Optical detection and discrimination between biomass and fossil fuel combustion: influence on air quality in different environments

Monitoring Ambient Air

London, 12 December 2011

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Aerosol d.o.o.

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LSCE/CEA Orme des Merisiers, Gif-sur-Yvette, France

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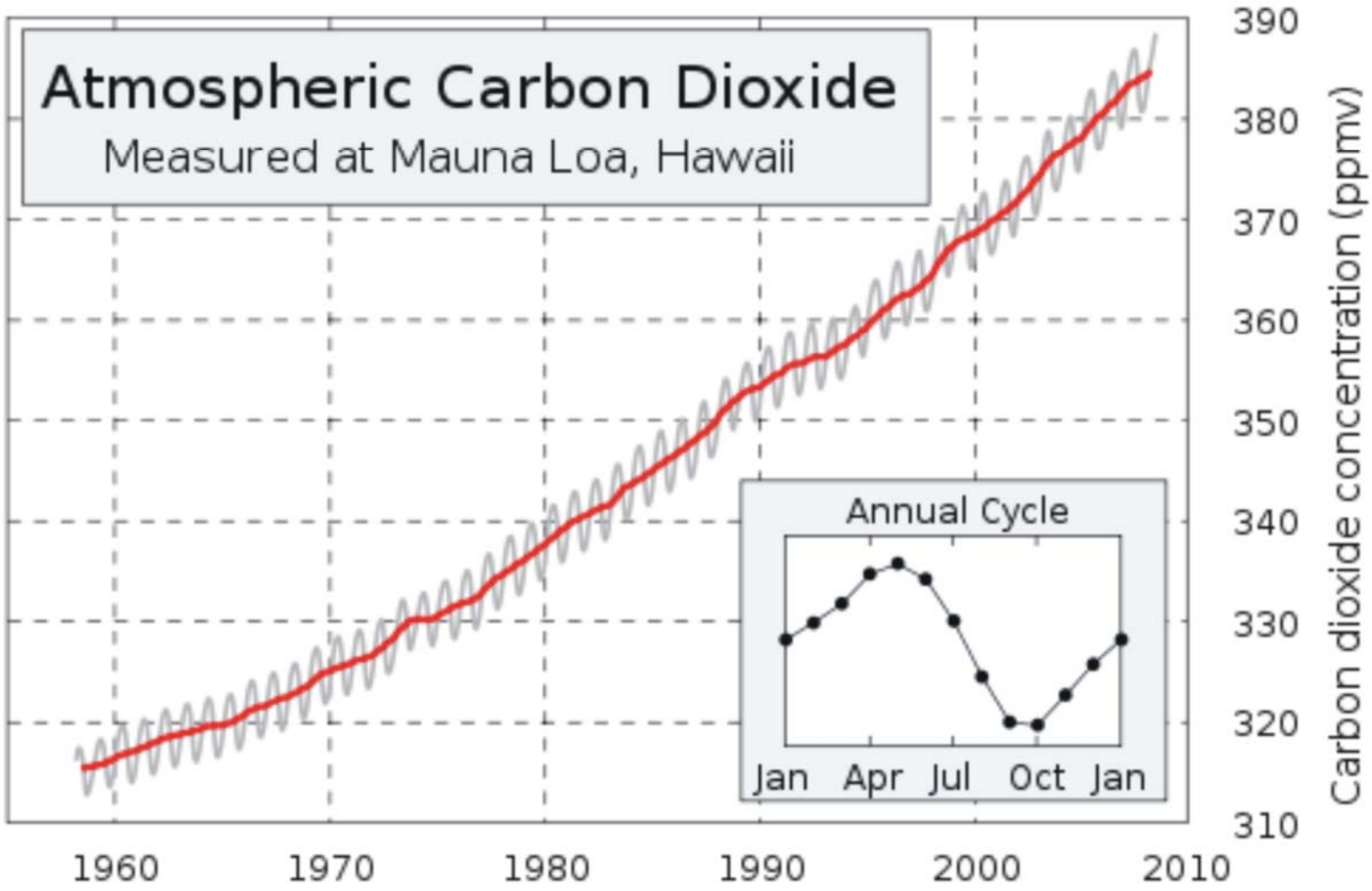
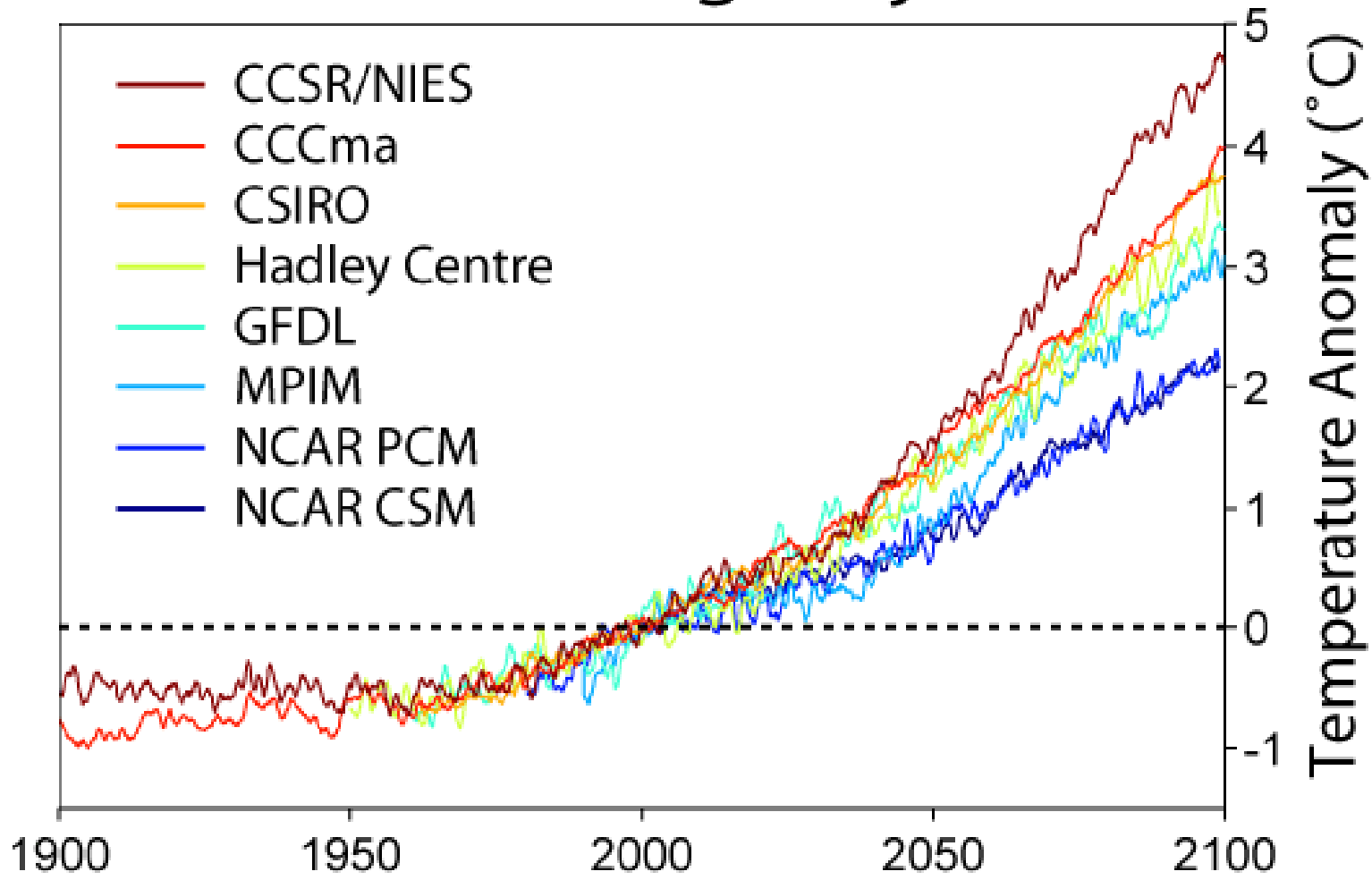
Climate change



