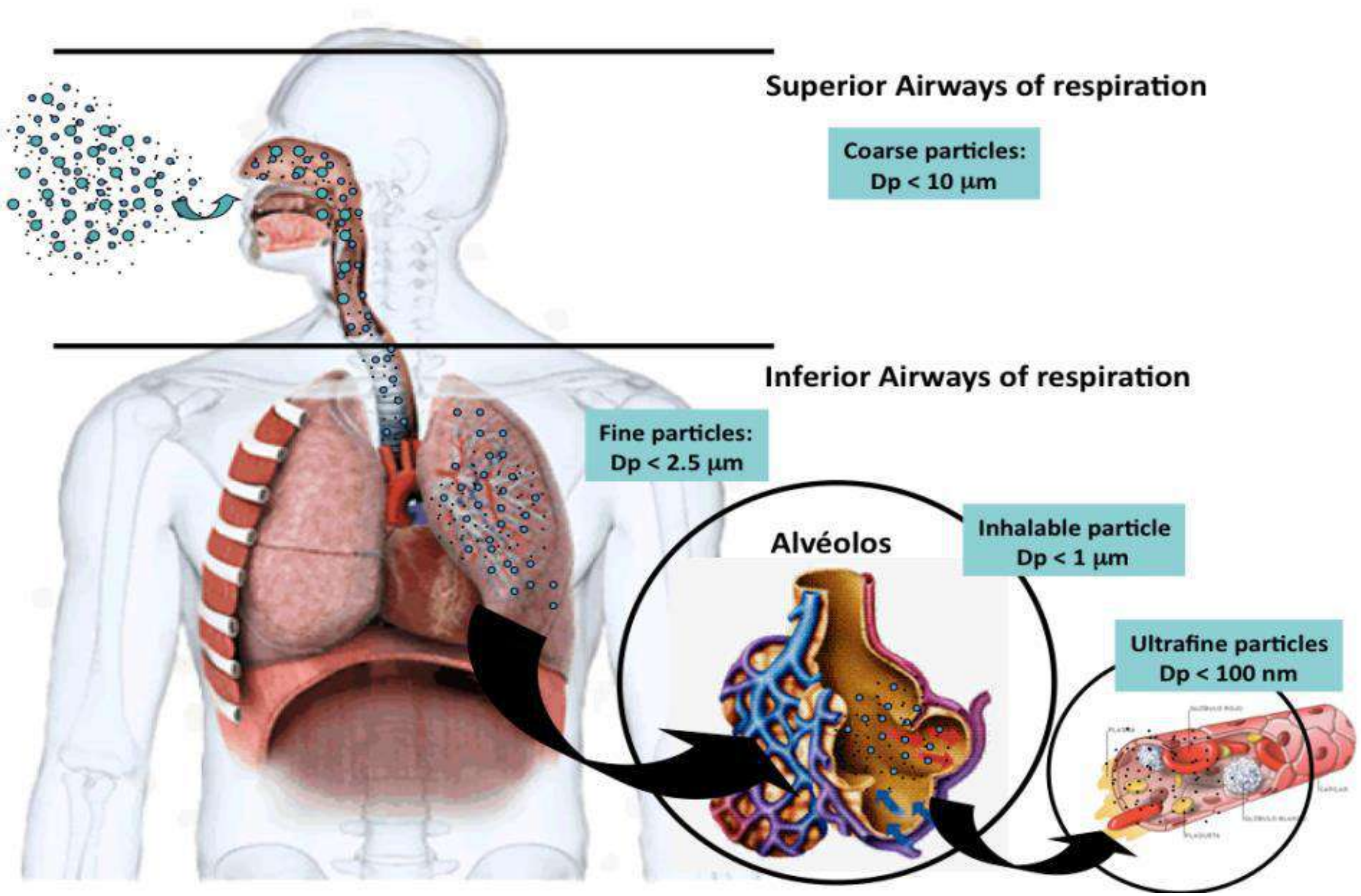
Pollutant	Averaging time	AQG level
$PM_{2.5}$, µg/m³	Annual	9
	24-hour[a]	35
PM_{10}, µg/m³	Annual	/
	24-hour[a]	150

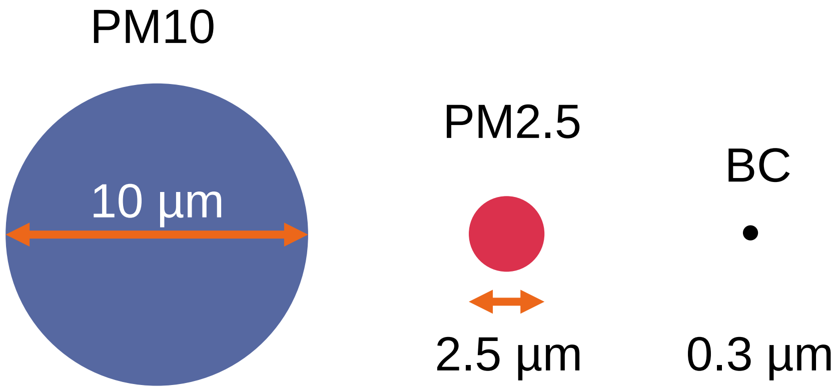
EU (2030*)

Pollutant	Averaging time	AQG level
$PM_{2.5}$, µg/m³	Annual	10
	24-hour[a]	25
PM_{10}, µg/m³	Annual	20
	24-hour[a]	45

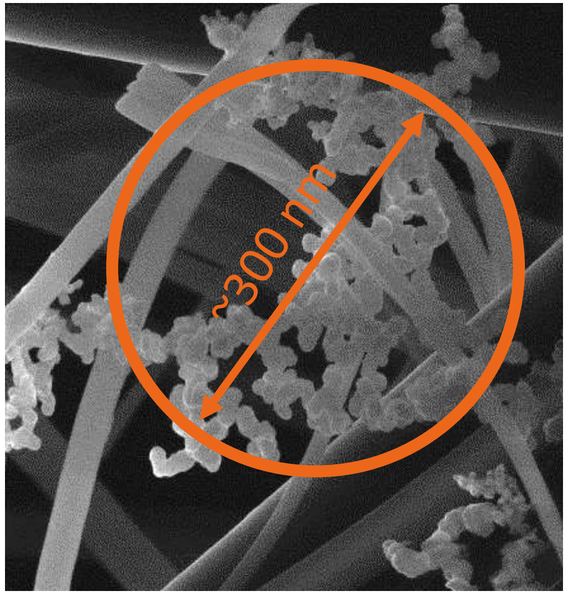
*In February 2024, the Council and the European Parliament reached a provisional agreement on the revised directive

Black Carbon (BC) as part of PM10

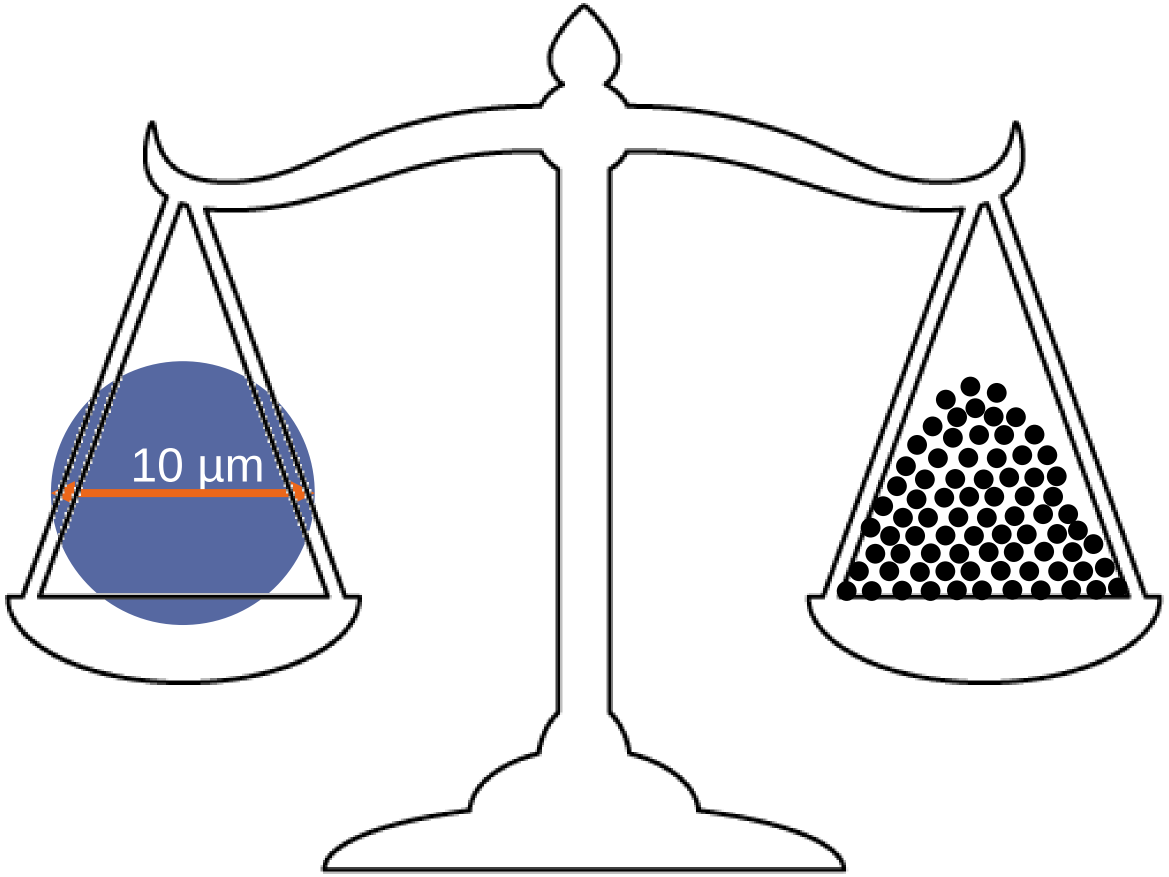


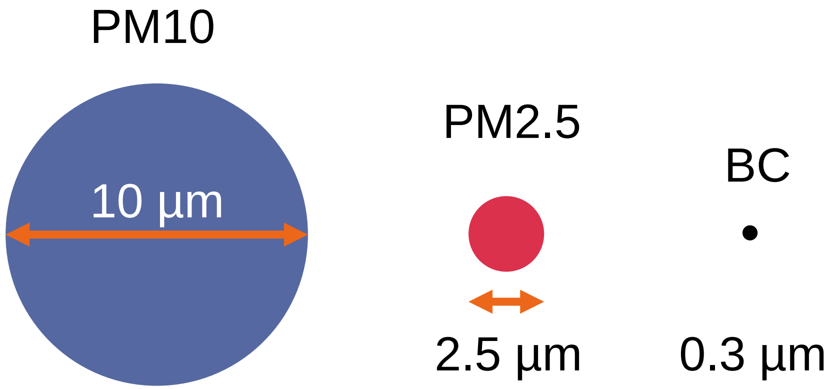


2r(BC) ~ 300 nm =0.3 µm

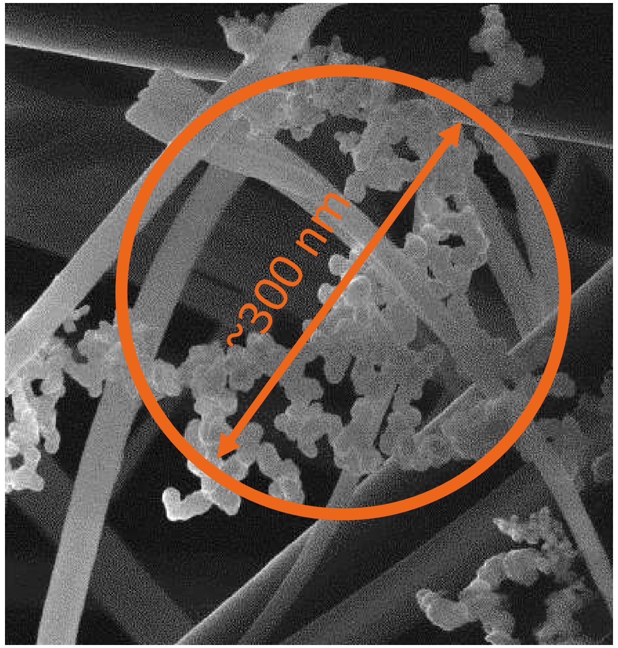


Larger aerosols dominate the mass concentration





2r(BC) ~ 300 nm =0.3 µm

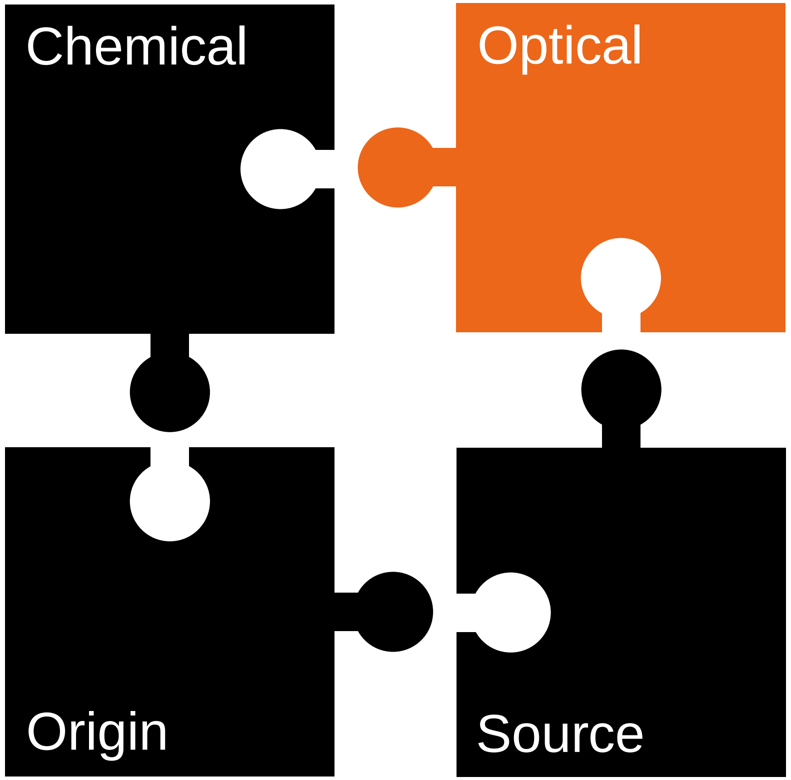


2r(PM10) ~ 33·2r(BC)

m(PM10) ~36.000· m(BC)

Carbonaceous aerosols

Elemental / organic



Absorbing/ non-absorbing

Primary / secondary

Natural / anthropogenic

Chemical composition of CA

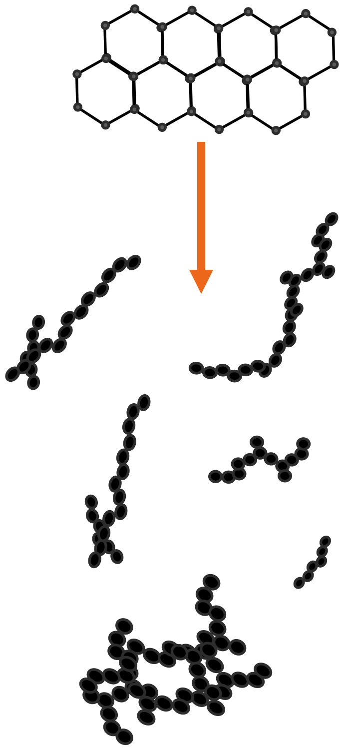
CA – Carbonaceous Aerosols
BC t Black Carbon
EC t Elemental Carbon
OA t Organic Aerosols
BrC t Brown Carbon
TC t Total Carbon
OC t Organic Carbon

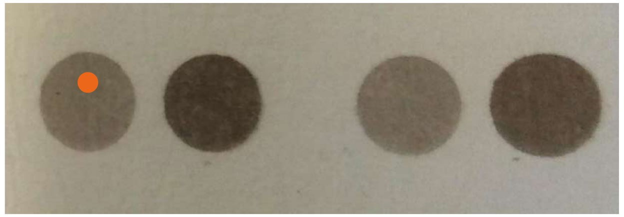
$$CA = BC + OA$$

$$TC = BC + OC$$

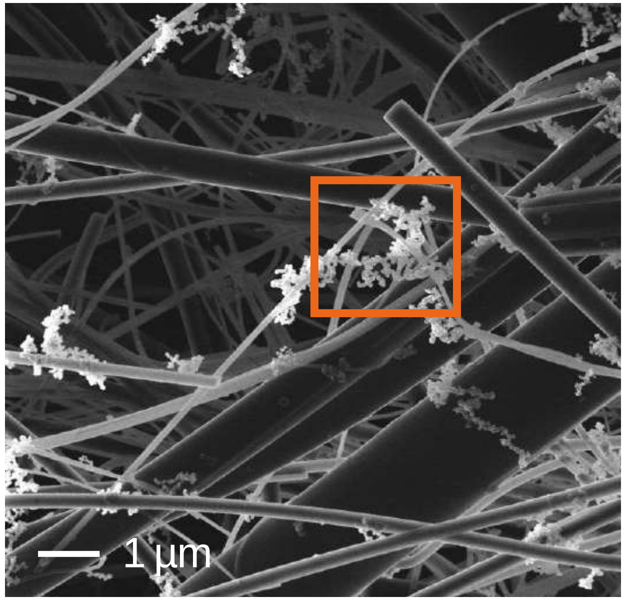
BC (black carbon)

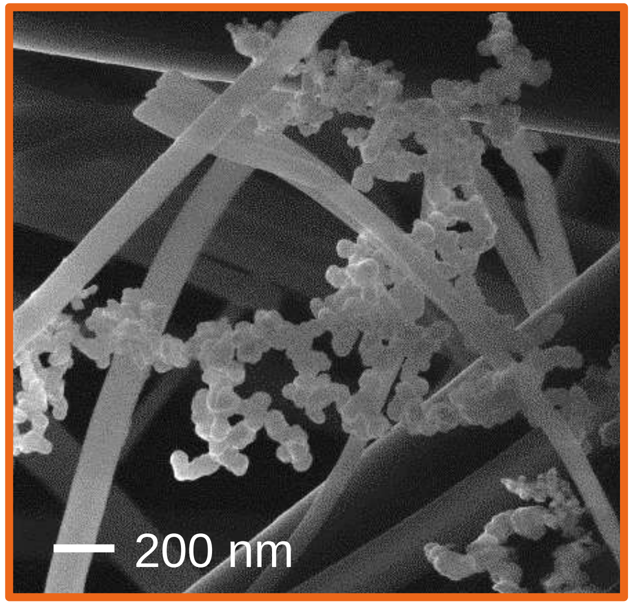
- soot
- graphite like carbon
- fractal structure
- pure, elemental carbon
- refractory
- chemically inert
- combustion tracer
- light absorbing





Fresh BC particles on AE33 filter tape (Helium Ion Microscopy)





Chemical composition of CA

TC is carbon fraction of CA

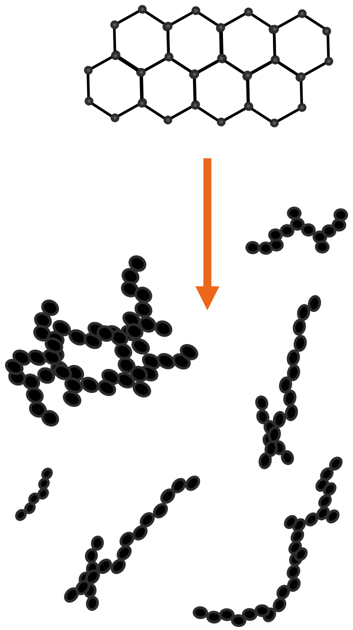
$$CA = BC + OA$$

$$TC = BC + OC$$

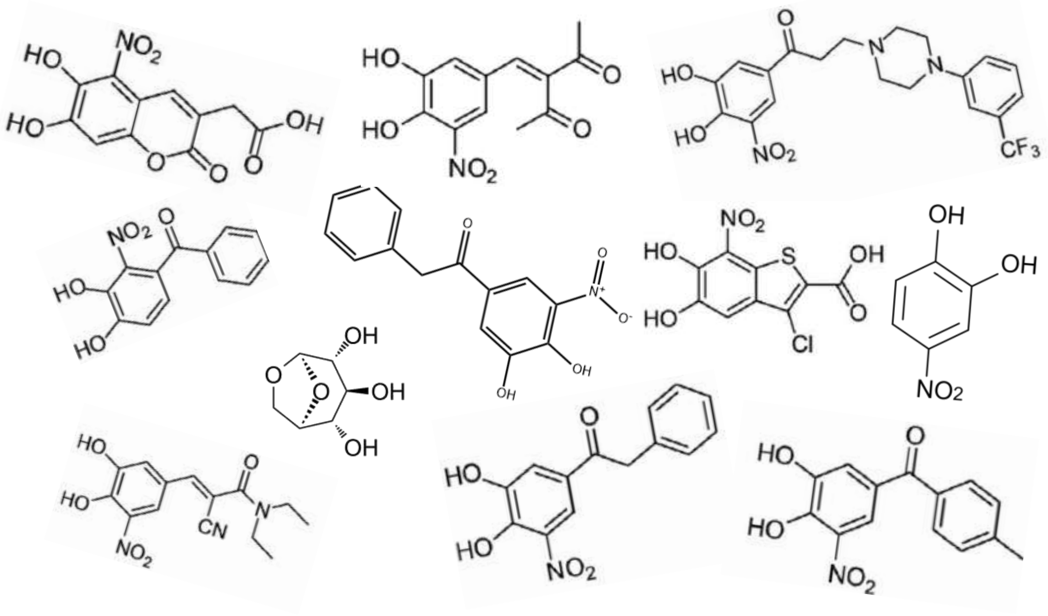
OC is carbon fraction of OA

CA– CarbonaceousAerosols
BC t BlackCarbon
EC t ElementalCarbon
OA t OrganicAerosols
BrC t Brown Carbon
TC t Total Carbon
OC t OrganicCarbon

BC

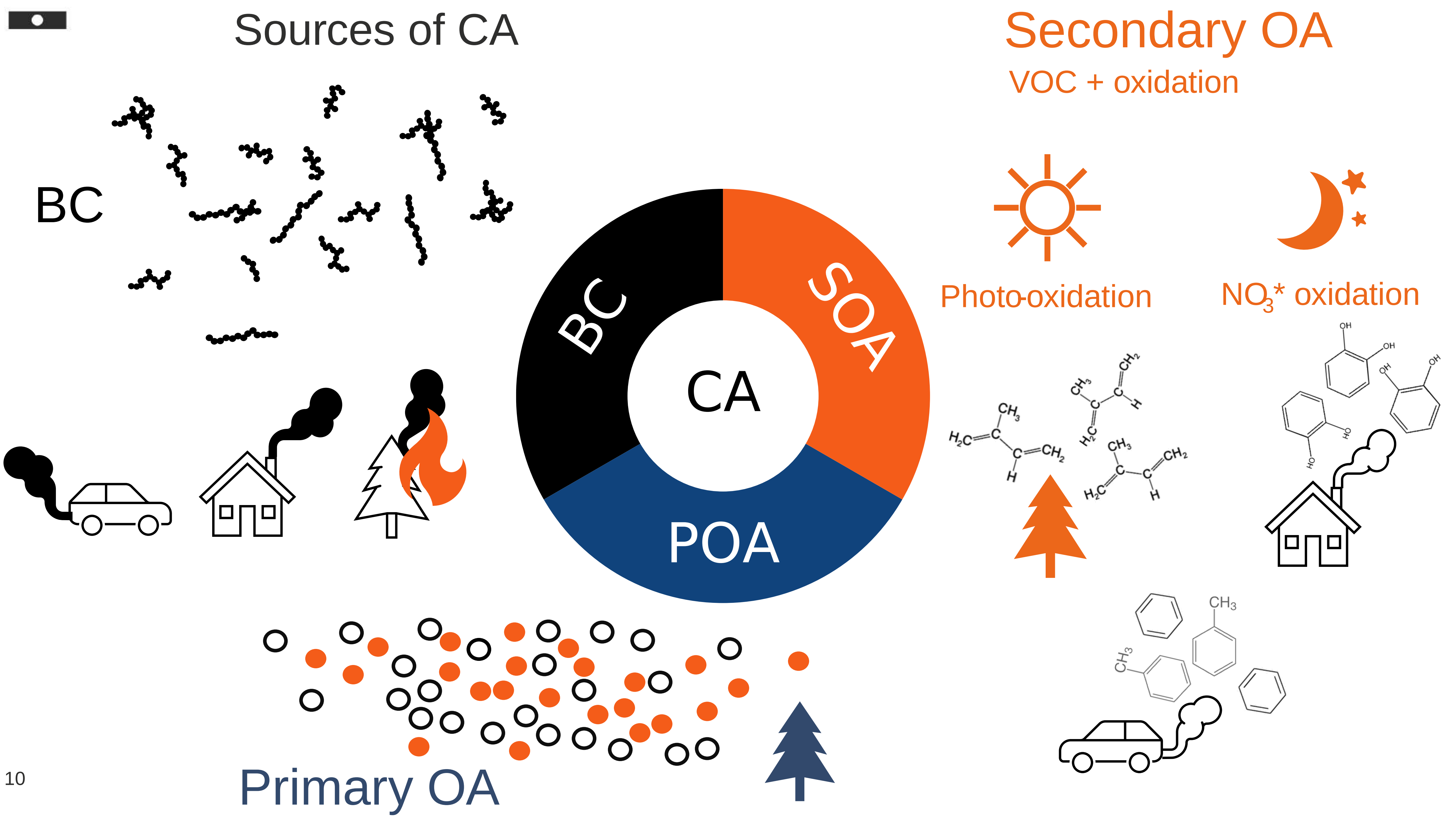


OA



Organic aerosols

- other elements:
  , U K U E U ^ U Y
- chemically not inert: chemical transformations
- aging: oxidation
- Complex structure