Aerosol

Global Warming Projections



SRES A2, IPCC

Aerosol

Renewable fuels: wood

- wood/biomass is a **sustainable fuel** – trees recycle CO2
- burning biomass is and has been a **major energy source**
- various combustion regimes: high-efficiency distric heating ovens – individual wood-stoves
- possible extreme emissions of particulate matter

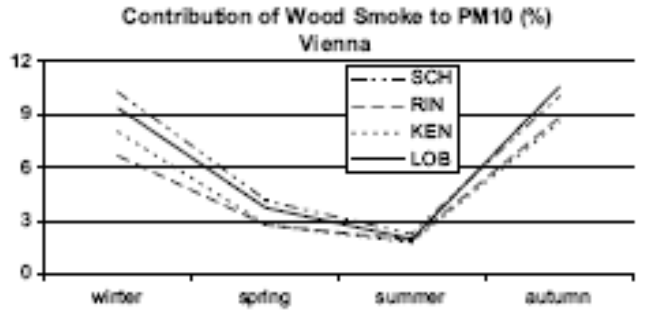
Wood-smoke – part of PM10

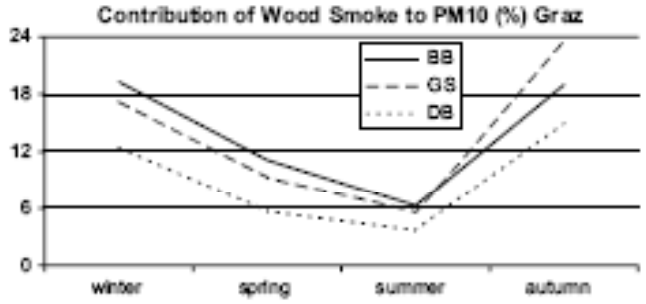
- **<u>rural areas</u>** (small villages in Lower Austria, Styria, Carinthia, Burgenland and Salzburg):

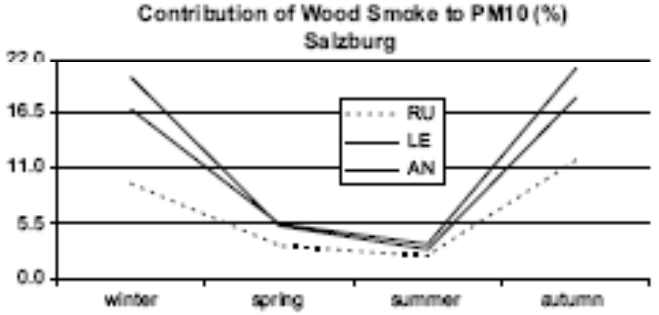
	WS	WS + HULIS
annual average	8 - 21%;	15 - 28%
winter	14 - 32%	19 - 42%

- **urban areas** (Vienna, Graz, Salzburg, Klagenfurt):

	WS	WS + HULIS
annual average	5 - 16%	9 - 20%
winter	8 - 22%	13 - 28%



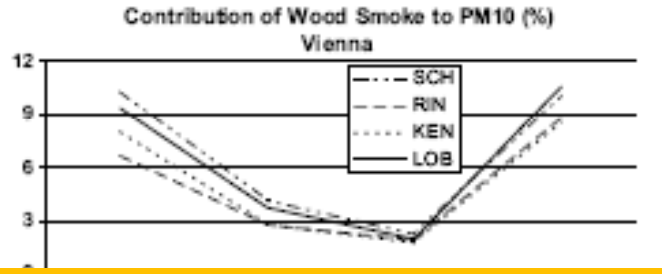




Aquella, TUW; A. Caseiro et al. / Atmospheric Environment 43 (2009) 2186–2195

Wood-smoke – part of PM10

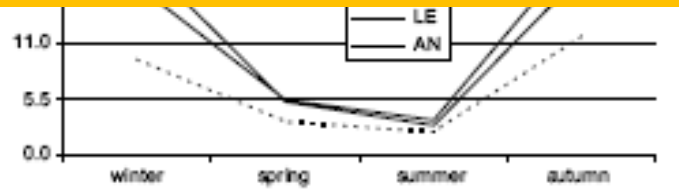
- **<u>rural areas</u>** (small villages in Lower Austria, Styria, Carinthia, Burgenland and Salzburg):



Up to 40% of all particulate matter is wood-smoke!