Sources of CA
Secondary OA
VOC + oxidation
BC
Photo-oxidation
NO3* oxidation
BC
SOA
CA
POA
Primary OA

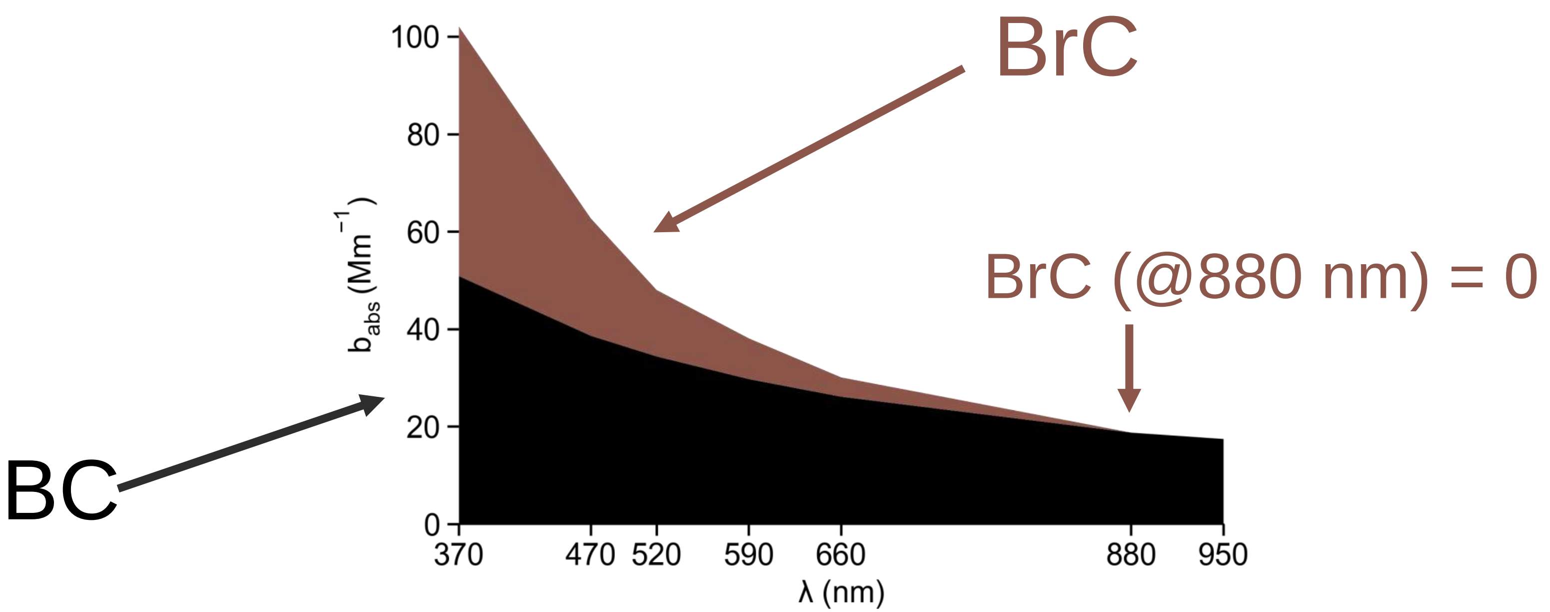
Optical properties of CA

CA – Carbonaceous Aerosols
BC t Black Carbon
OA t Organic Aerosols
BrC t Brown Carbon
$OA_{non-abs}$ t Non-absorbing OA
LAA t Light Absorbing Aerosols

$$CA = BC + \overbrace{OA}^{}$$

$$\underbrace{BC + BrC}_{LAA} + OA_{non-abs}$$

$$LAA + OA_{non-abs}$$



Aethalometer – filter photometer for measuring BC

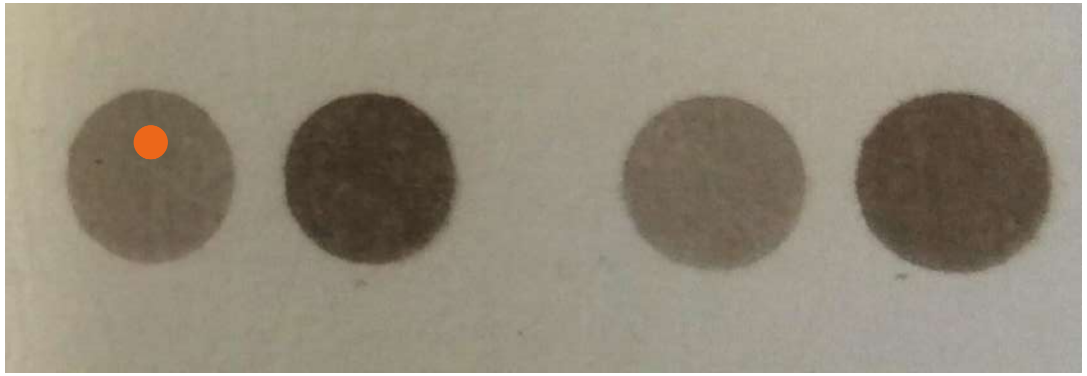
AE33(7λ)

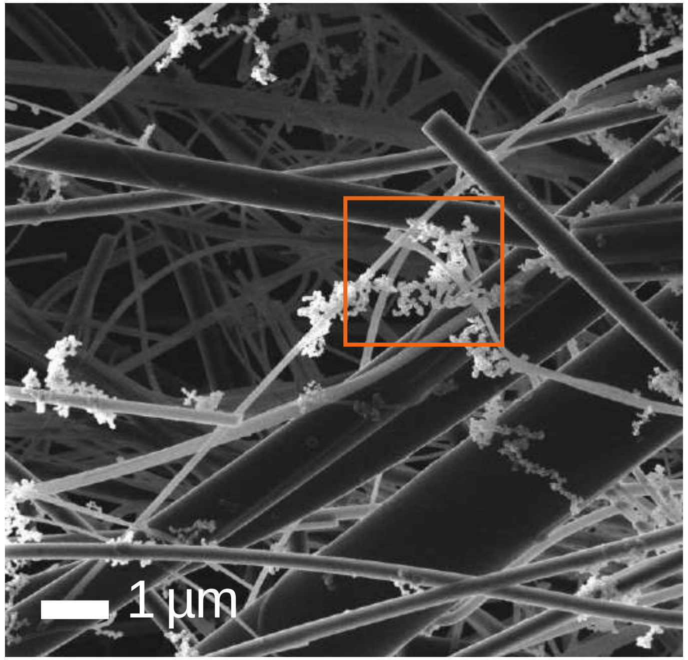
AE36(7λ)

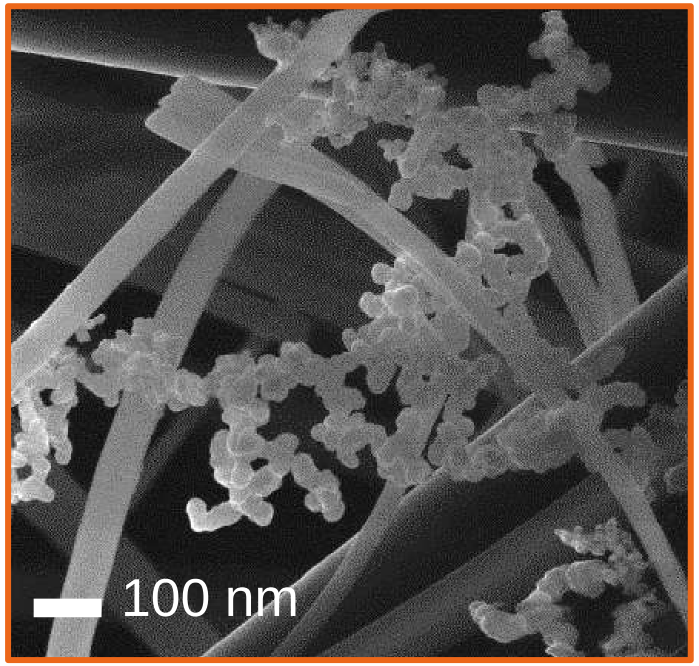
AE36s(9λ)

Aethalometer - principle of operation

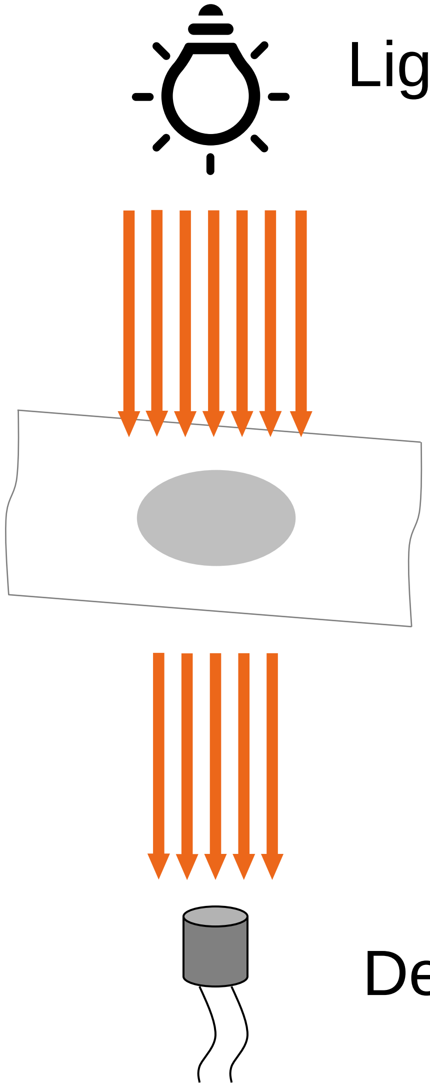
AE36s







Aethalometer - principle of operation

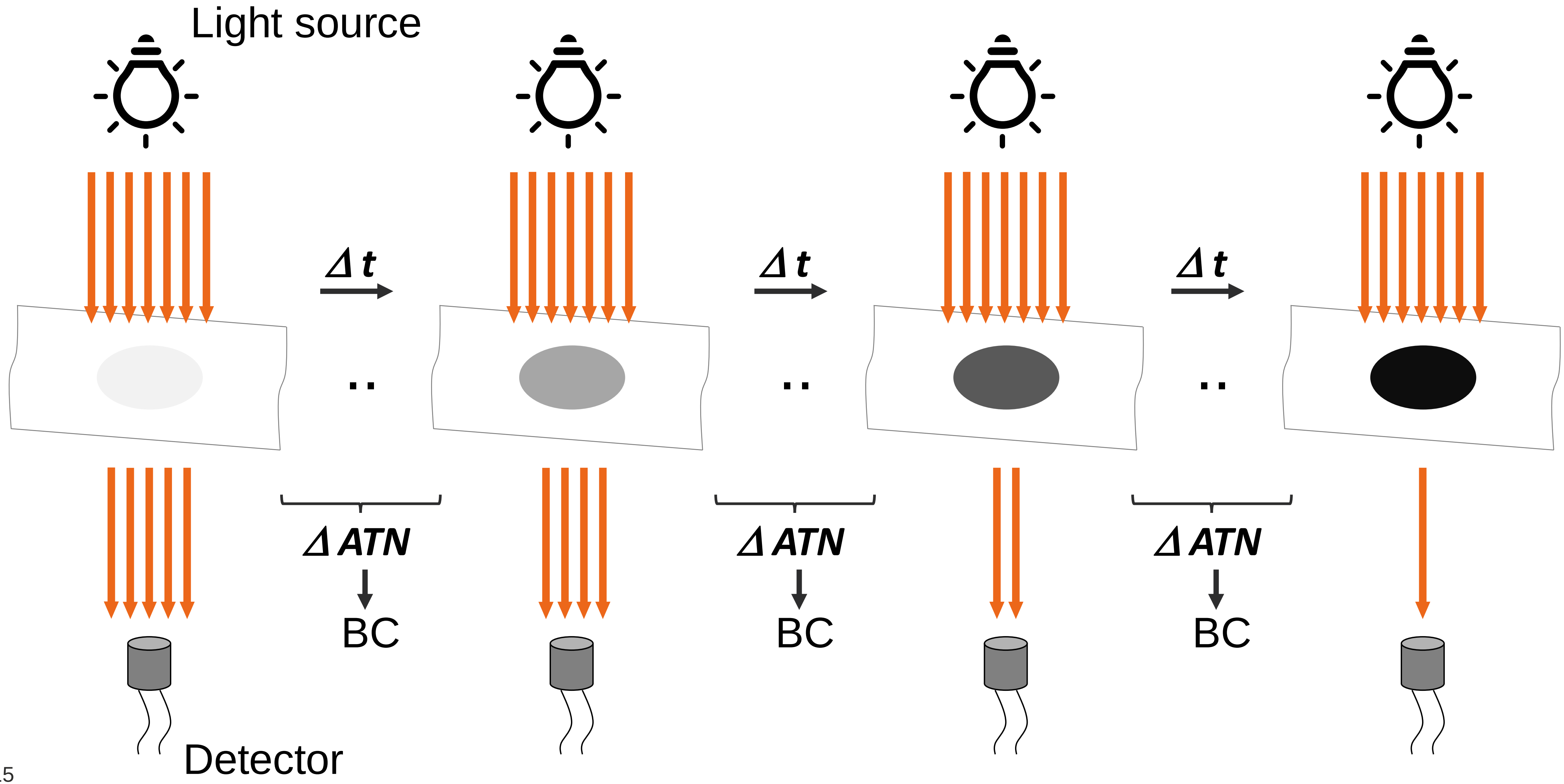


Light source

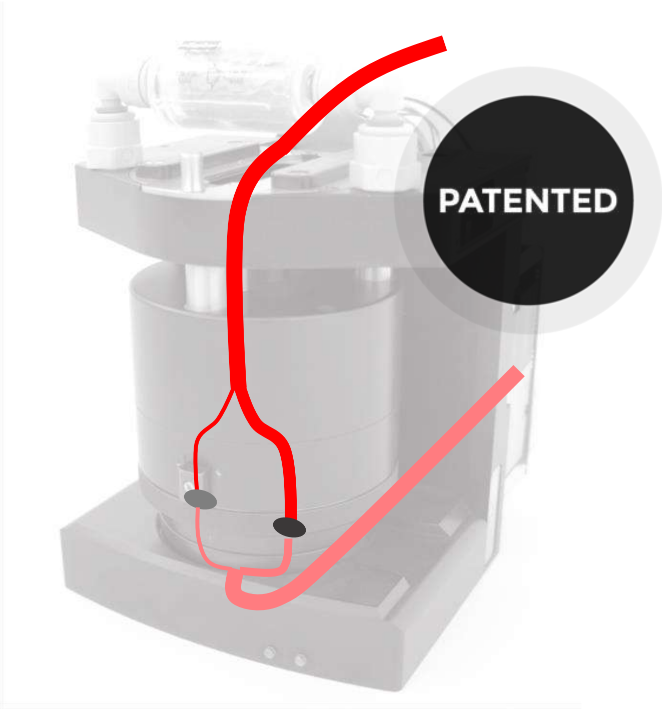
Light attenuation

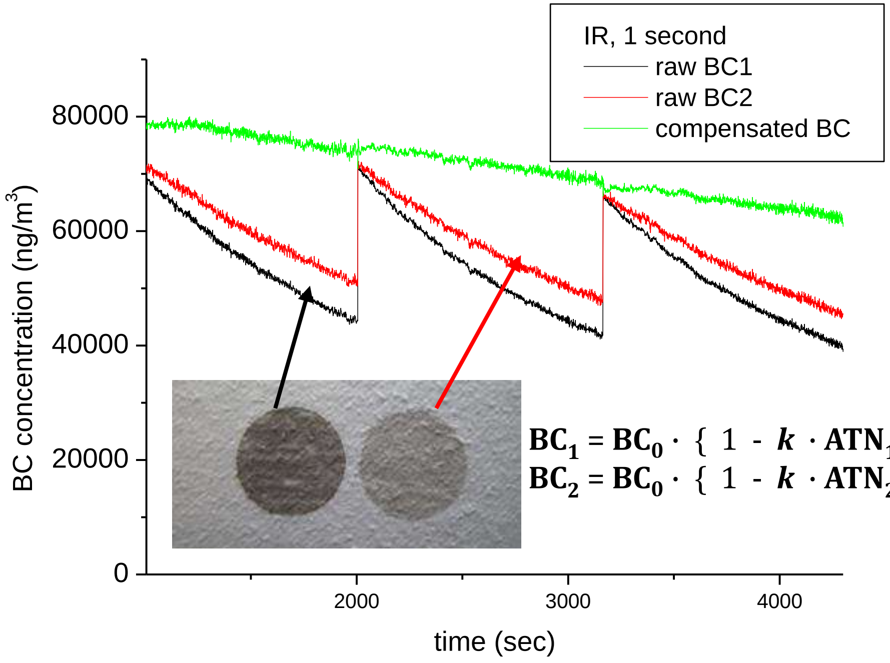
Detector

Aethalometer - principle of operation

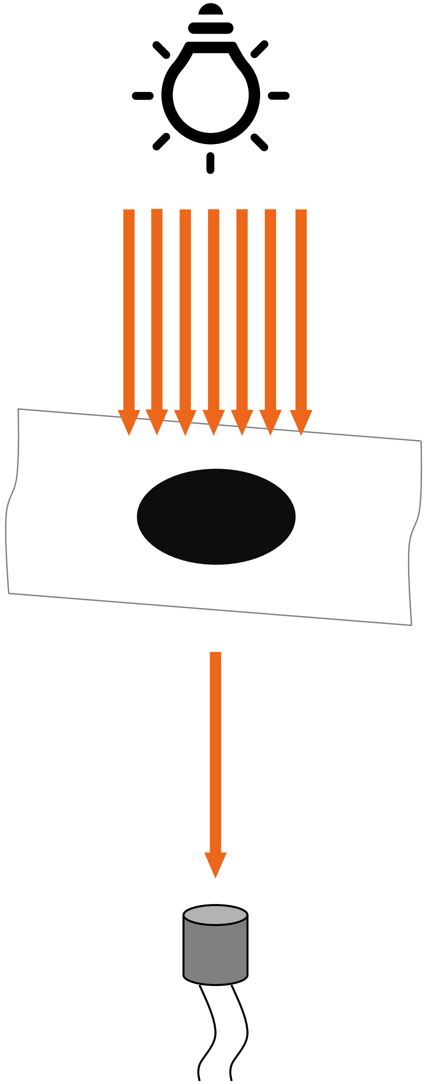


Aethalometer DualSpot^{TM} – real-time loading effect correction



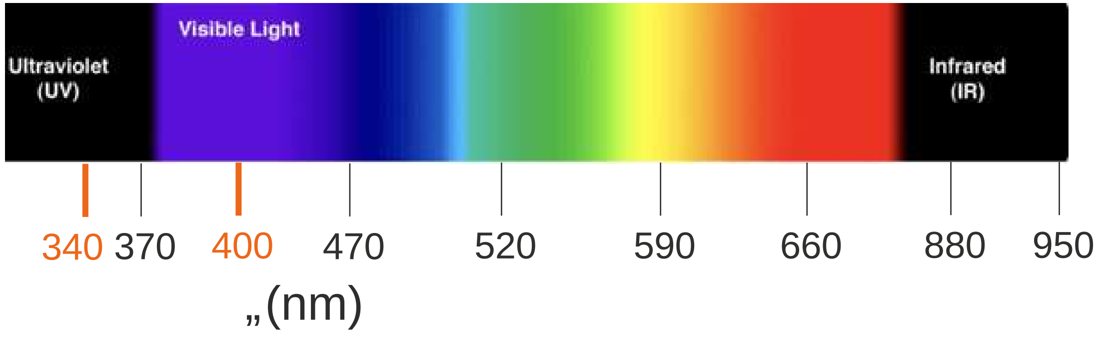


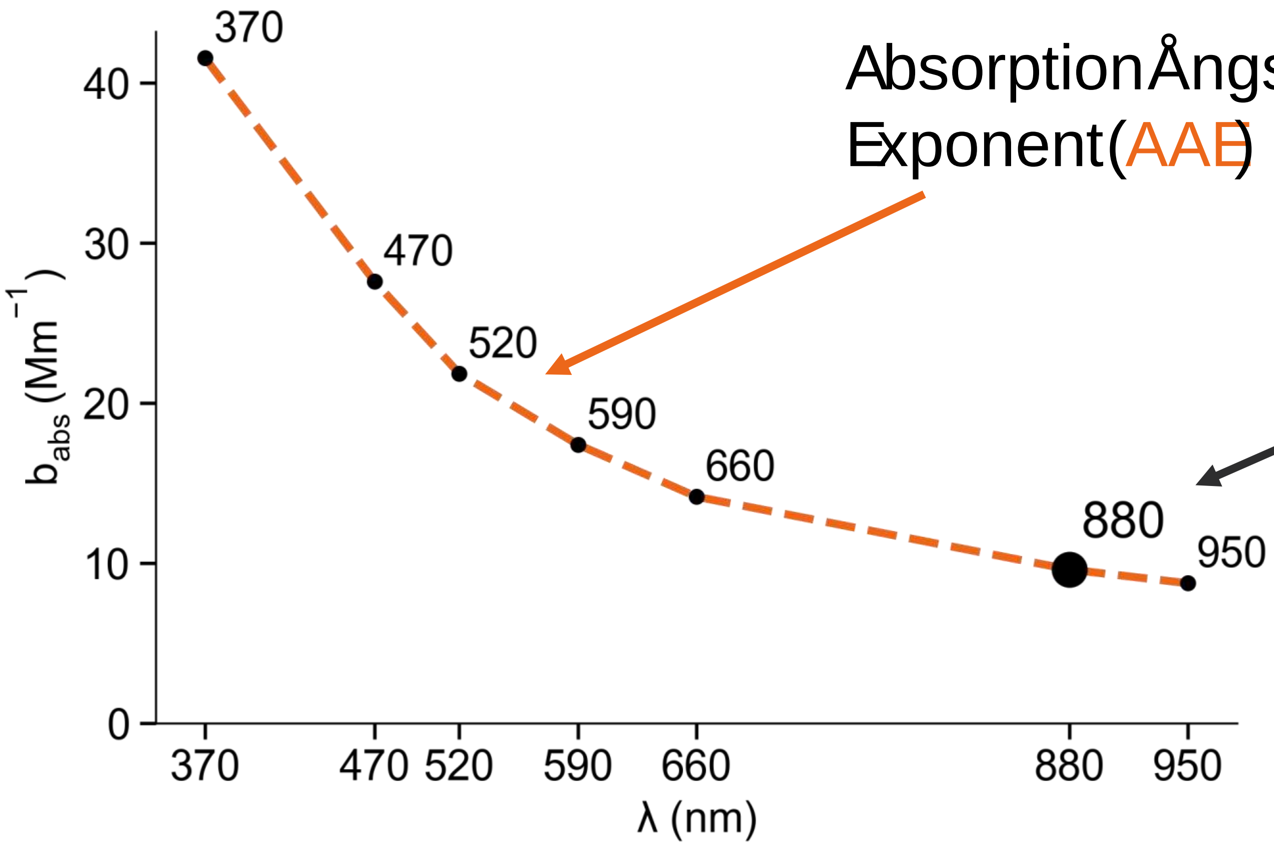
$$BC_1 = BC_0 \cdot \{ 1 - \boldsymbol{k} \cdot ATN_1 \}$$
$$BC_2 = BC_0 \cdot \{ 1 - \boldsymbol{k} \cdot ATN_2 \}$$



Aethalometer multi-wavelength measurements

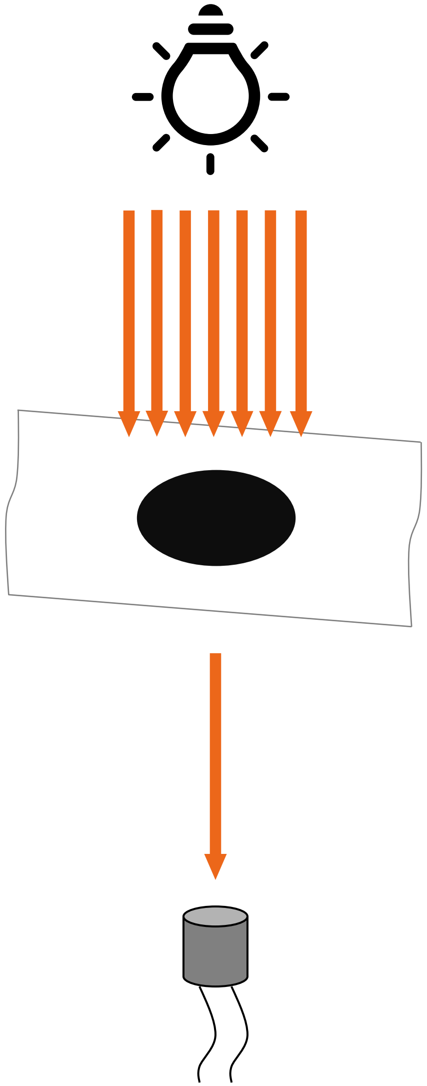
7 (AE33, AE36) or 9 (AE36s) wavelengths





Absorption Ångström Exponent (AAE)

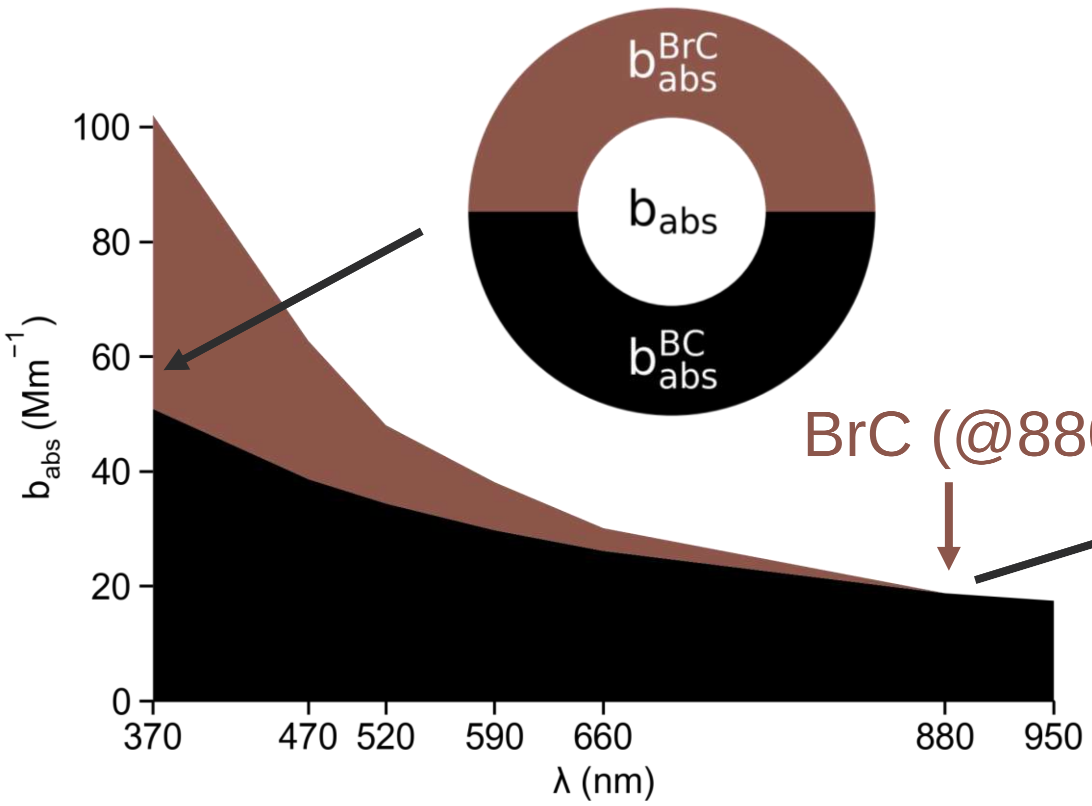
Black Carbon (BC)



Aethalometer multi-wavelength measurements

Brown carbon (BrC) model

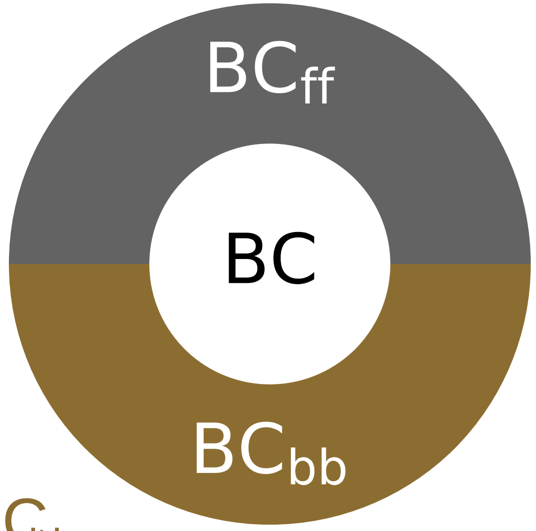
(Zhang et al., *Sci. Total Environ.*, 2020; Saleh, *Curr. Pollut. Rep.*, 2020)



BrC (@880 nm) = 0

Aethalometer (Sandradewi) model

(Sandradewi et al., *Environ.Sci.Technol.*, 2008; Zotter et al., *ACP*, 2017)



BC (@880 nm) = BC_{ff} + BC_{bb}

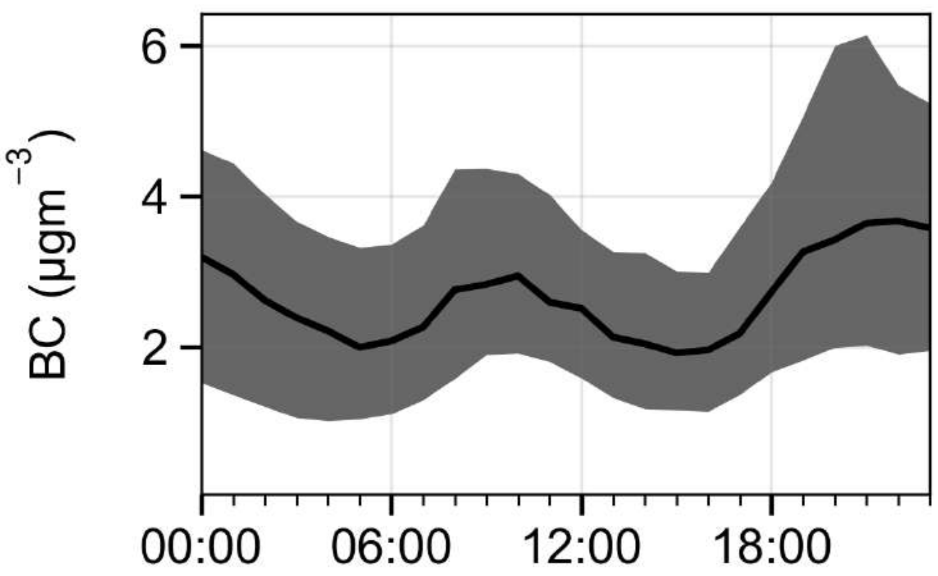
BC_{ff} (liquid/fossil fuels) AAE_{ff} ~ 1.0 t 1.15

BC_{bb} (solid fuels/biomass burning) AAE_{bb} ~ 2.0

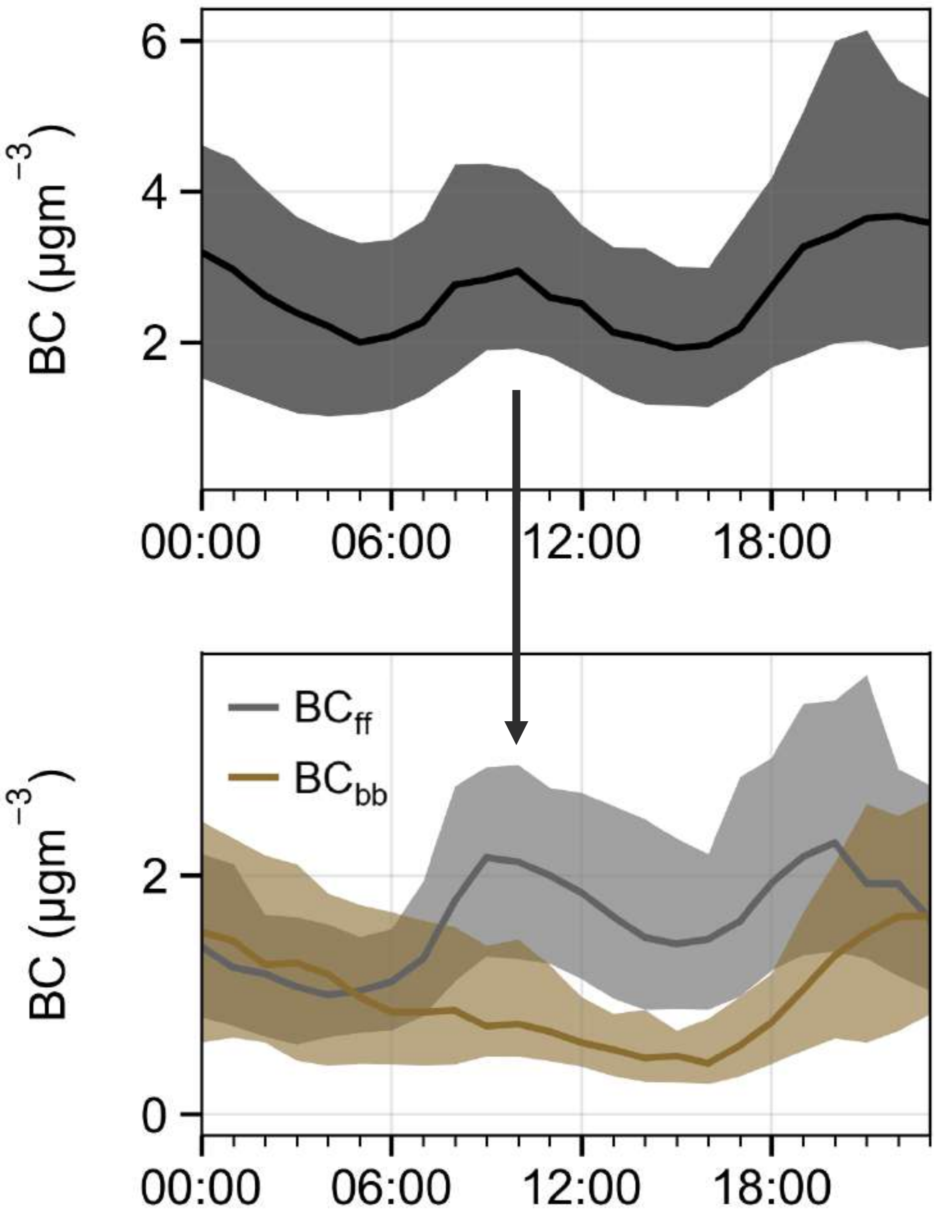
Approx: BrC (@880 nm) = 0, BC is only LAA @880 nm

AAE_{BC} ~ AAE_{ff} ~ 1.0 - 1.15

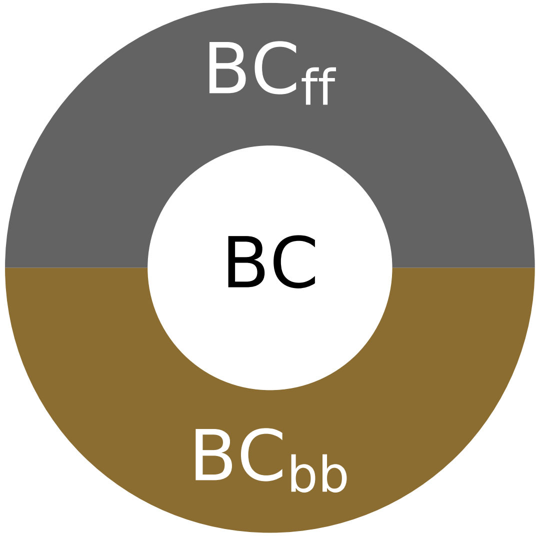
Aethalometer source apportionment model



Aethalometer source apportionment model



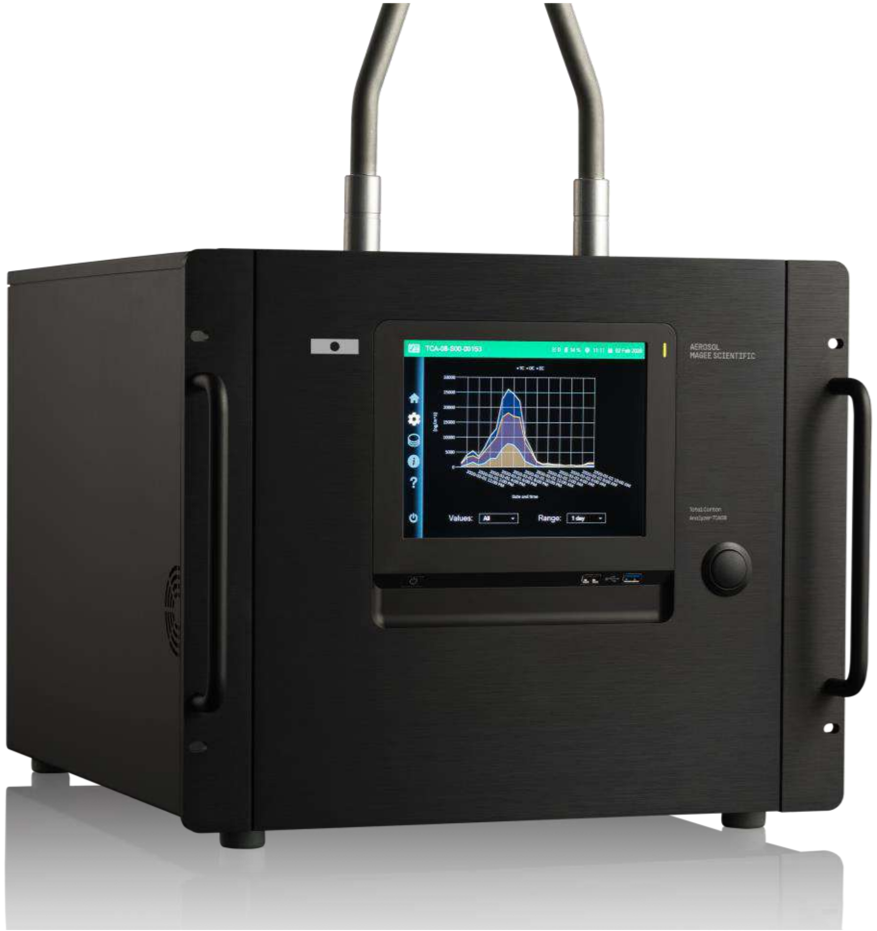
Traffic (fossil fuels)



Biomass burning

Total Carbon Analyzer TCA08

Simplified thermal protocol 900°C



PATENTED

2 chambers

1 for sampling & 1 for analyzing

-> Continuous operation

CASS: Carbonaceous aerosol specification system TC-BC(λ) method

CASS

TCA08
+
AE36s

(Rigler et al., *Atmos. Meas. Tech.*, 2020;
Drinovec et al., *Atmos. Meas. Tech.*, 2015;
/ À v] *Sci. Total Environ.*, 2022)

TCA08:

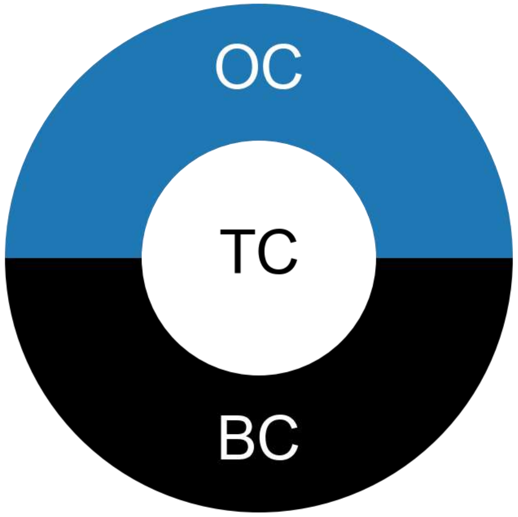
- Simplified thermal protocol for TC
- Two chambers continuous data
- 20 min t 24 h time resolution

Aethalometer (AE33 or AE36s or AE36):

- Optical method: 79 „optical absorption
- Up to 1s time resolution
- Optical attenuation -> BC mass
- BC ~ EC

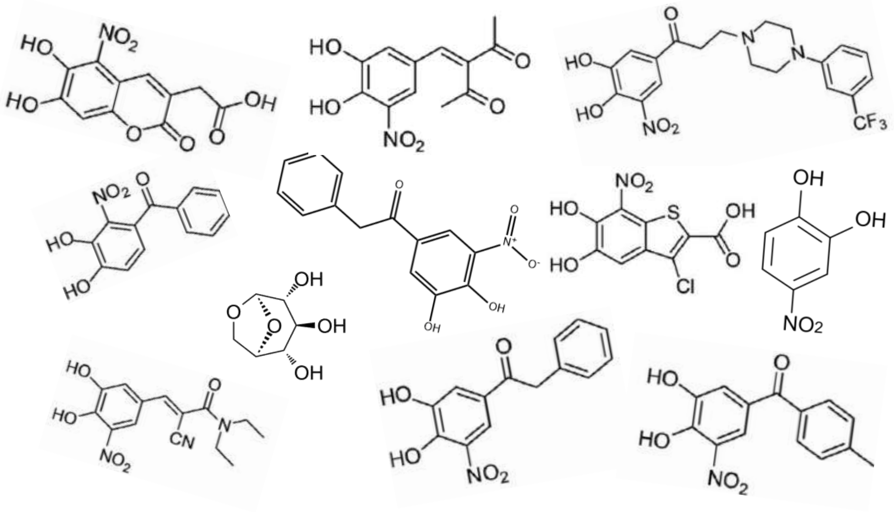
CASS:

OC(t) = TC(t) – BC(t)

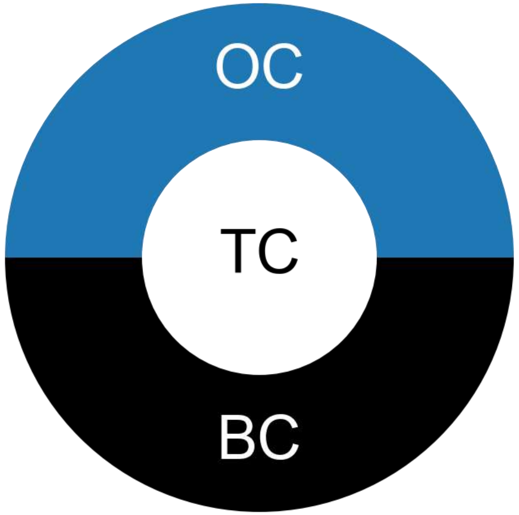


CASS: TC-BC(λ) method

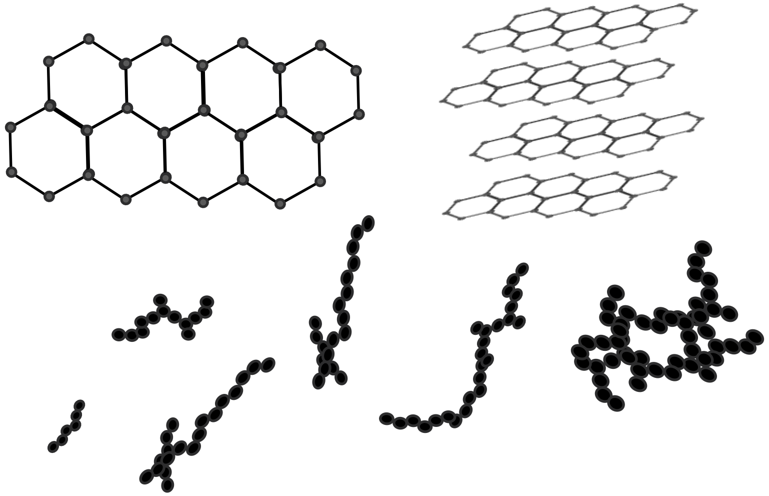
OC t organic carbon



TC = BC + OC
Total carbon



BC t black carbon



1D EC (BC) tracer model

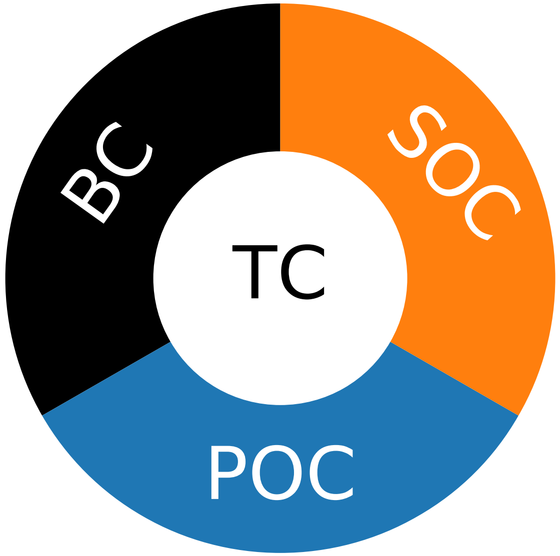
(Turpin &Hunticker, *Atmos.Environ.*, 1995,

/ À v] *Sči. TotalX Environ.*, 2022)

$$\mathrm{POC(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim}} \cdot \mathrm{BC(t)},$$

$$\mathrm{SOC(t)} = \mathrm{OC(t)} - \mathrm{POC(t)}$$

Black carbon



Secondary OC

Primary OC

1 free model parameter: $(\mathrm{OC/BC})_{\mathrm{prim}}$

1D EC (BC) tracer model

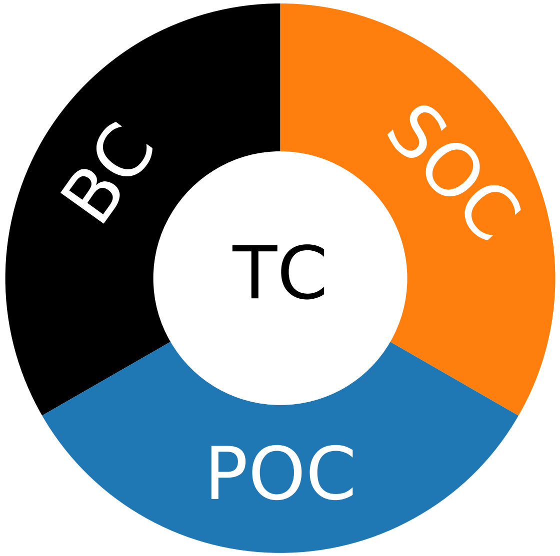
(Turpin & Hunticker, *Atmos. Environ.*, 1995,

/ À v] *Sci. Total Environ.*, 2022)

$$\mathrm{POC(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim}} \cdot \mathrm{BC(t)},$$

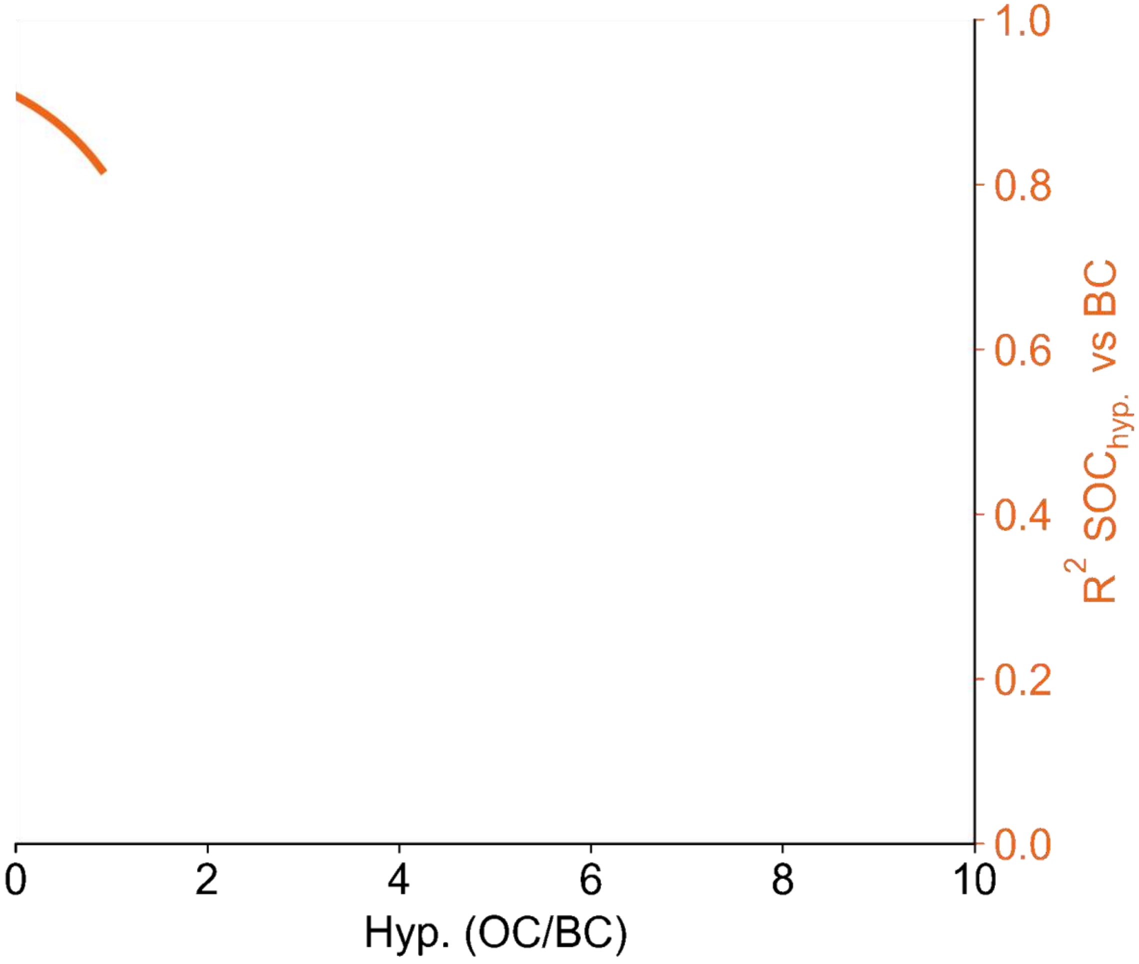
$$\mathrm{SOC(t)} = \mathrm{OC(t)} - \mathrm{POC(t)}$$