Woodsmoke is a local and regional air quality problem!

annual average	5 - 16%	9 - 20%
winter	8 - 22%	13 - 28%



Aerosol

Aquella, TUW; A. Caseiro et al. / Atmospheric Environment 43 (2009) 2186–2195

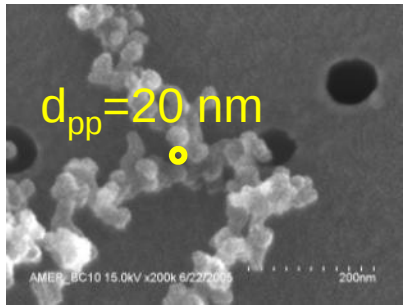
Aerosol Black Carbon

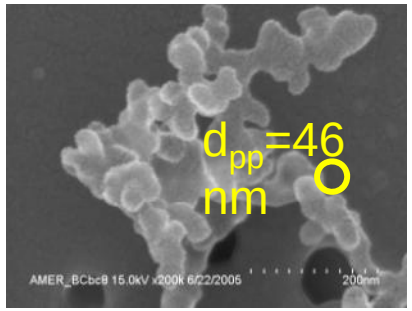
- BC is a product of incomplete **combustion**
- BC <u>not</u> automatically related to CO_2 emission
- BC emissions can <u>not</u> be predicted:

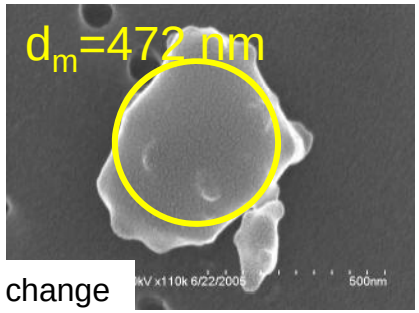
  must be measured

- BC particles from <u>different sources</u> can have <u>different characteristics</u> that produce <u>different effects</u> in the atmosphere:

  (Coal/Diesel/Biomass, USA/Asia/Europe)