Black carbon



Secondary OC

Primary OC



$(OC/BC)_{prim}$ from minimum R^2 (MRS)

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

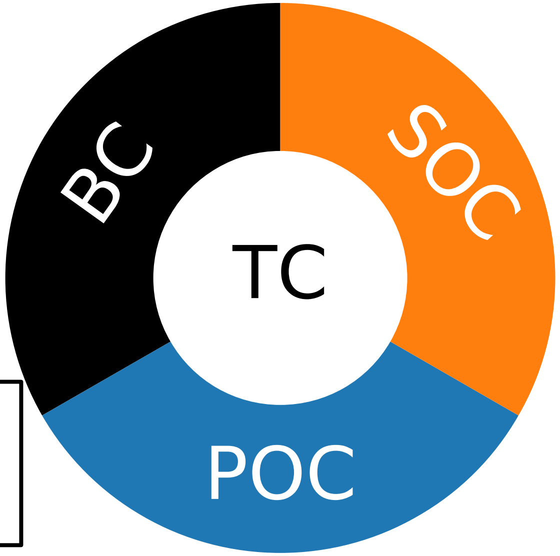
1D EC (BC) tracer model

(Turpin &Hunticker, *Atmos.Environ.*, 1995,
/ À v] *Sci. Total Environ.*, 2022)

$$POC(t) = \left(\frac{OC}{BC}\right)_{prim} \cdot BC(t),$$

$$SOC(t) = OC(t) - POC(t)$$

Black carbon



Secondary OC

Primary OC

1 free parameter:
$(OC/BC)_{prim}$

2D BC tracer model

~ / À v] *manuscript in preparation*)

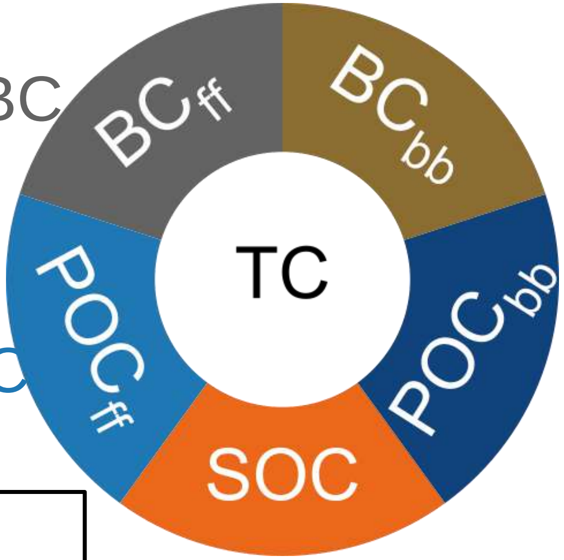
$$POC_{ff}(t) = \left(\frac{OC}{BC}\right)_{prim,ff} \cdot BC_{ff}(t),$$

$$POC_{bb}(t) = \left(\frac{OC}{BC}\right)_{prim,bb} \cdot BC_{bb}(t),$$

$$SOC(t) = OC(t) - POC_{ff}(t) - POC_{bb}(t),$$

Traffic BC

Biomass BC



Traffic POC

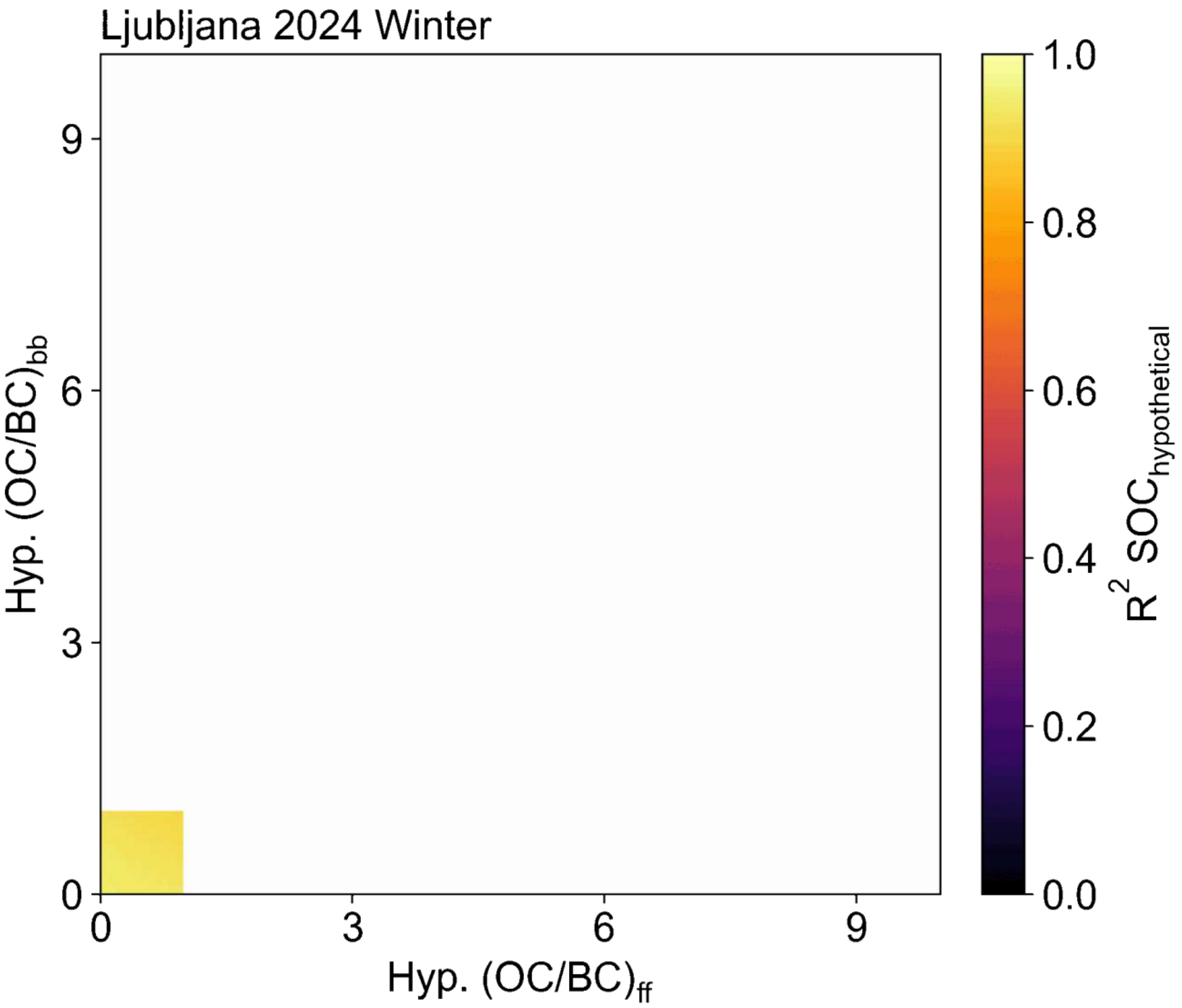
Biomass PO

Secondary OC

2 free parameters:
$(OC/BC)_{prim,ff}$ & $(OC/BC)_{prim,bb}$

2D BC tracer model

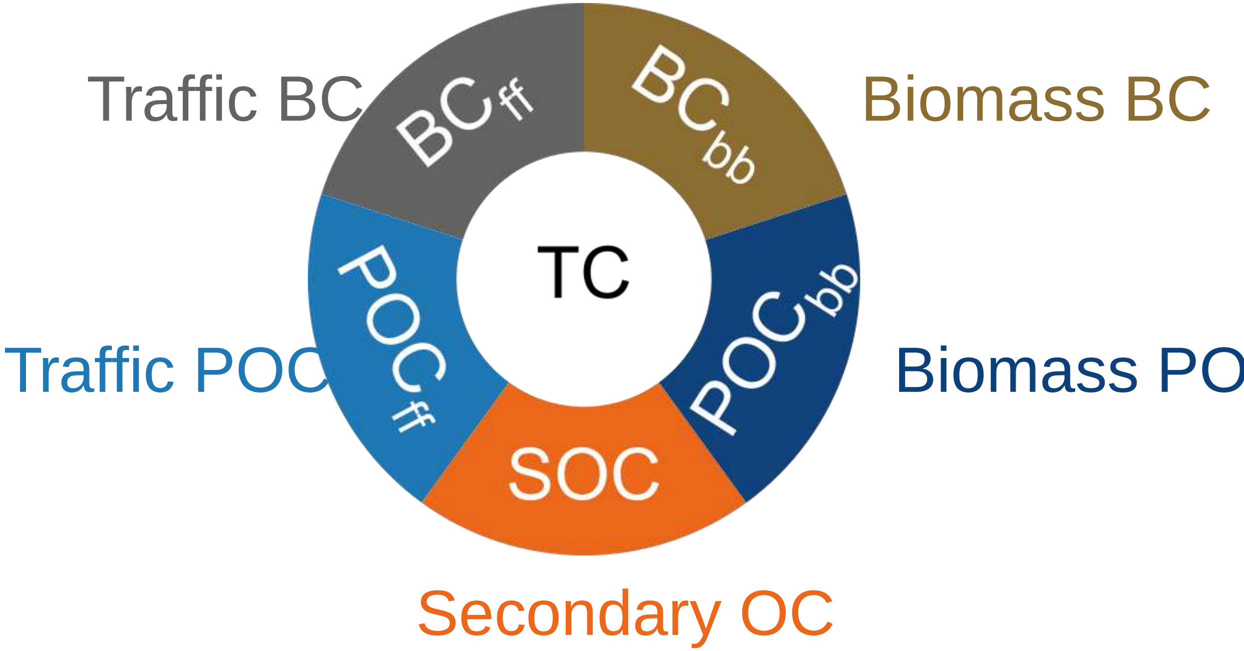
~ / À v] *manuscript in preparation*)



$$\mathrm{POC_{ff}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,ff}} \cdot \mathrm{BC_{ff}(t)},$$

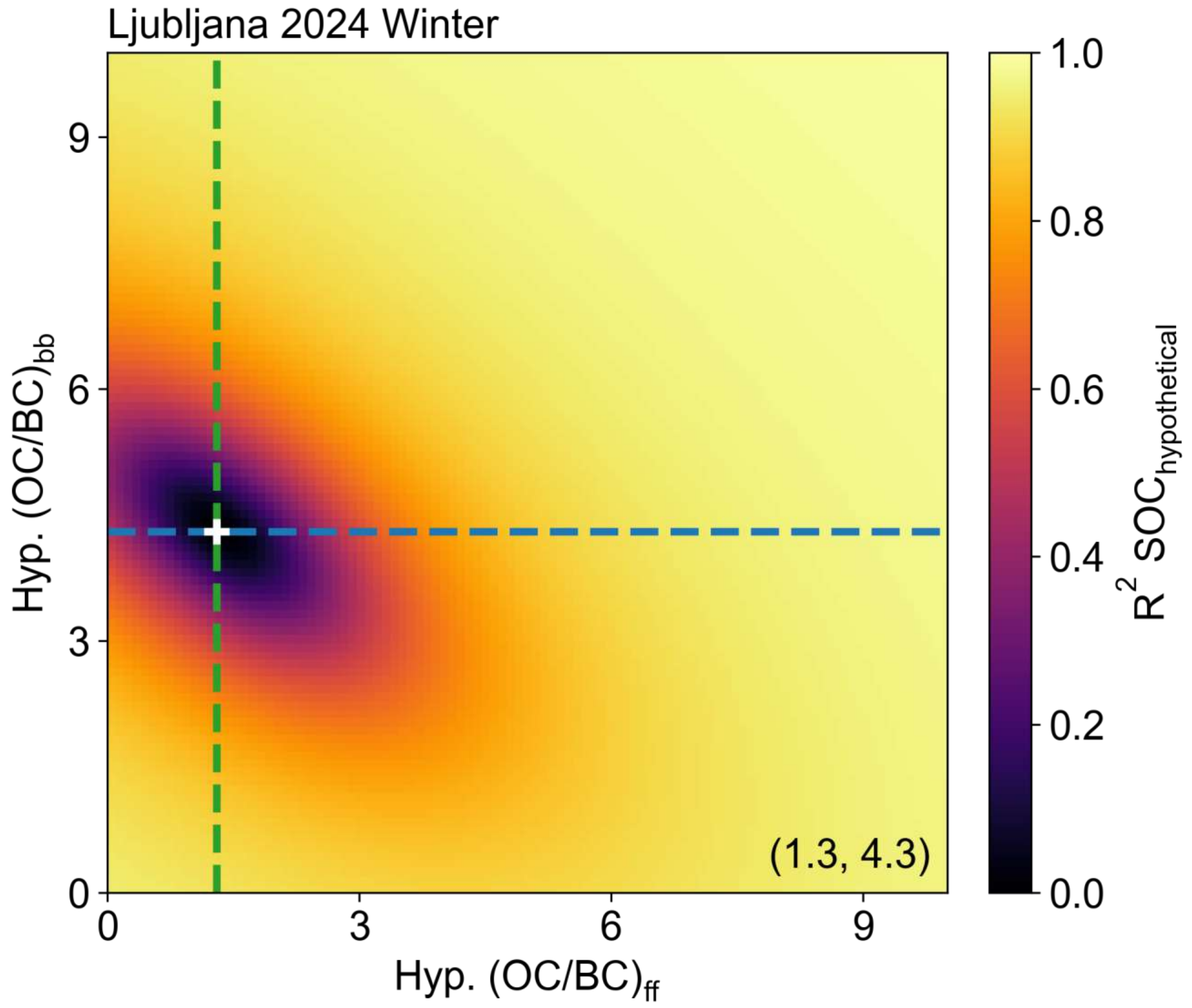
$$\mathrm{POC_{bb}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,bb}} \cdot \mathrm{BC_{bb}(t)},$$

$$\mathrm{SOC(t)} = \mathrm{OC(t)} - \mathrm{POC_{ff}(t)} - \mathrm{POC_{bb}(t)},$$



2D BC tracer model

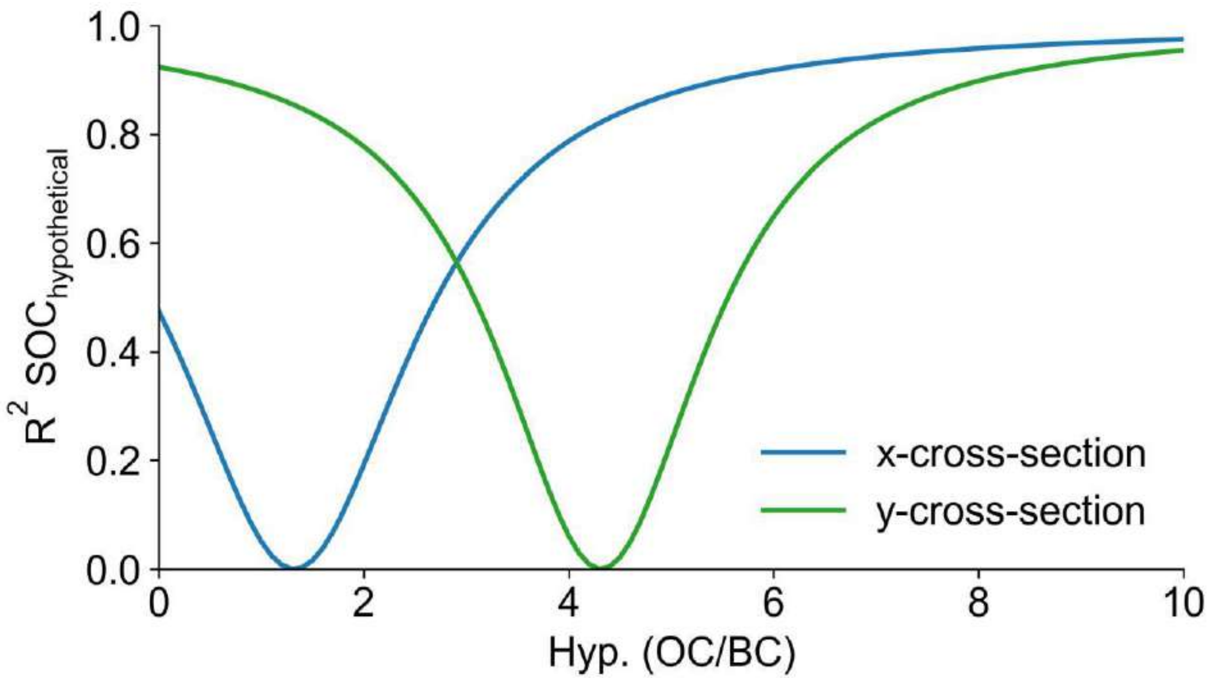
~ / À v] *manuscript in preparation*)

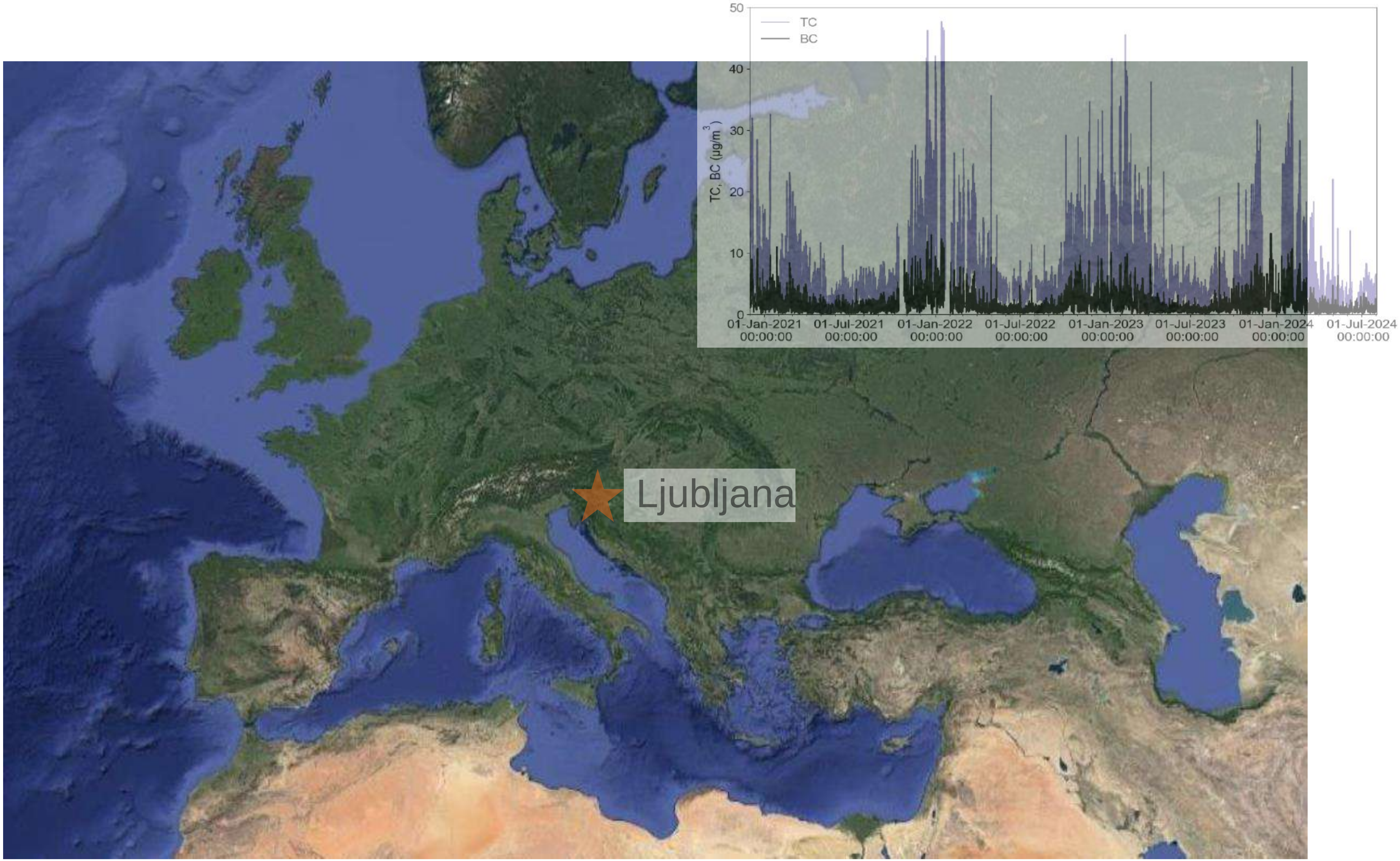


$$\mathrm{POC_{ff}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,ff}} \cdot \mathrm{BC_{ff}(t)},$$

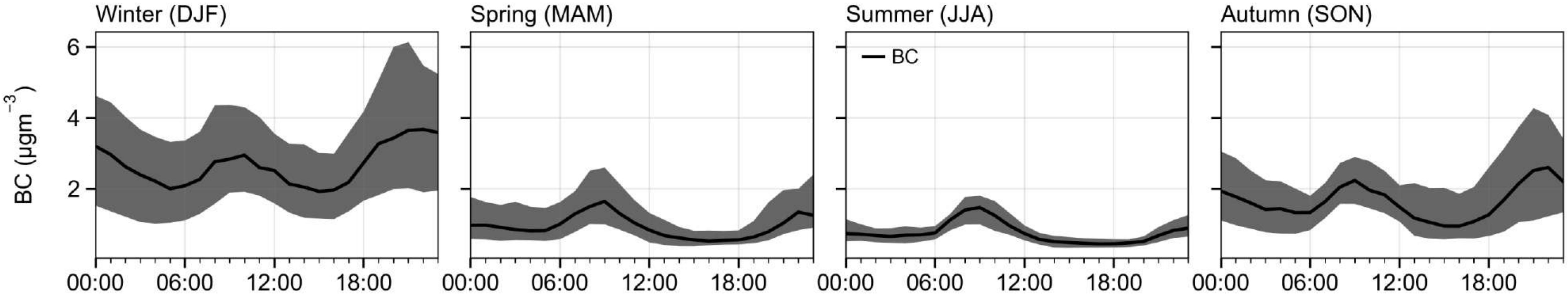
$$\mathrm{POC_{bb}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,bb}} \cdot \mathrm{BC_{bb}(t)},$$

$$\mathrm{SOC(t)} = \mathrm{OC(t)} - \mathrm{POC_{ff}(t)} - \mathrm{POC_{bb}(t)},$$




TC
BC
TC, BC (µg/m3)
50
40
30
20
10
0
01-Jan-2021 00:00:00
01-Jul-2021 00:00:00
01-Jan-2022 00:00:00
01-Jul-2022 00:00:00
01-Jan-2023 00:00:00
01-Jul-2023 00:00:00
01-Jan-2024 00:00:00
01-Jul-2024 00:00:00
Ljubljana

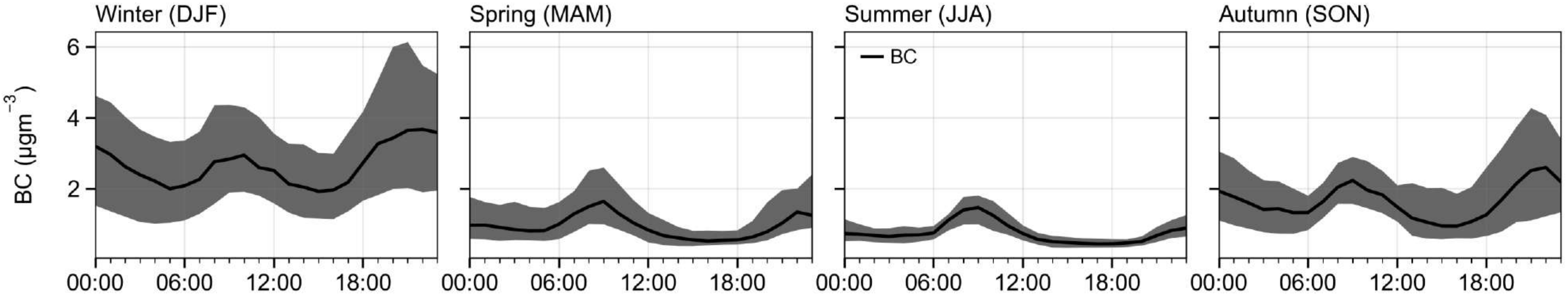
Black carbon typical diurnal profiles



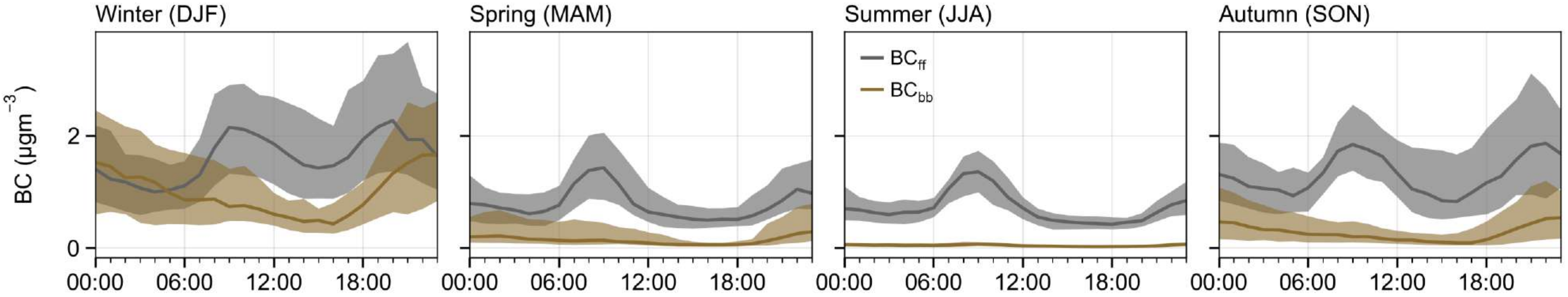
Higher concentrations in winter
- Lower temperatures
  -> Higher demand for heating
- Lower planetary boundary (PBL)
- Shorter day

Lower concentrations in summer
- Higher temperatures
  -> No need for heating
- Higher planetary boundary (PBL)
  -> Higher volume available for mixing
- Longer day

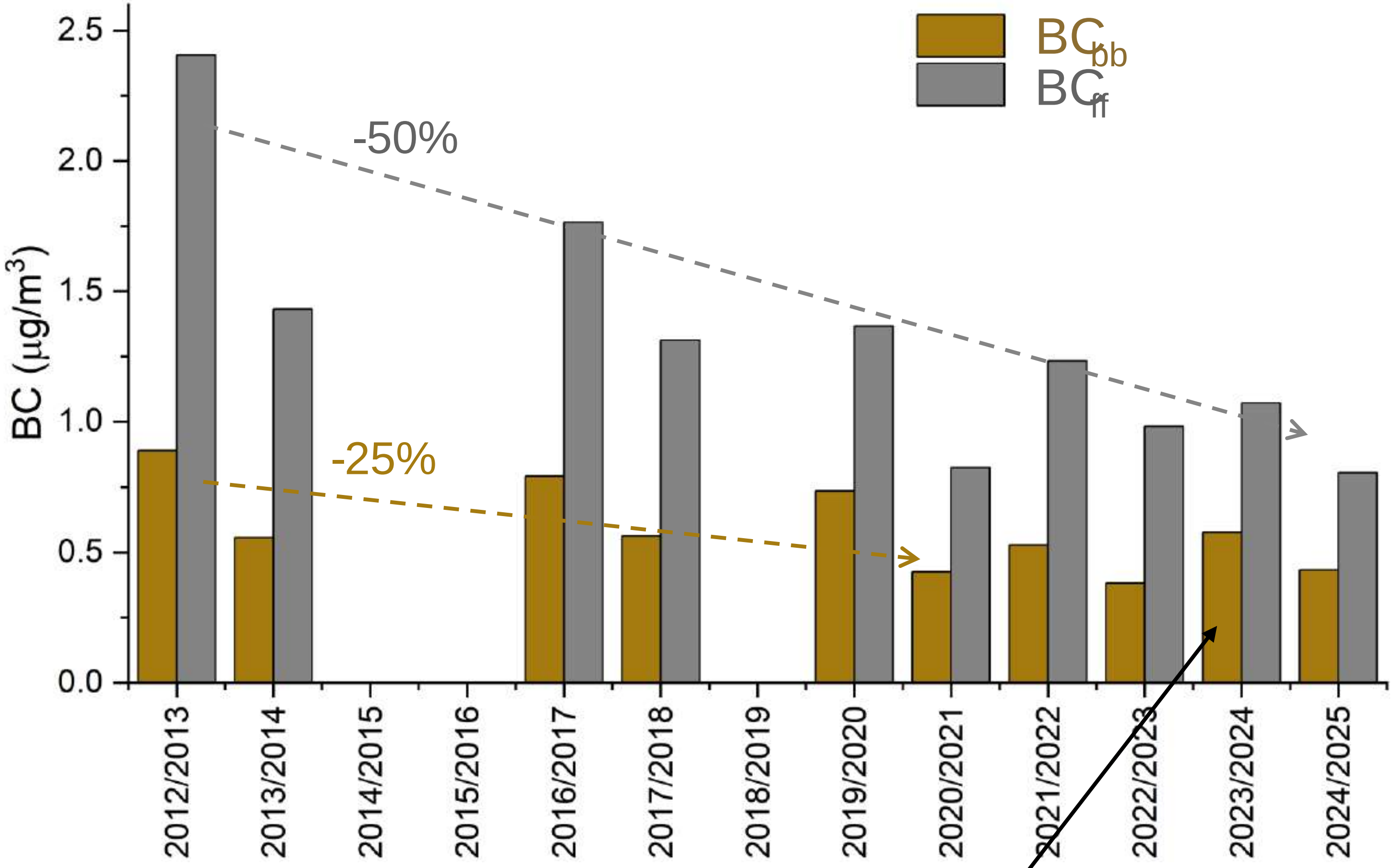
Black carbon diurnal profiles & source apportionment



Aethalometer model: traffic-related BC_{ff} and biomass burning-related BC_{bb}



BC concentrations decrease in Ljubljana 2012–2025



Year-to-year variations:

Weather conditions changes,
no significant emission improvements

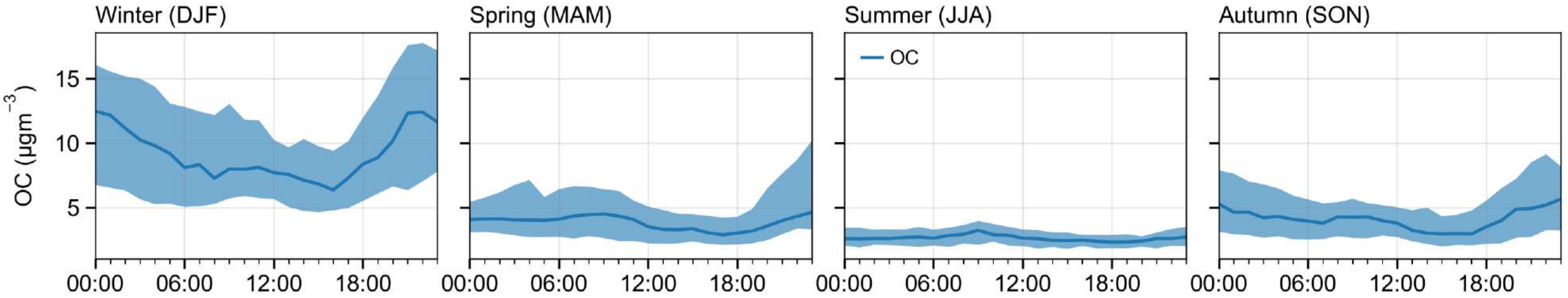
- Newer cars – new emission standards
  - -> lower emissions
    - ->> lower BC_{ff}

  Preprint egusphere, 2025)

- Milder winters
  - -> lower need for heating
    - ->> lower BC_{bb}

- BC_{bb} has no trend between 2020 to 2025

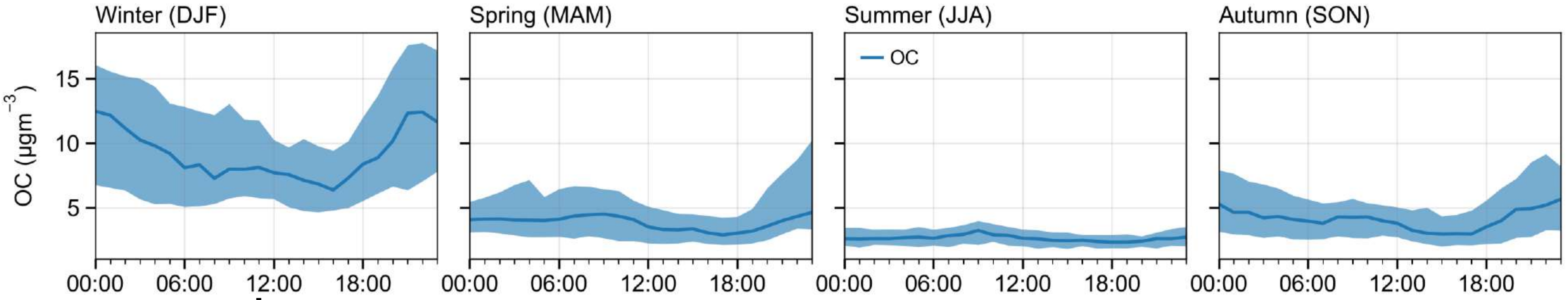
Organic carbon typical diurnal profiles



Similar pattern to BC: highest concentrations in winter and lowest in summer

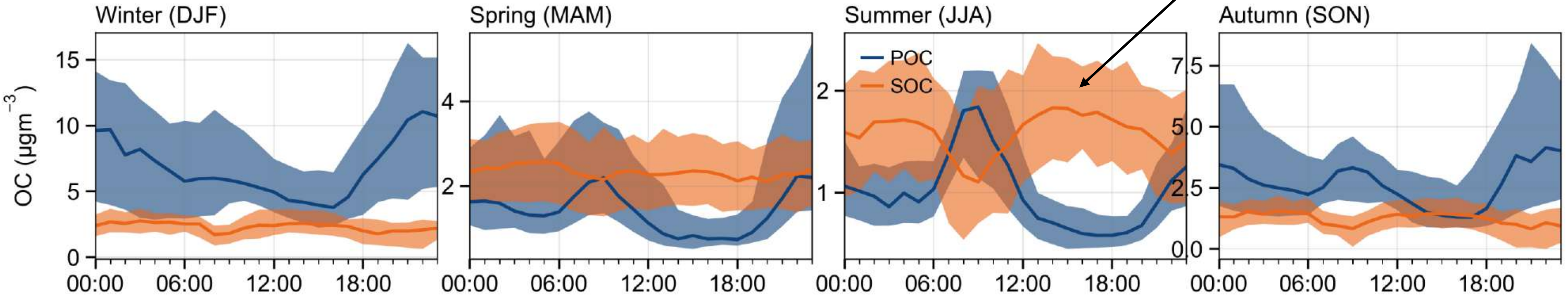
- Lower planetary boundary (PBL) & shorter day in winter
- Higher planetary boundary (PBL) & longer day in summer better mixing of pollution

Organic carbon typical diurnal profiles & apportionment

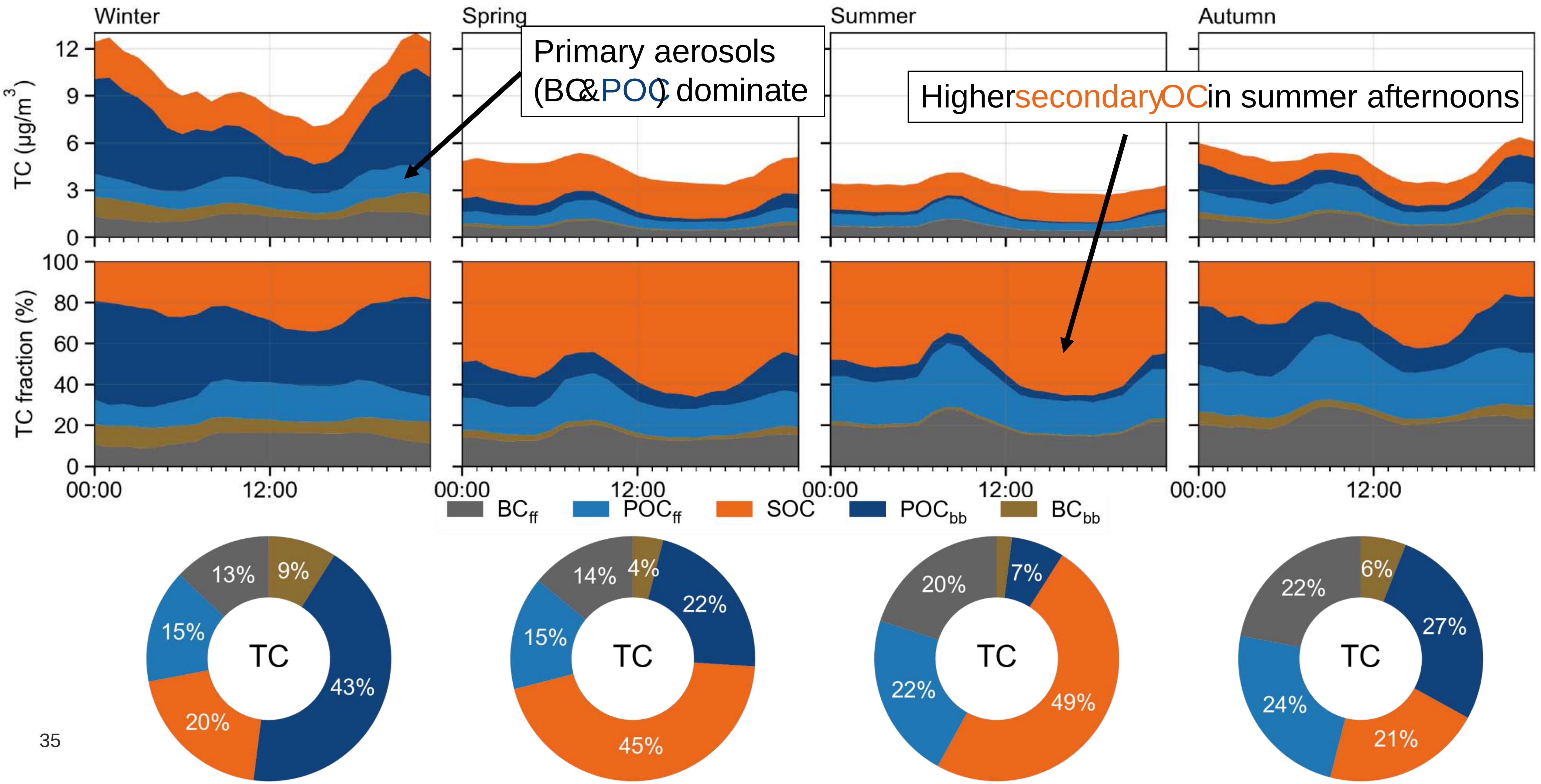


2D BC tracer model: split between primary and secondary OC

Sumer afternoon SOC peak



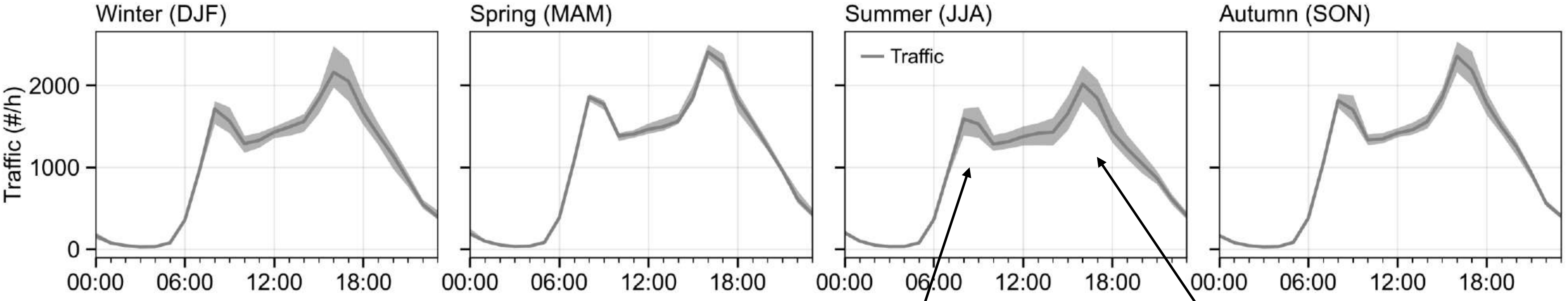
TC apportionment: Aethalometer + BC tracer models



Primary aerosols (BC & POC) dominate

Higher secondary OC in summer afternoons

Intercomparison of traffic density and BC_{ff} diurnals



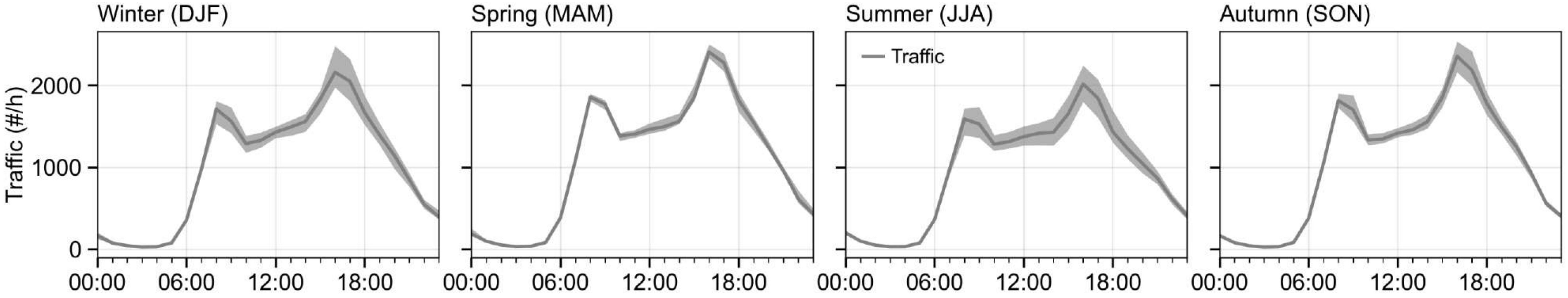
Traffic counters
- The same pattern in all 4 seasons
- Slightly lower traffic in summer due to holidays

Morning rush hour:
from home to work

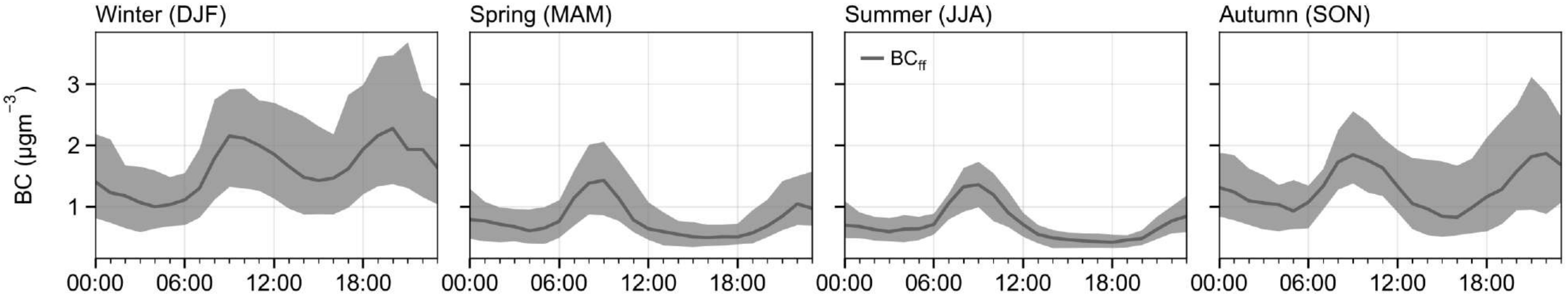
Afternoon rush hour:
from work to home
+ afternoon activities

-> higher traffic

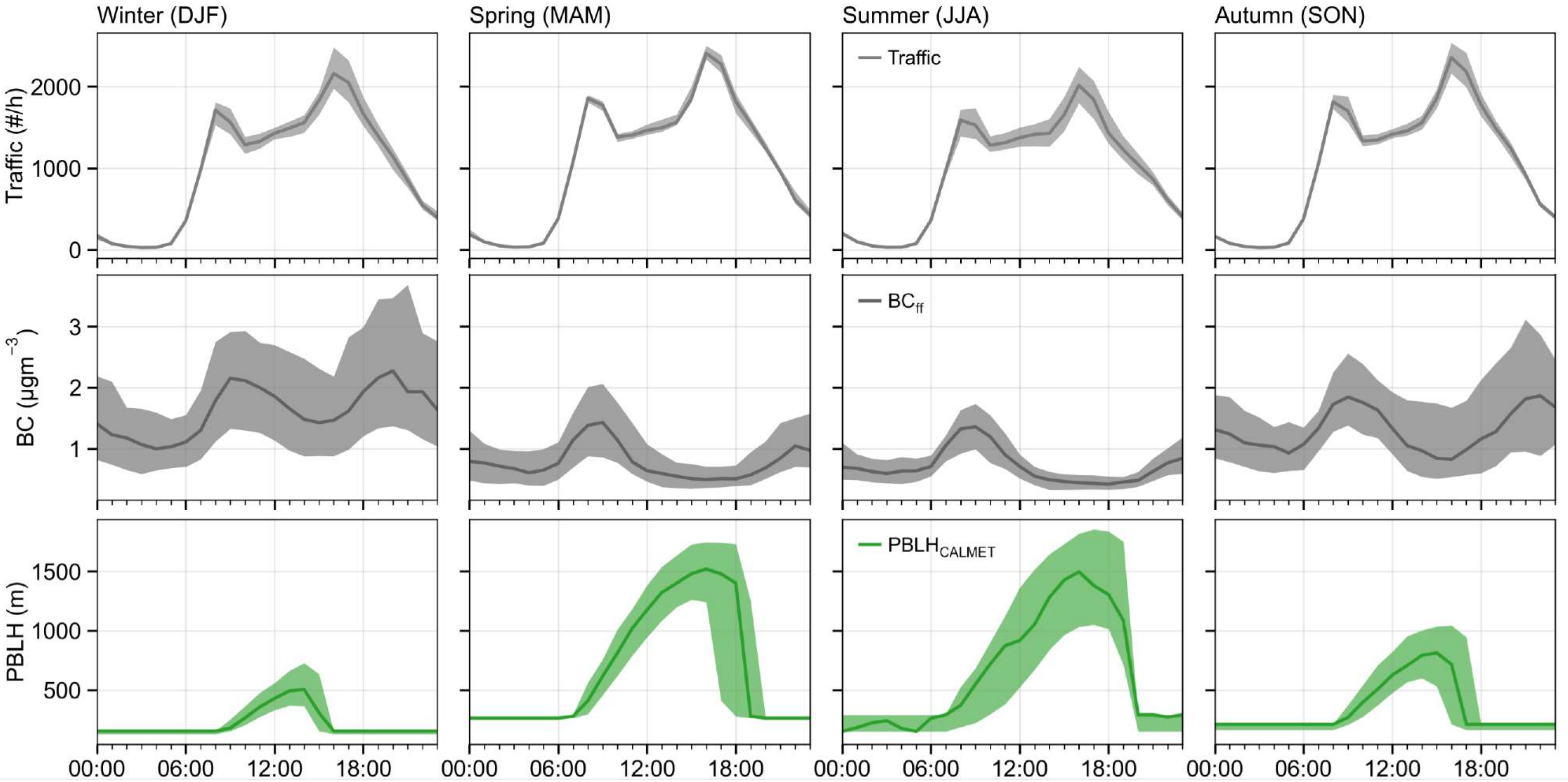
Intercomparison of traffic density and BC_{ff} diurnals



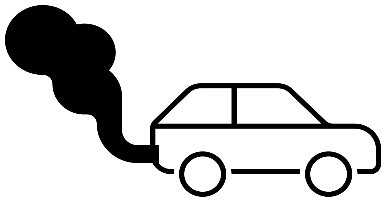
BC_{ff} does not follow the traffic pattern



Traffic & BC_{ff} diurnals and planetary boundary layer - PBL

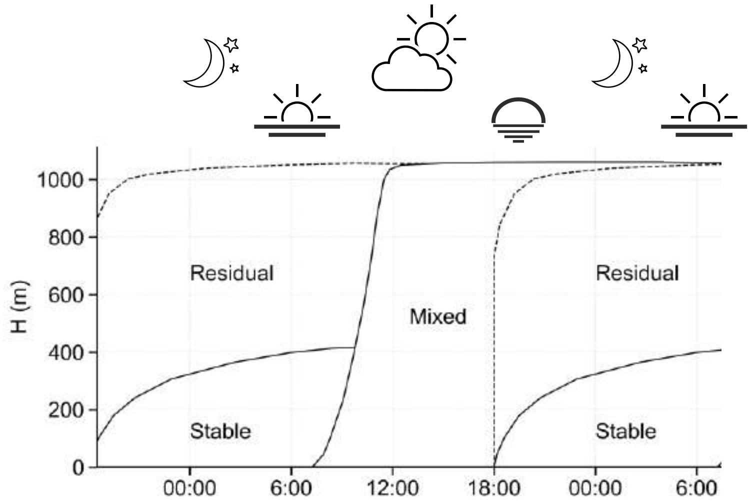


Emission & production rates + meteorology



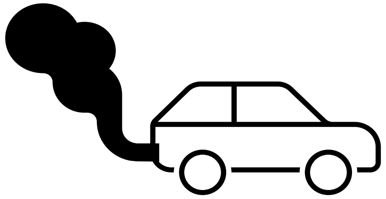
Emissions from traffic

+



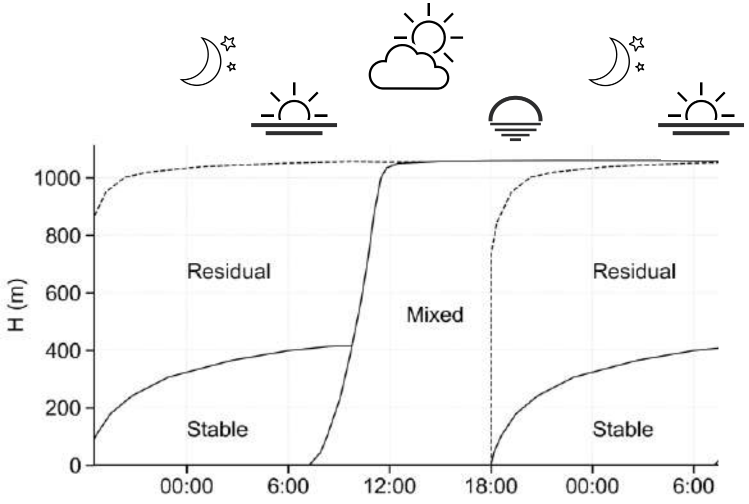
PBL t planetary boundary layer

Emission & production rates + meteorology



Emissions from traffic

+



PBL t planetary boundary layer

Concentration (C) in column of air (h)