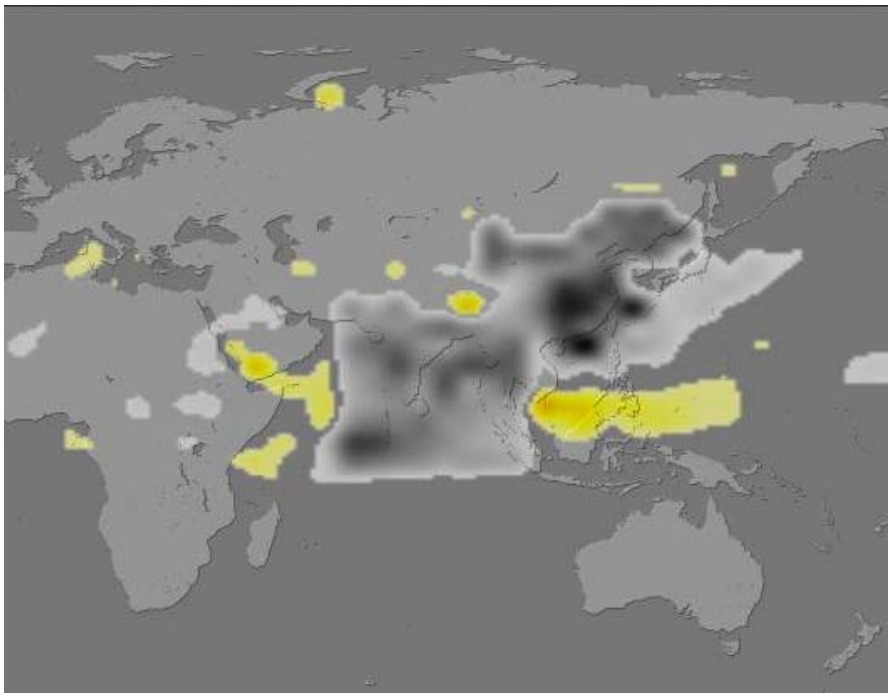




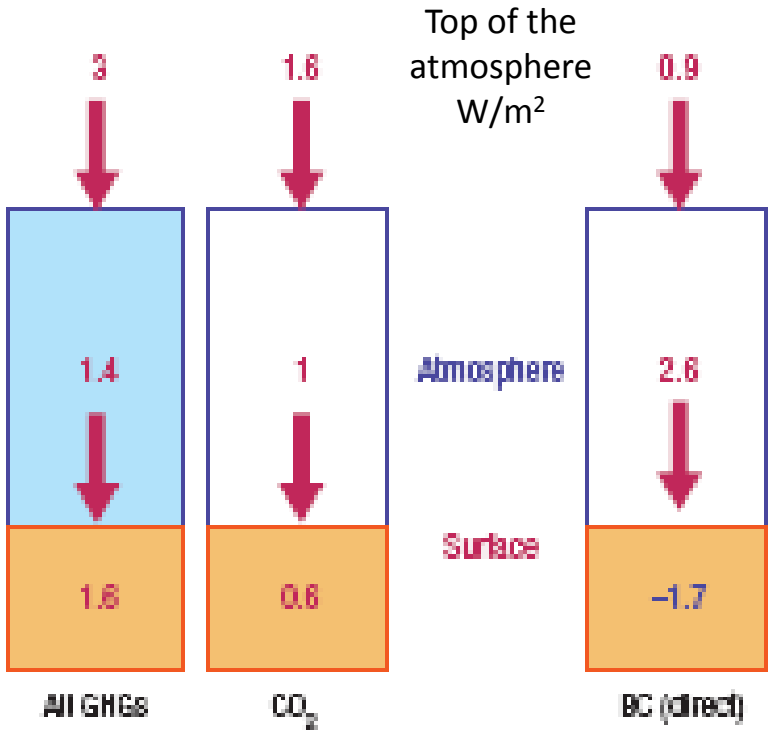
Note change in scale

Aerosol

Climate Change Effects of Aerosols



S. Menon, J. Hansen et al. *Science* (2002) 2250



V. Ramanathan, G. Charmichael, Nature Geosci (2008) 221

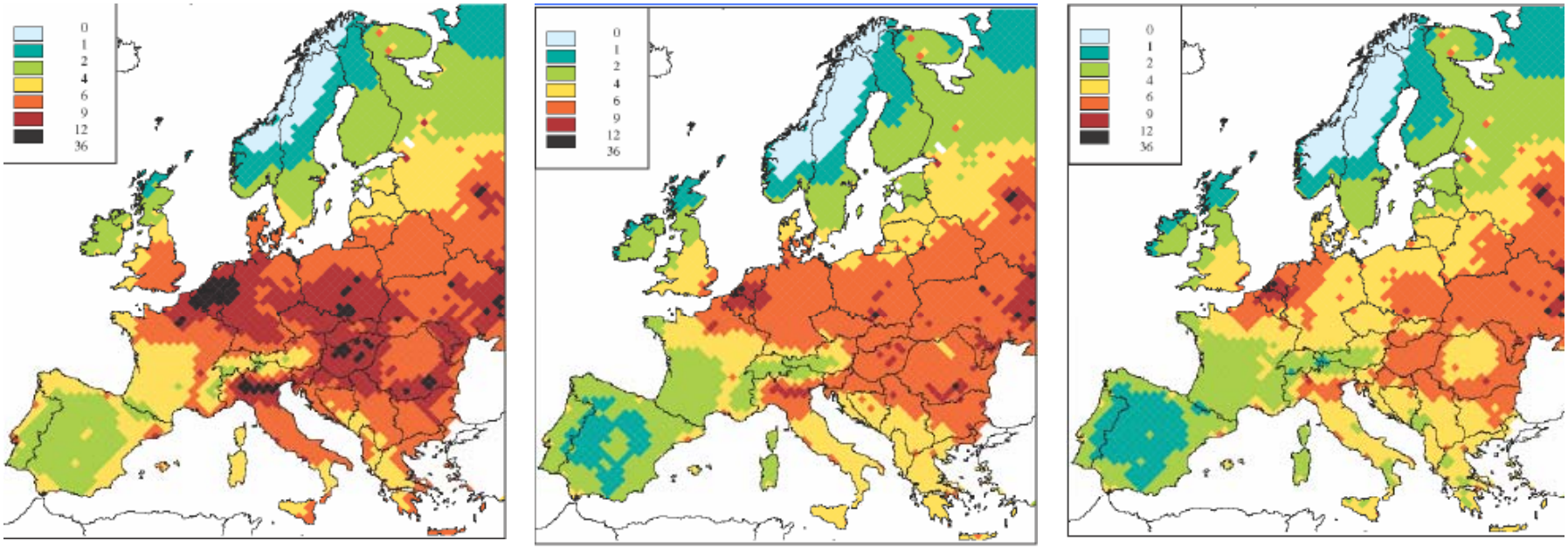
Haze over Asia: up to 40% of sunlight absorbed. Crop yields reduced ; local rainfall changed.