Emission or production rates

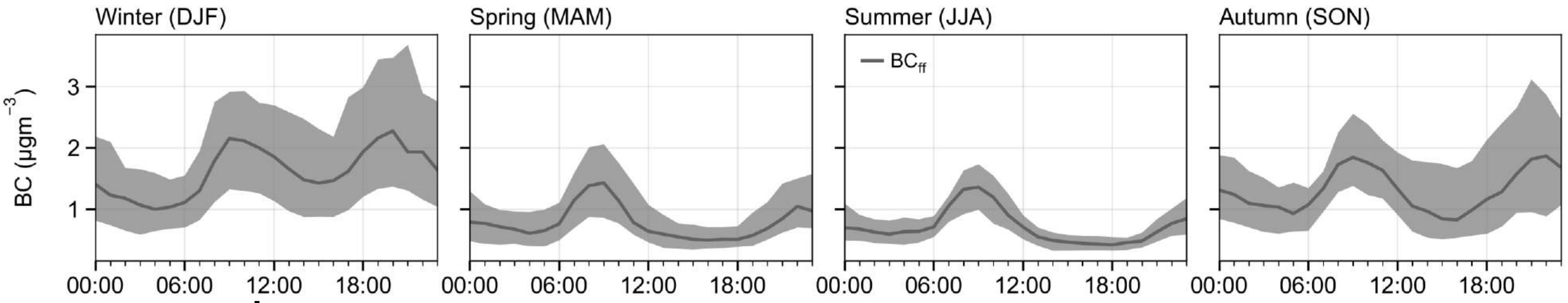
Decayed remaining

Exchanged by entrainment or shrinking of PBL

$$Ch = \boxed{\boldsymbol{E\Delta T}} + C_0 h_0 e^{-\lambda'(t-t_0)} + \left\{ \begin{array}{ll} C_0(h-h_0)e^{-\lambda'(t-t_0)} & \text{for } \frac{dh}{dt} \leq 0 \\ C_{residual}(h-h_0)e^{-\lambda'(t-t_0)} & \text{for } \frac{dh}{dt} > 0 \end{array} \right\}$$

~'Œ P}Œ] *Atmos. Chem. Phys.*, 2020)

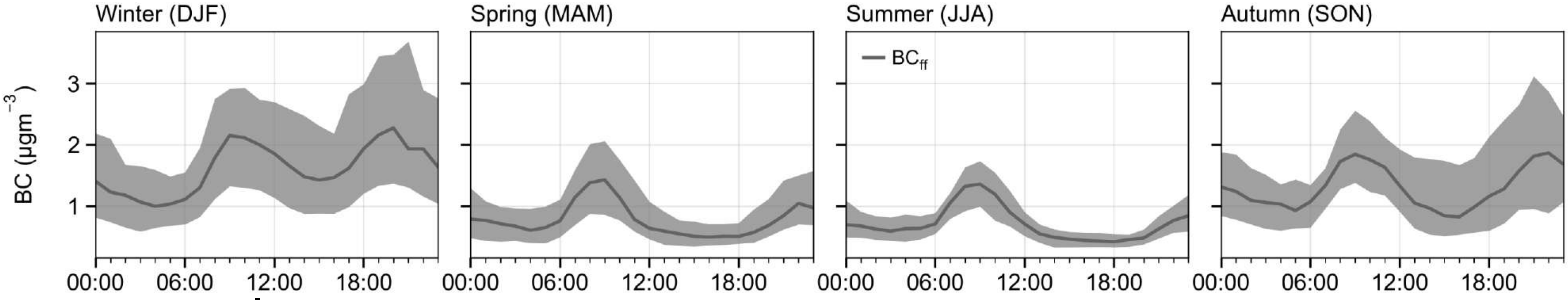
Concentrations: Emission rate + meteorological conditions



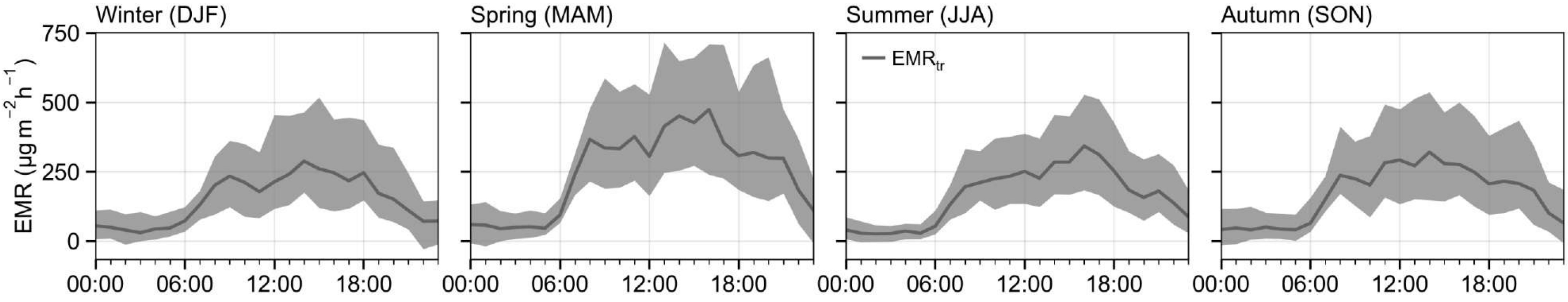
BC_{ff} concentrations -> Emission rates EMR from traffic - better characterization of sources

~'Œ P}Œ] *Atmos. Chem. Phys.*, 2020)

Concentrations: Emission rate + meteorological conditions

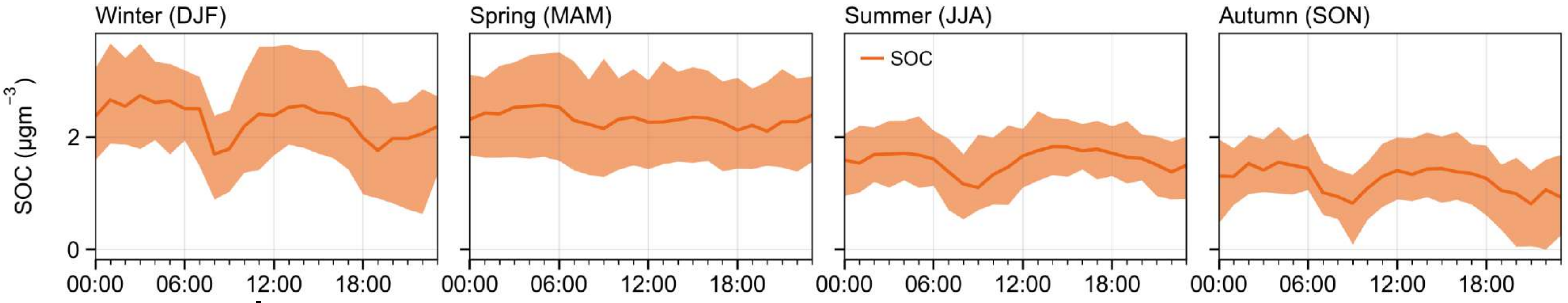


BC$_{ff}$ concentrations -> Emission rates EMR from traffic - better characterization of sources



~'Œ P}Œ] *Atmos. Chem. Phys.*, 2020)

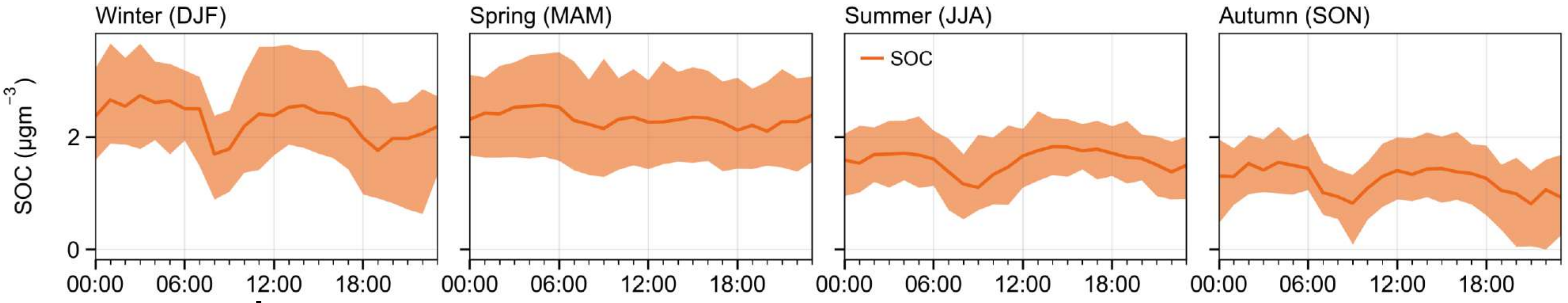
Concentrations: Production rate + meteorological conditions



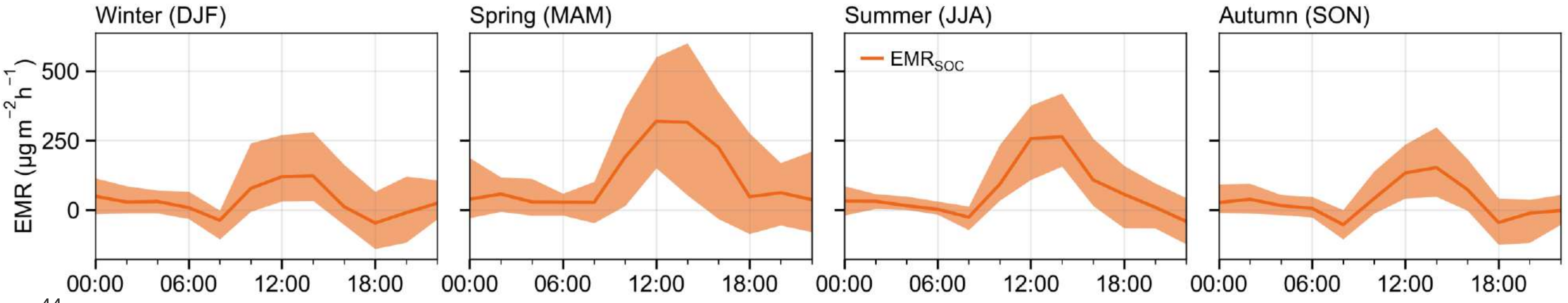
SOC concentrations -> Production rate

~'Œ P}Œ] *Atmos. Chem. Phys.*, 2020)

Concentrations: Production rate + meteorological conditions



SOC concentrations -> Production rate - high volume available in afternoon, huge production



Conclusions

Carbonaceous aerosols

- Public health
- Climate change

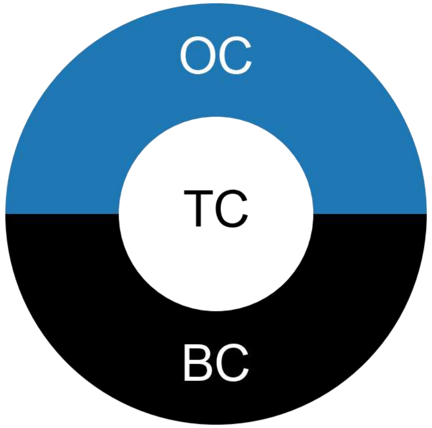
CASS: TC-BC (,,)

- TCA + Aethalometer
- On-line OC/EC, high time resolution
- Primary and secondary CA
- Typical seasonal & diurnal profiles

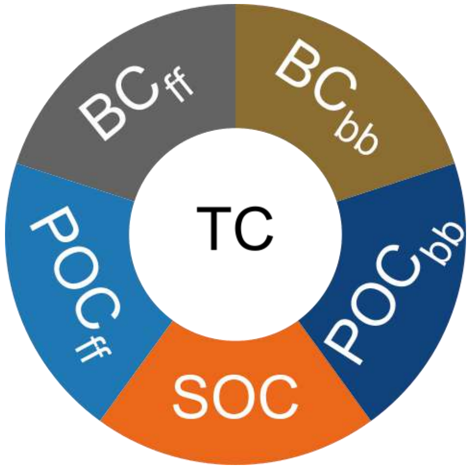
BC emission rates / SOA production rates

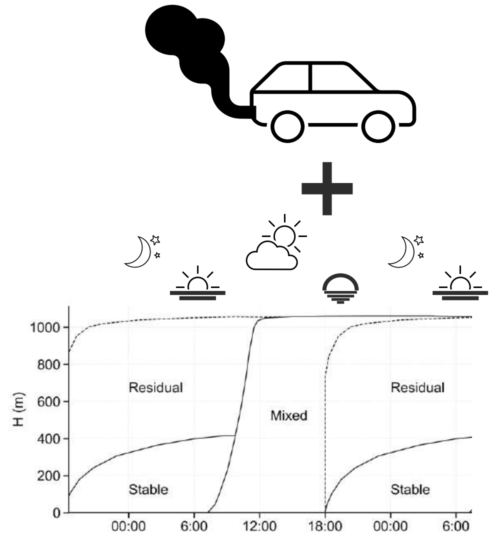
- Isolate anthropogenic activity, weather influence excluded
  -> Better trends
- Production rate for bulk SOA

CASS



TCA08
+
Aethalometer



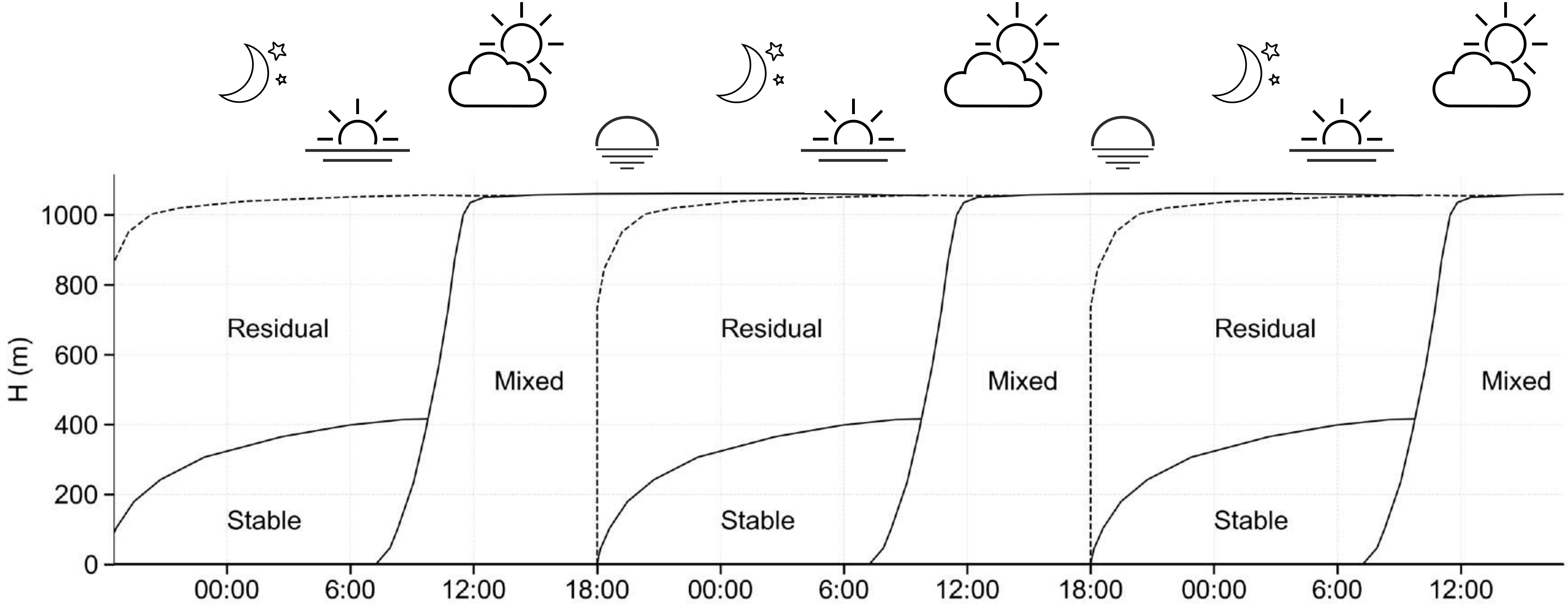


Thank you for your attention!

mivancic@aerosolmageesci.com

This study was supported by Slovenian Research and Innovation Agency, research project L1-4386.

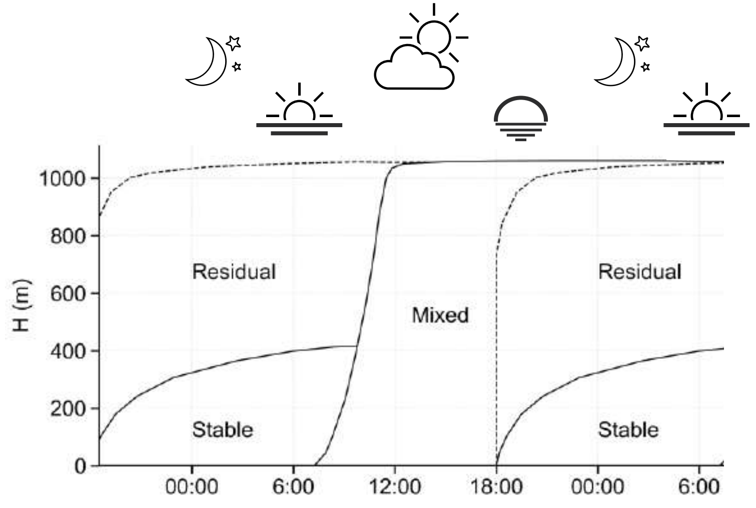
Planetary Boundary Layer



Planetary Boundary Layer

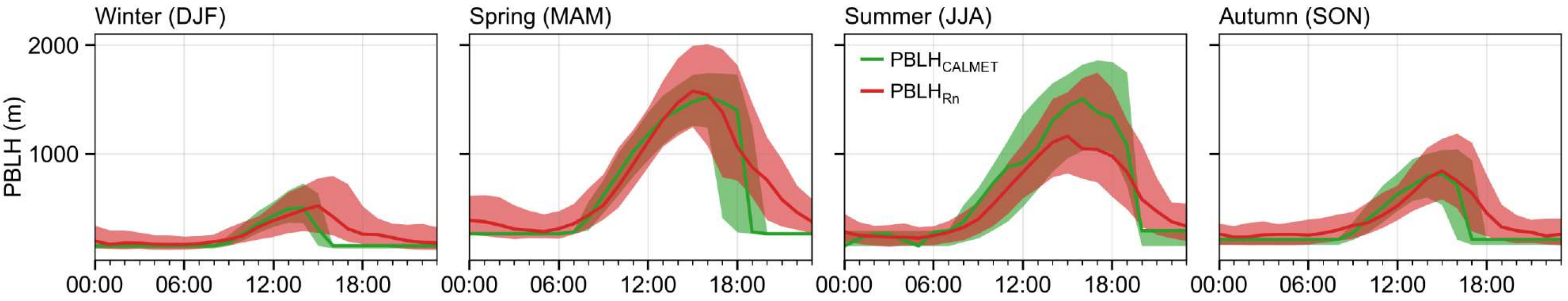
Meteorological model (ALADIN + CALMET):

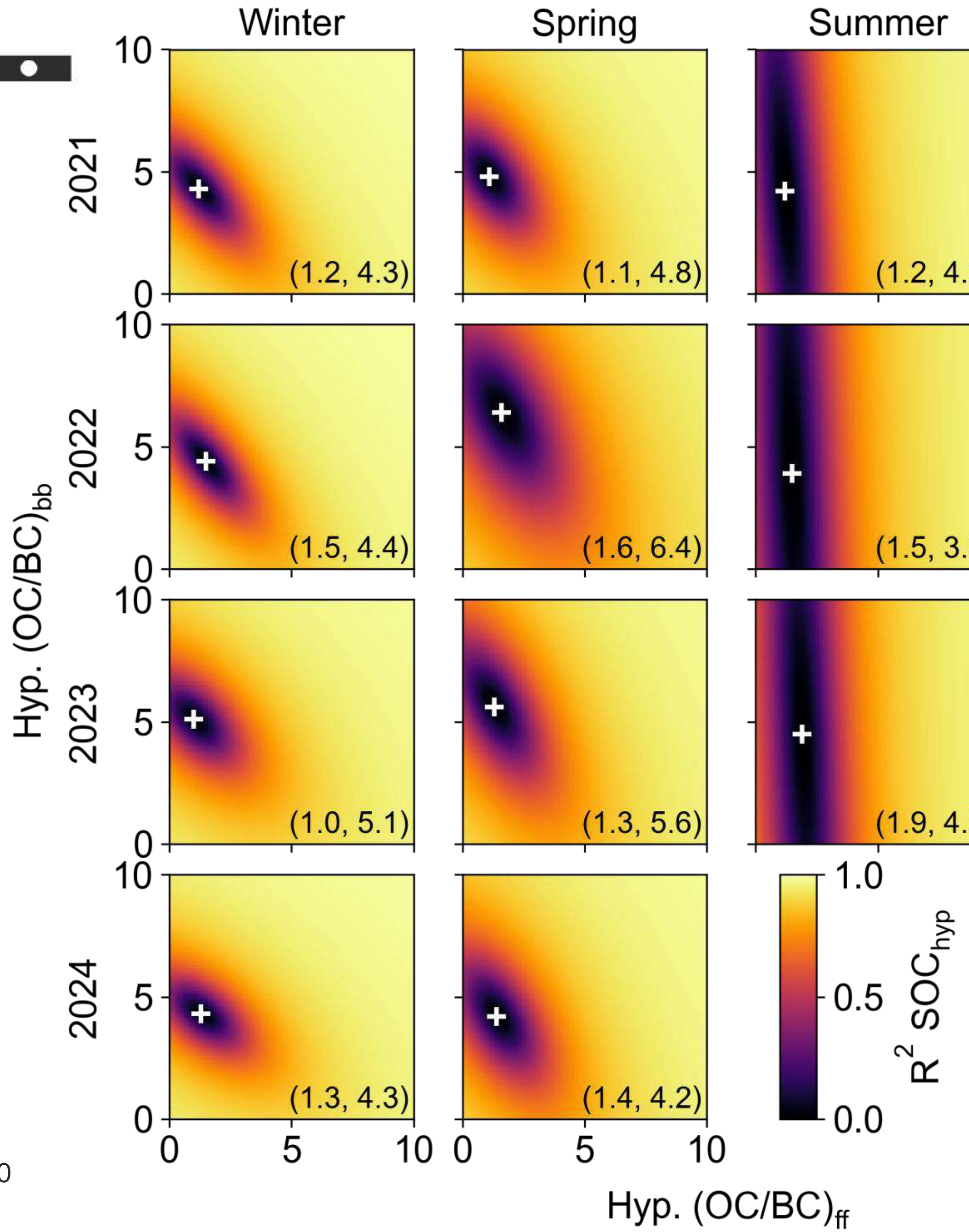
- Empirical equations



Radon (Rn) as tracer:

- Known decay time
- Stable exhalation from soil and rocks on a monthly scale
- Main daily variation Rn concentration due to the change of PBL





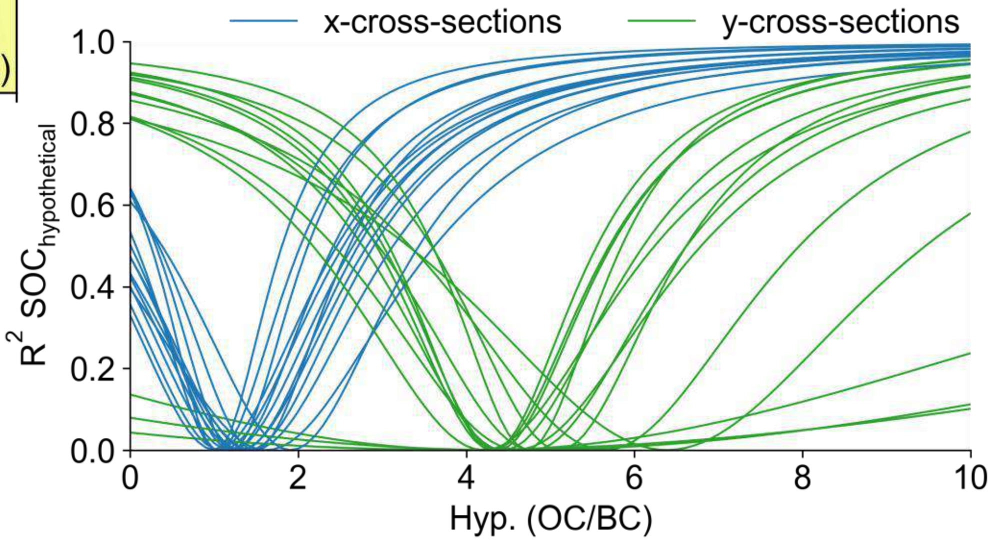
2D BC tracer model

~ / À v] manuscript in preparation)