BC forcing is almost 1/3 of the total TOA GHG forcing!
Heat redistribution → weather

Why are atmospheric aerosols important?

- **Public Health: loss of life** in months due to PM2.5

(CAFE baselines, RAINS 2004)



2000 2010 2020

Even with reduced emissions: statistical life loss still around **5 months average in EU in 2020**!

Health Effects

THE "HARVARD 6-CITIES" STUDY

Dockery et al., *N. Engl. J. Med.* 329: 1753 (1993)

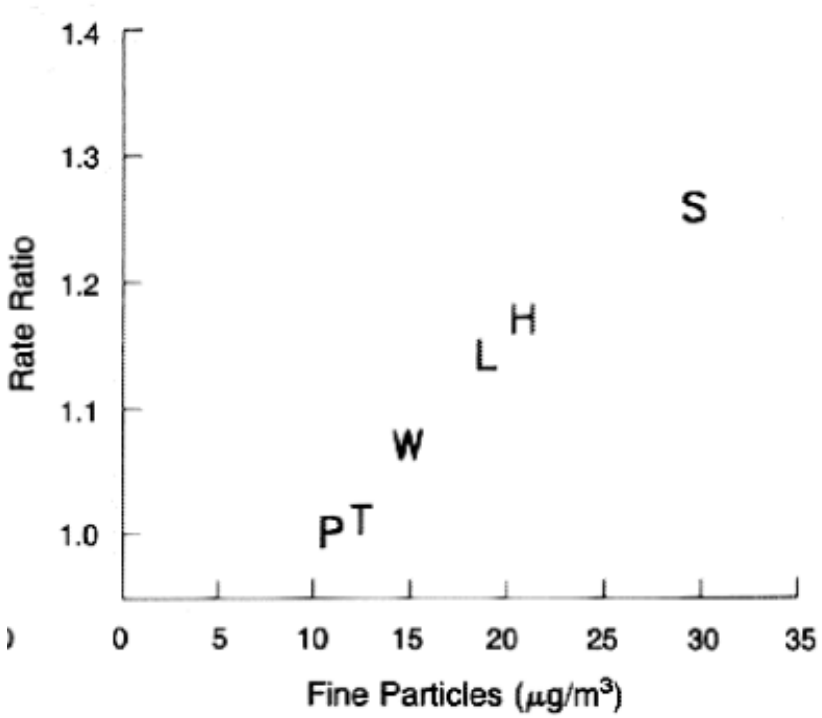
- **Longitudinal cohort study of 8111 adults, 1974 – 1977**

Steubenville, OH (S) Harriman, TN (H) St. Louis, MO (L)
Watertown, MA (W) Topeka, KS (T) Portage, WI (P)

- **1401 death certificates after 14-16 yr follow-up**

Smoking-adjusted mortality rates (deaths/1000 population)

Mortality	Mortality Ratio Highest *vs.* Lowest PM
All causes	**1.26 (1.08 – 1.47)**
Lung cancer	**1.37 (0.81 – 2.31)**
Other cardiopulmonary	**1.37 (1.11 – 1.68)**
Non-cardiopulmonary	**1.01 (0.79 – 1.30)**



Wood is a major energy source

- wood/biomass is a **sustainable fuel** – trees recycle CO2
- burning biomass is a **major energy source** in the Alps
- various combustion regimes: high-efficiency distric heating ovens – individual wood-stoves
- possible extreme emissions of particulate matter
- local and regional air quality issue – up to **40% of all particulate matter is wood-smoke**
- **woodsmoke is composed of light absorbing carbonaceous aerosols**