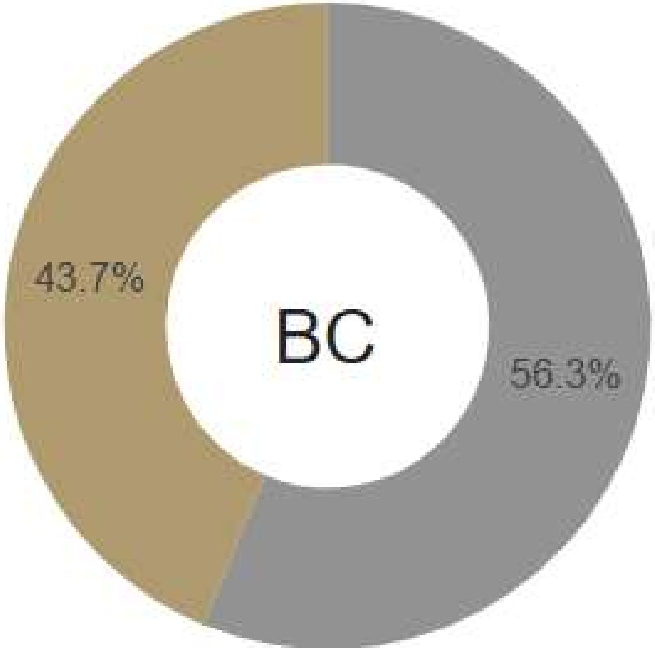
$$\mathrm{POC_{ff}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,ff}} \cdot \mathrm{BC_{ff}(t)},$$

$$\mathrm{POC_{bb}(t)} = \left(\frac{\mathrm{OC}}{\mathrm{BC}}\right)_{\mathrm{prim,bb}} \cdot \mathrm{BC_{bb}(t)},$$

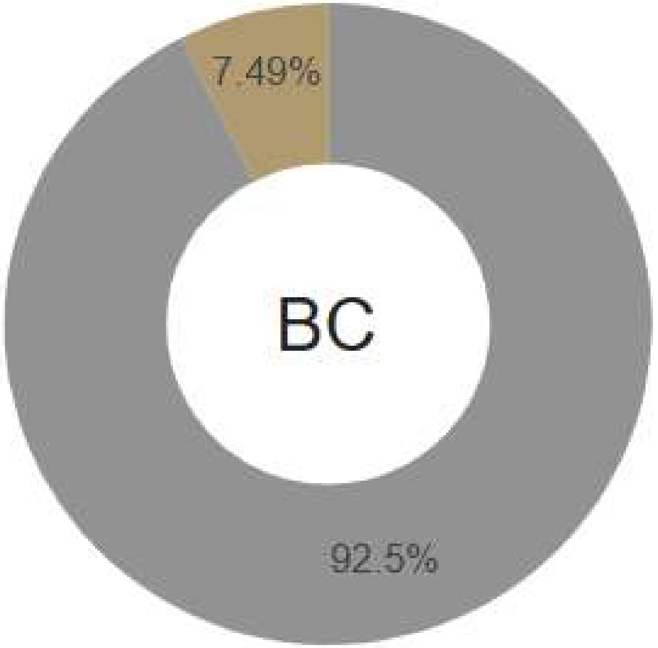
$$\mathrm{SOC(t)} = \mathrm{OC(t)} - \mathrm{POC_{ff}(t)} - \mathrm{POC_{bb}(t)},$$



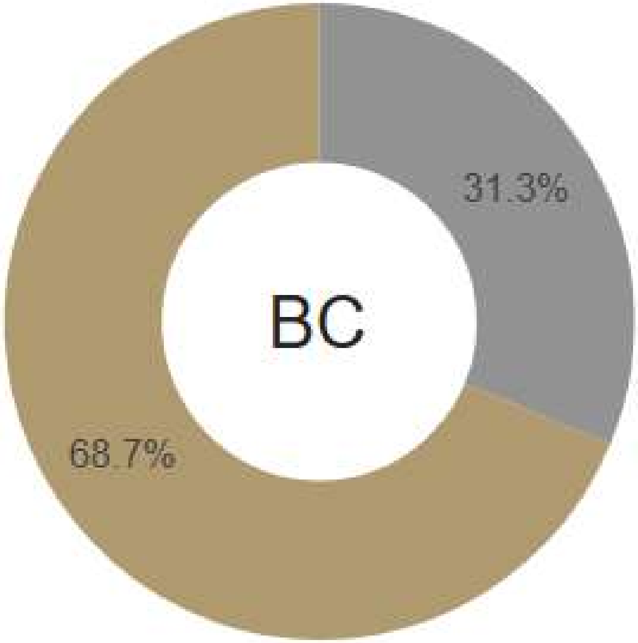
Ljubljana
(Urban background)



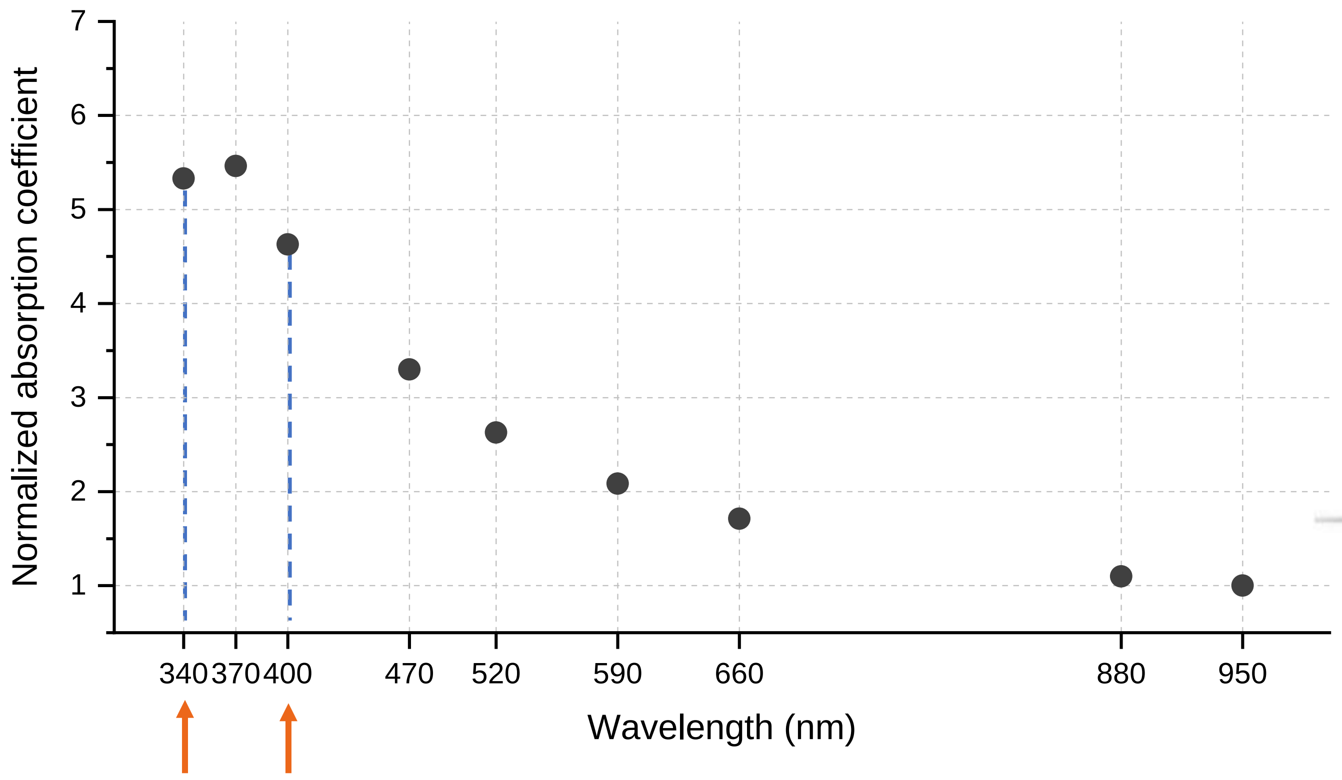
Barcelona
(Urban background)



Velenje(Rural)



Analyses of absorption spectral features: AE36s

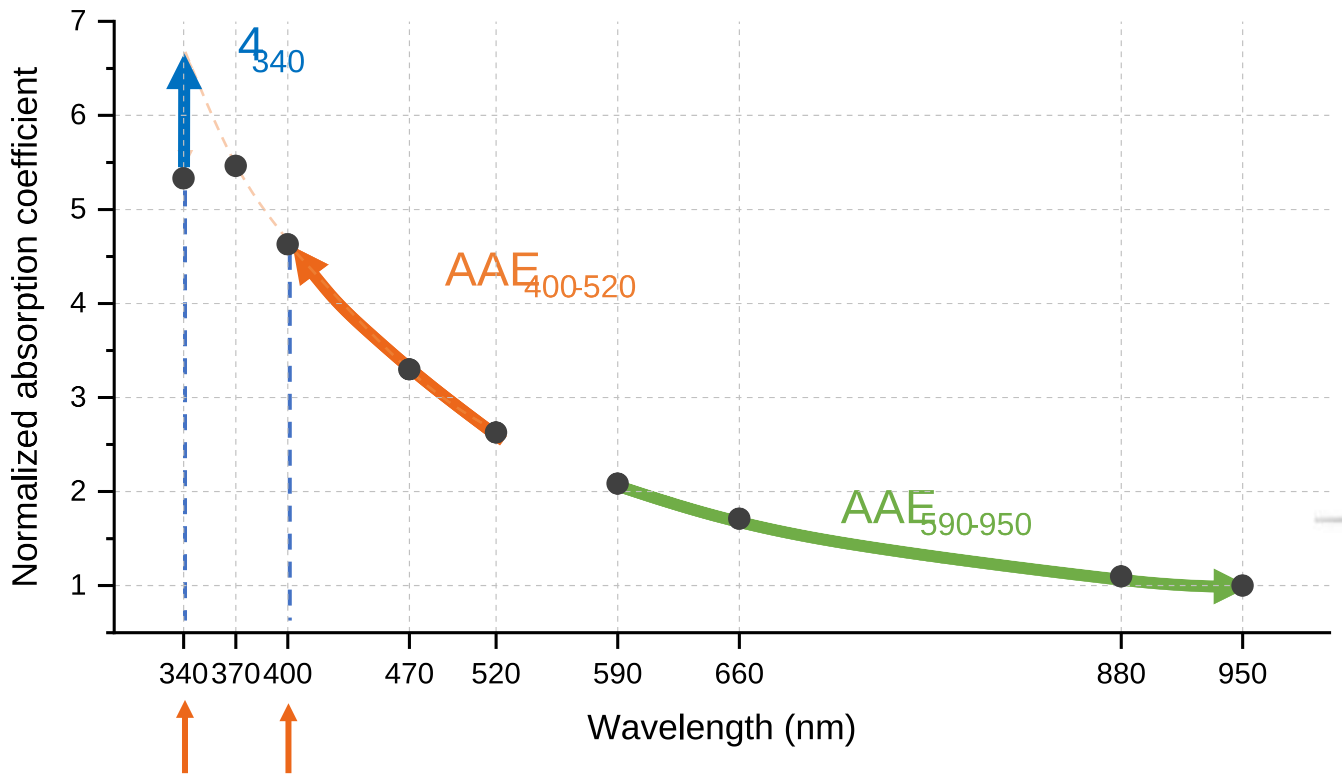


AE36s

~'Œ P}Œ](*manuscript in preparation*)

Reconstructed from: Yuan et al., ACP, 2020

Analyses of absorption spectral features: AE36s



AE36s

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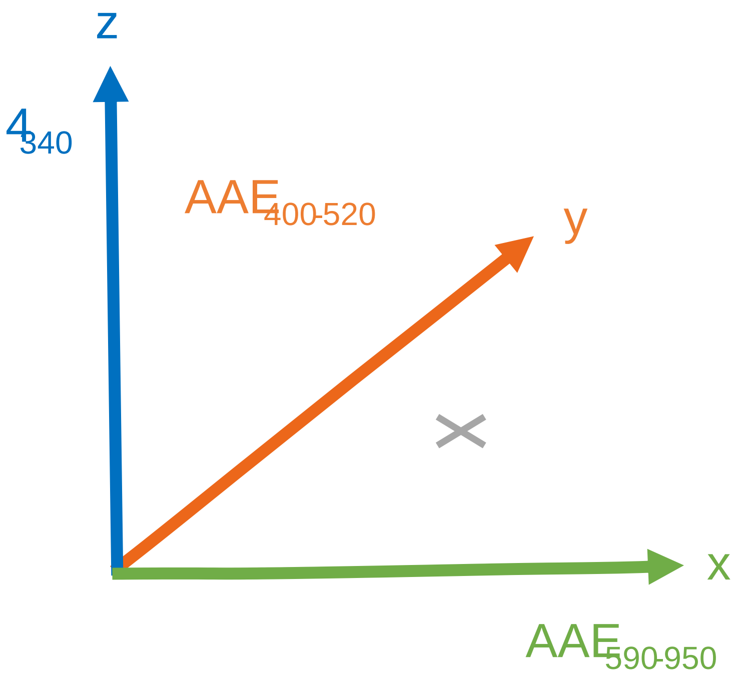
Analyses of absorption spectral features: AE36s



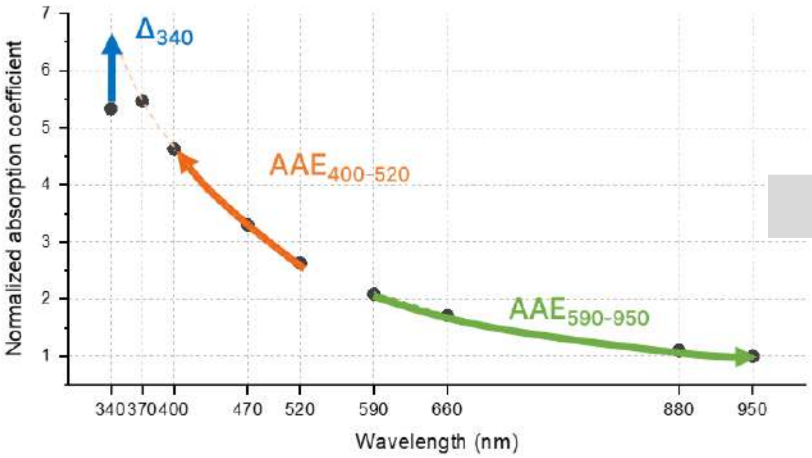
AE36s

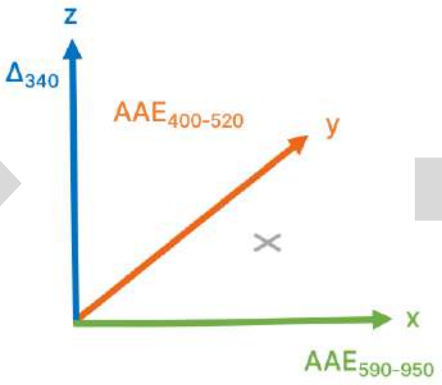
~'Œ P}Œ] *manuscript in preparation)*

Reconstructed from: Yuan et al., ACP, 2020

Results – measurement campaign in Athens

Advanced 9-wavelength apportionment

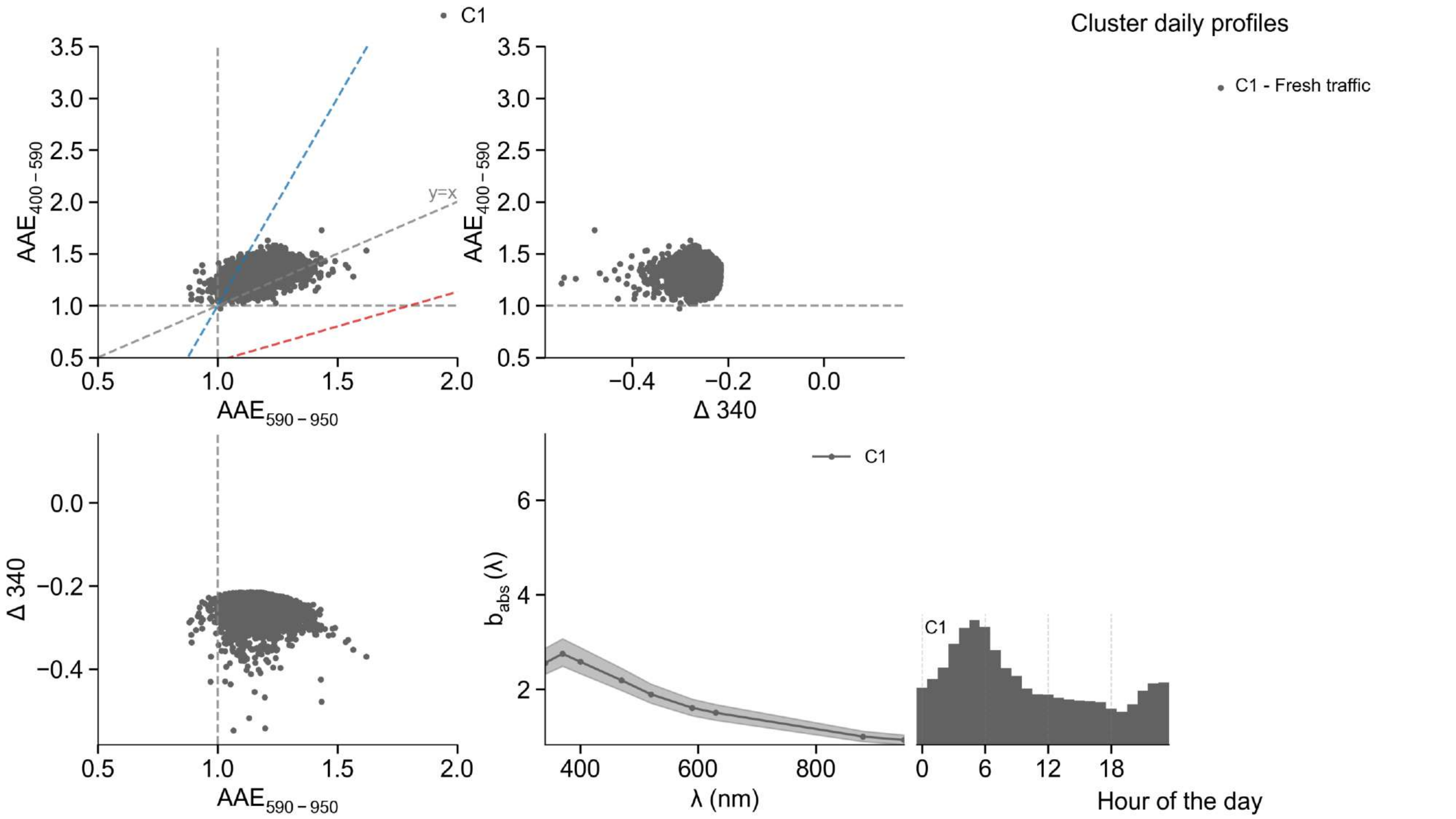




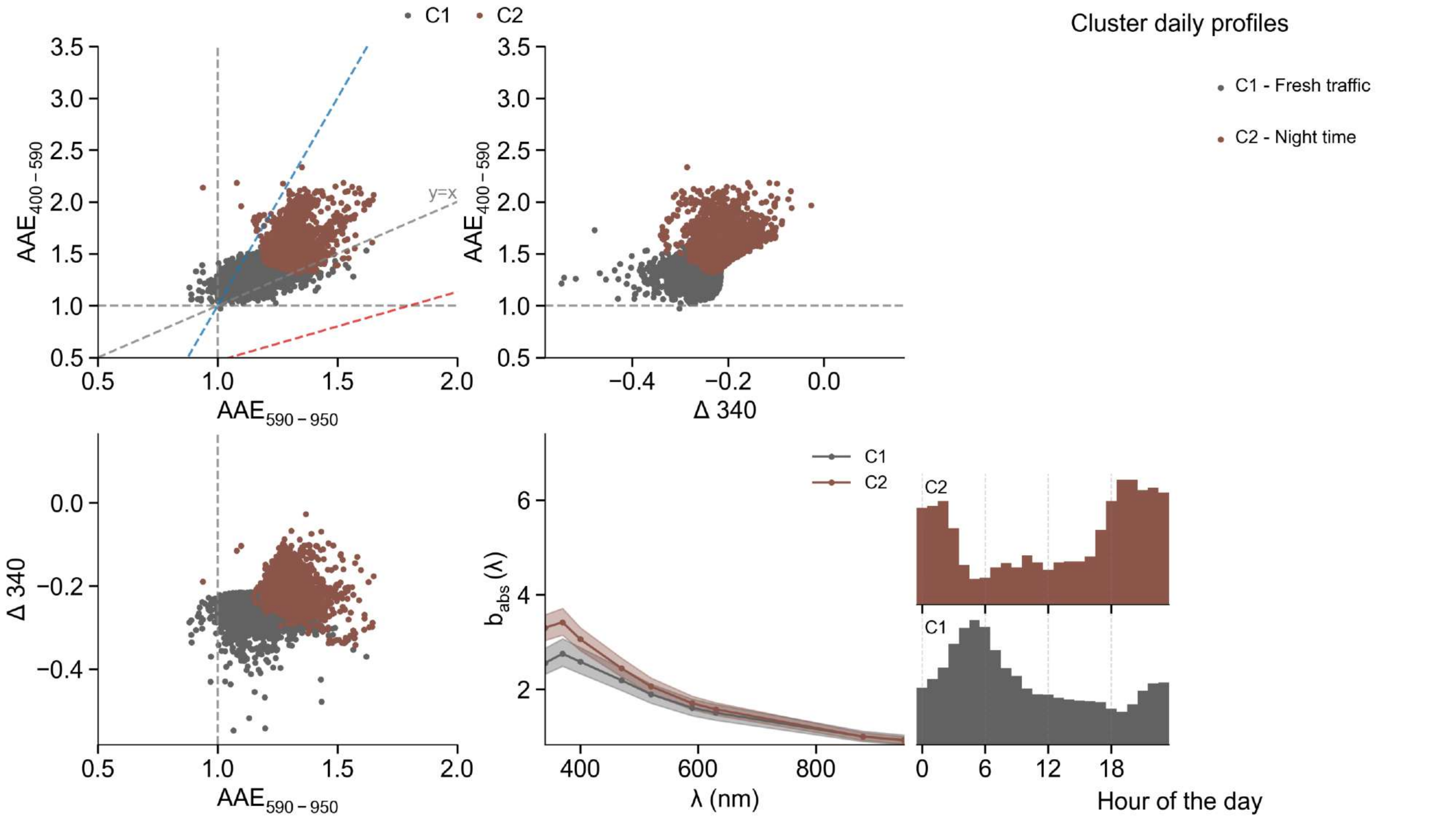
SPECTRAL CLUSTERING

low-dimension embedding of the affinity matrix between samples

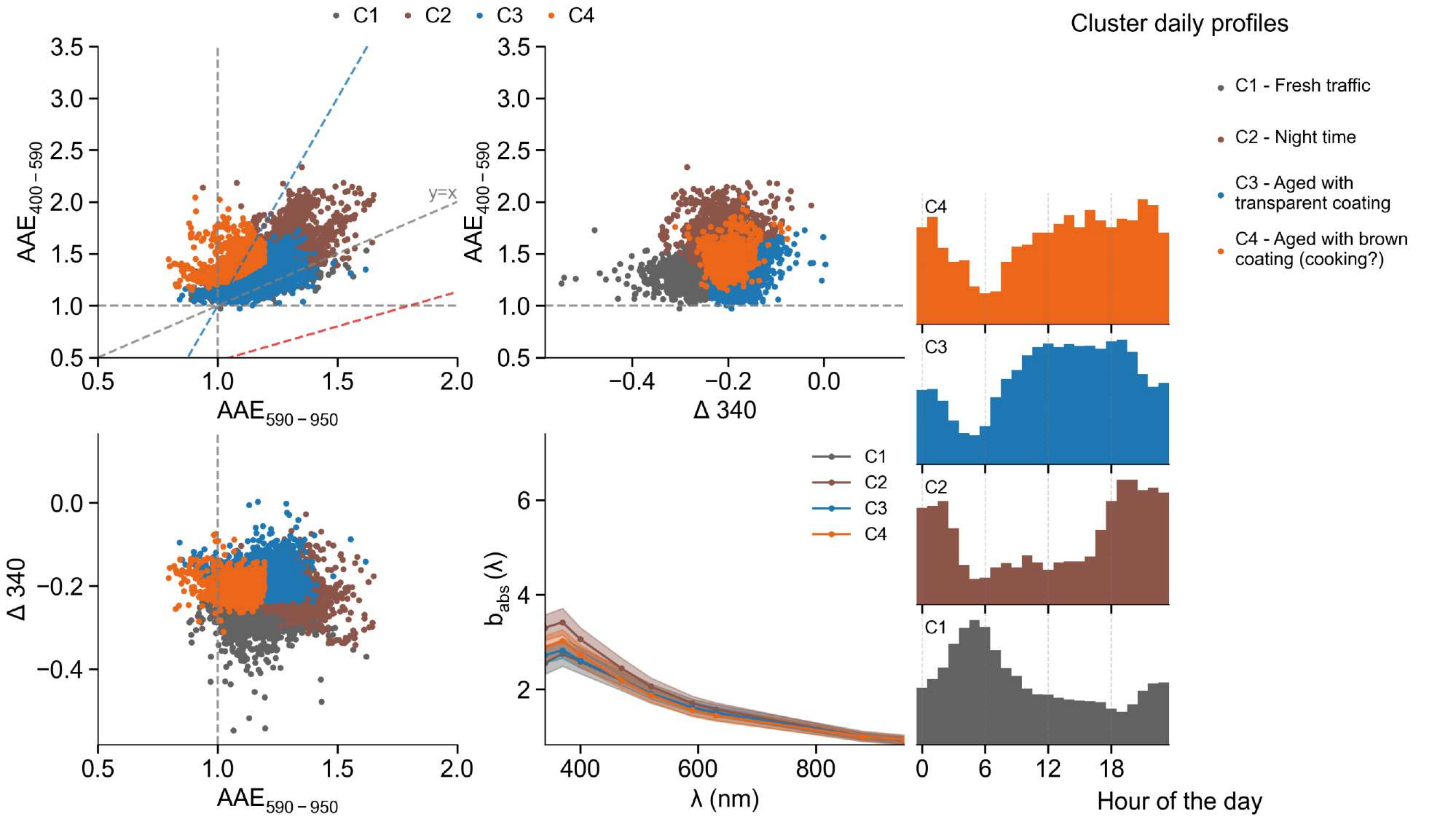
~ ' Œ P } Œ] *manuscript in preparation*)



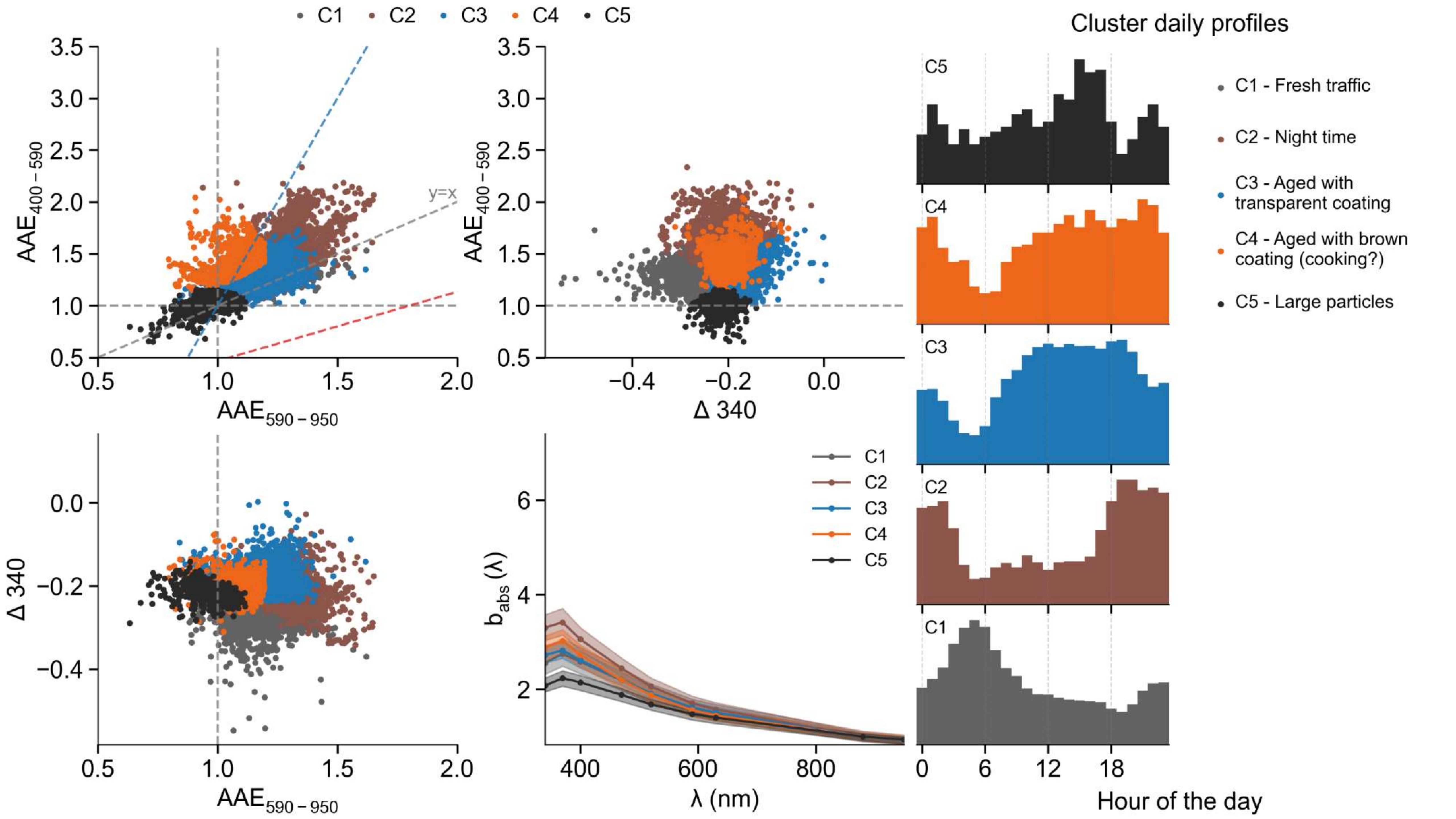
C1
Cluster daily profiles
C1 - Fresh traffic
y=x
$AAE_{400-590}$
$AAE_{590-950}$
Δ 340
C1
b_{abs} (λ)
λ (nm)
C1
Hour of the day



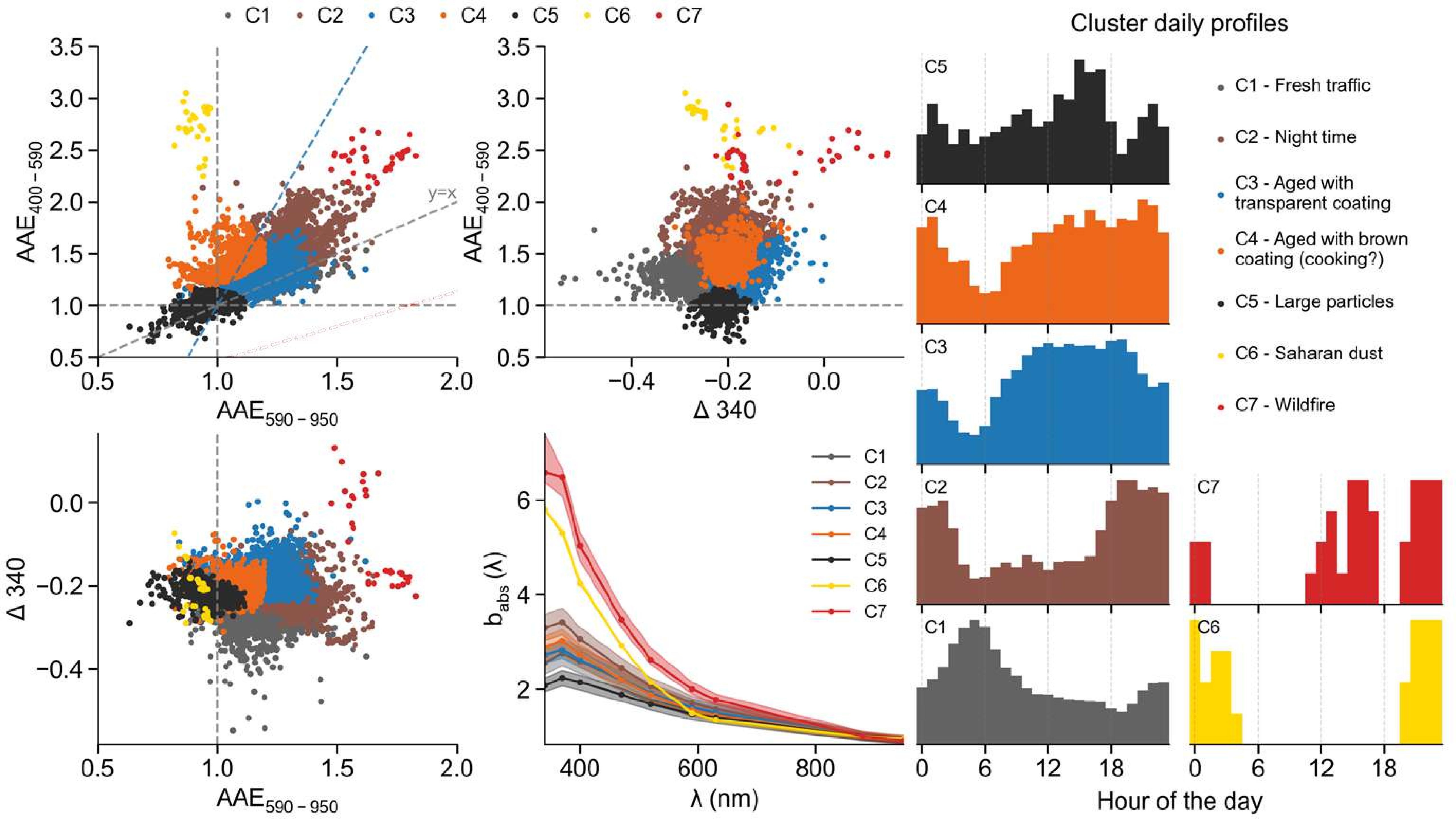
C1
C2
Cluster daily profiles
C1 - Fresh traffic
C2 - Night time
y=x
AAE400 − 590
AAE590 − 950
Δ 340
babs (λ)
λ (nm)
Hour of the day



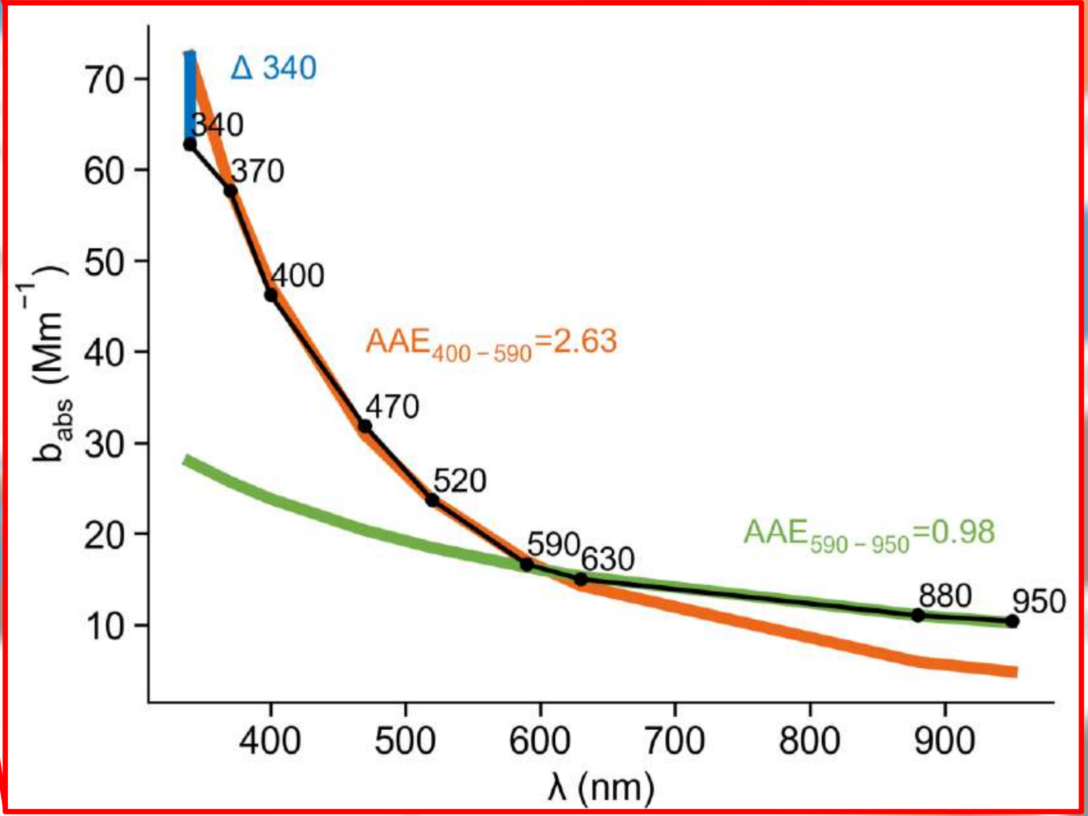
C1
C2
C3
C4
Cluster daily profiles
C1 - Fresh traffic
C2 - Night time
C3 - Aged with transparent coating
C4 - Aged with brown coating (cooking?)
y=x
$AAE_{400-590}$
$AAE_{590-950}$
Δ 340
b_{abs} (λ)
λ (nm)
Hour of the day



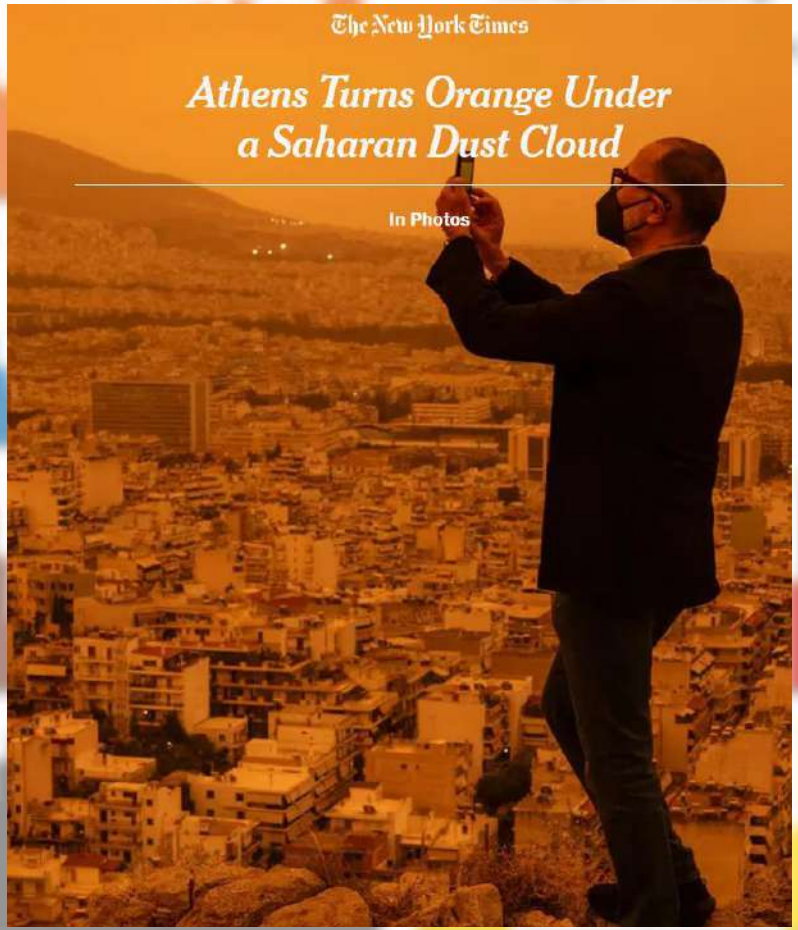
C1
C2
C3
C4
C5
Cluster daily profiles
y=x
$AAE_{400-590}$
$AAE_{590-950}$
Δ 340
b_{abs} (λ)
λ (nm)
Hour of the day
C1 - Fresh traffic
C2 - Night time
C3 - Aged with transparent coating
C4 - Aged with brown coating (cooking?)
C5 - Large particles



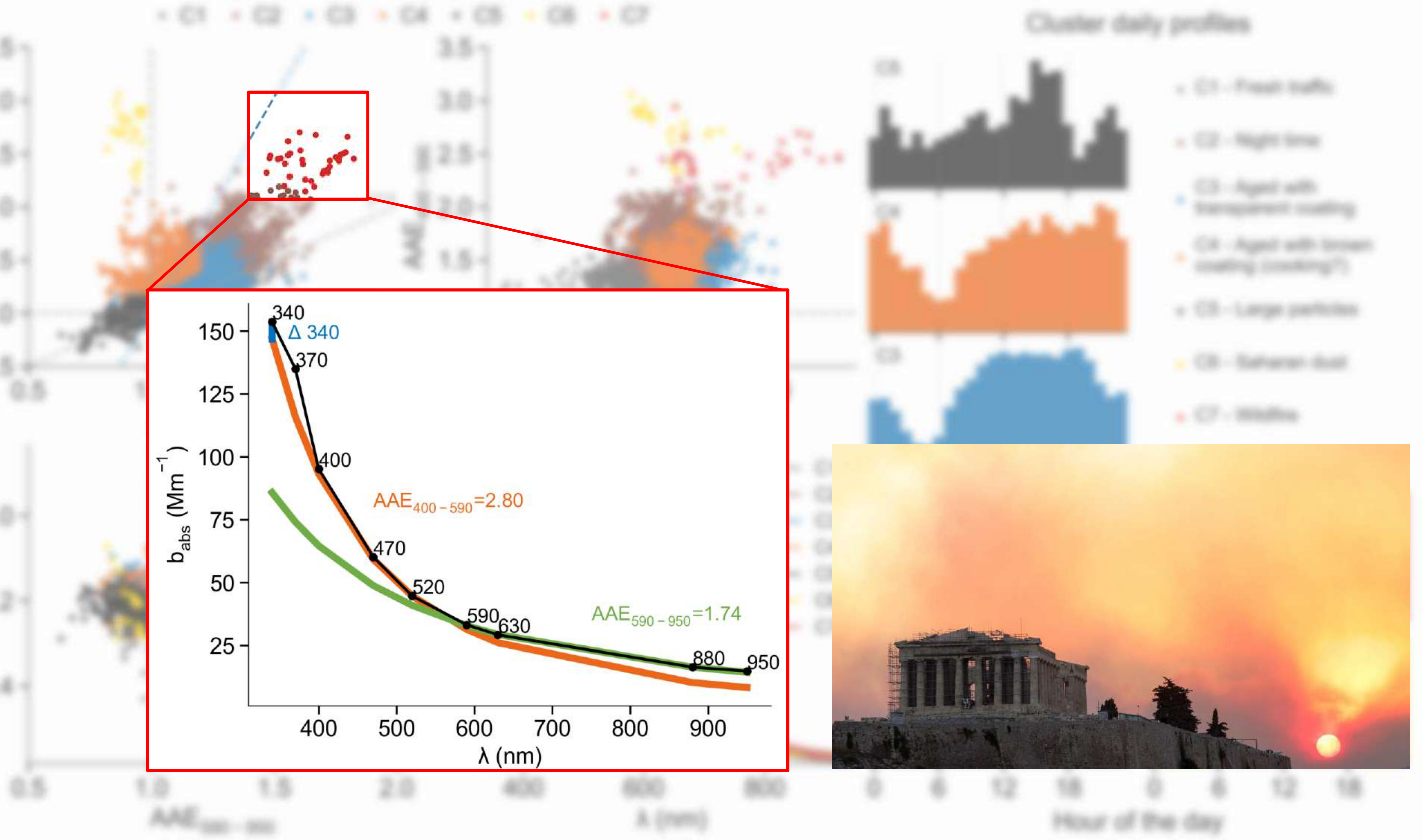
C1
C2
C3
C4
C5
C6
C7
AAE$_{400-590}$
AAE$_{590-950}$
y=x
Δ 340
b_{abs} (λ)
λ (nm)
Cluster daily profiles
C1 - Fresh traffic
C2 - Night time
C3 - Aged with transparent coating
C4 - Aged with brown coating (cooking?)
C5 - Large particles
C6 - Saharan dust
C7 - Wildfire
Hour of the day

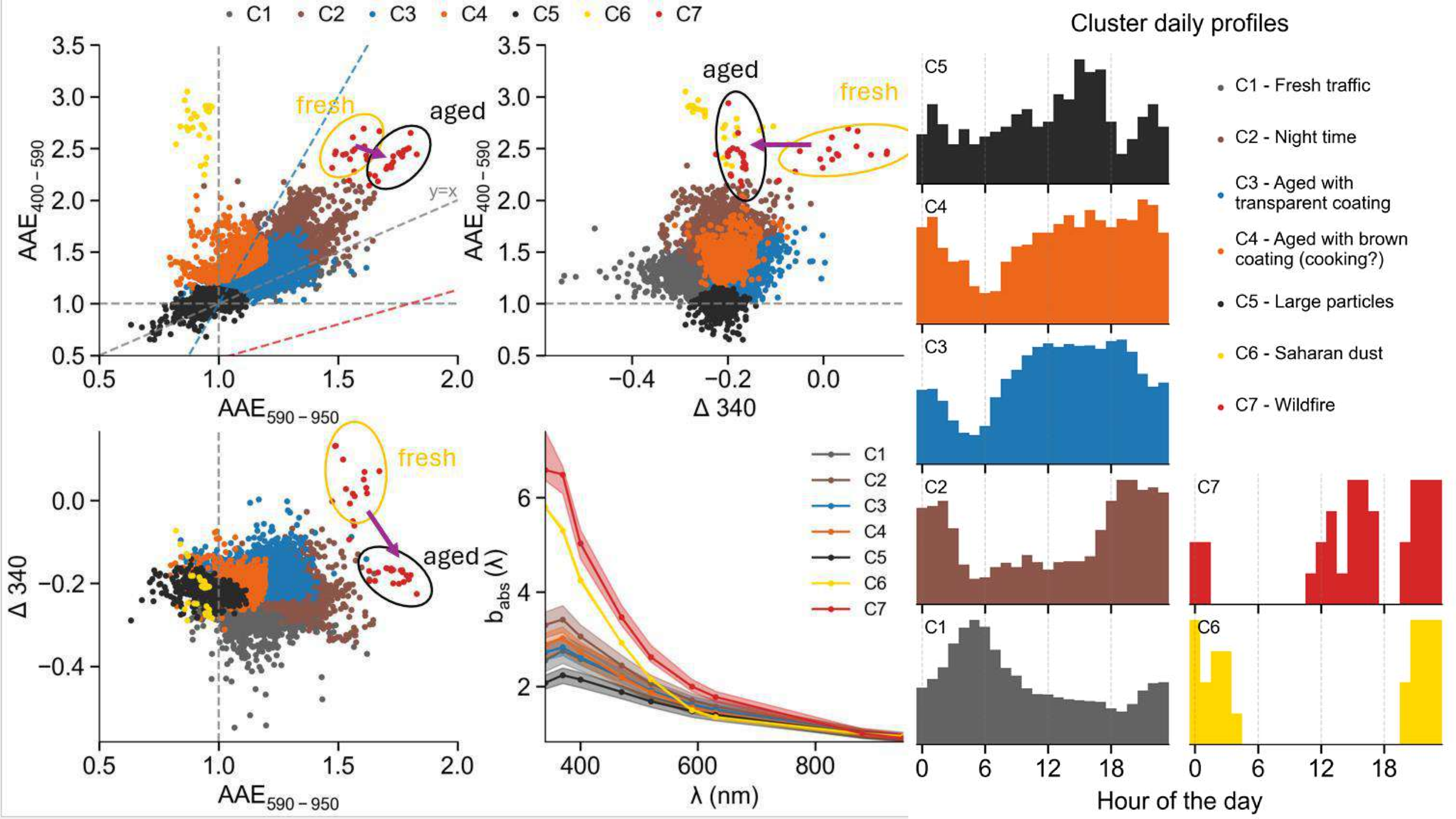


Δ 340
340
370
400
470
520
590
630
880
950
$AAE_{400-590}$=2.63
$AAE_{590-950}$=0.98
b_{abs} (Mm^{-1})
λ (nm)
10
20
30
40
50
60
70
400
500
600
700
800
900



The New York Times
Athens Turns Orange Under a Saharan Dust Cloud
In Photos


340
Δ 340
370
400
470
520
590
630
880
950
$AAE_{400-590}$=2.80
$AAE_{590-950}$=1.74
b_{abs} (Mm^{-1})
λ (nm)
150
125
100
75
50
25
400
500
600
700
800
900


C1 C2 C3 C4 C5 C6 C7
fresh
aged
y=x
$AAE_{400-590}$
$AAE_{590-950}$
Δ 340
b_{abs} (λ)
λ (nm)
Cluster daily profiles
C1 - Fresh traffic
C2 - Night time
C3 - Aged with transparent coating
C4 - Aged with brown coating (cooking?)
C5 - Large particles
C6 - Saharan dust
C7 - Wildfire
Hour of the day

AEROSOL
MAGEE SCIENTIFIC

Future research work