Aerosol

Advantages / Attributes of Optical Analysis

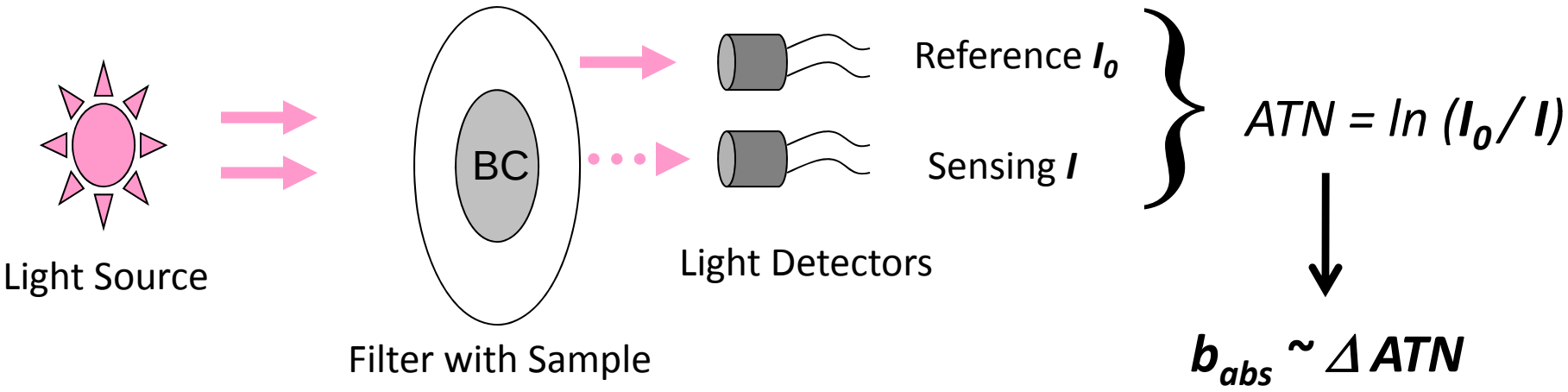
Typical **chemical speciation** time resolution – hours, **day**!

Optical methods – minute!

- Instantaneous
- Non-destructive
- Mobile / Portable
- Added dimension - *time*
- Added dimension – *wavelength*

Aerosol

Optical Analysis Method for Black Carbon



Analytical Instrument : Aethalometer™

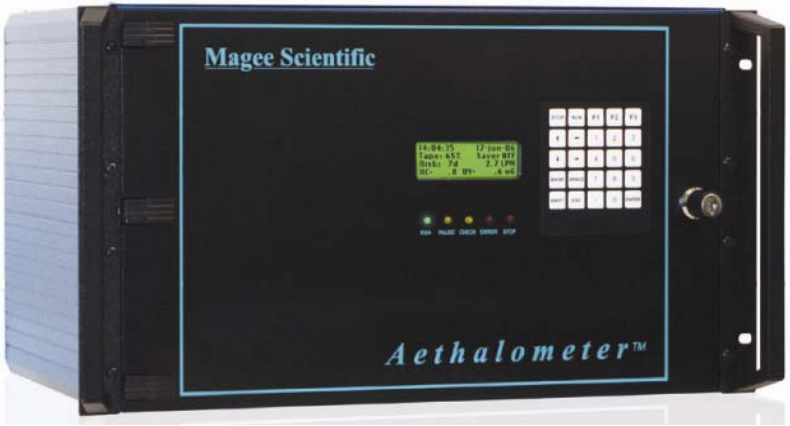
- Collect sample **continuously**.
- ***Optical absorption*** ~ change in ATN.
- Measure optical absorption continuously :
  optical wavelengths from 370 nm to 950 nm.
- Convert ***optical absorption*** to ***concentration of BC:***

$$BC\,(t) = b(t) / \sigma$$

- Real-time data: 1 s / 1 min / **5 minutes**
  - *Dynamical, real-time measurement, updated each period*

Aerosol

Aethalometer – Continuous rack mount instruments

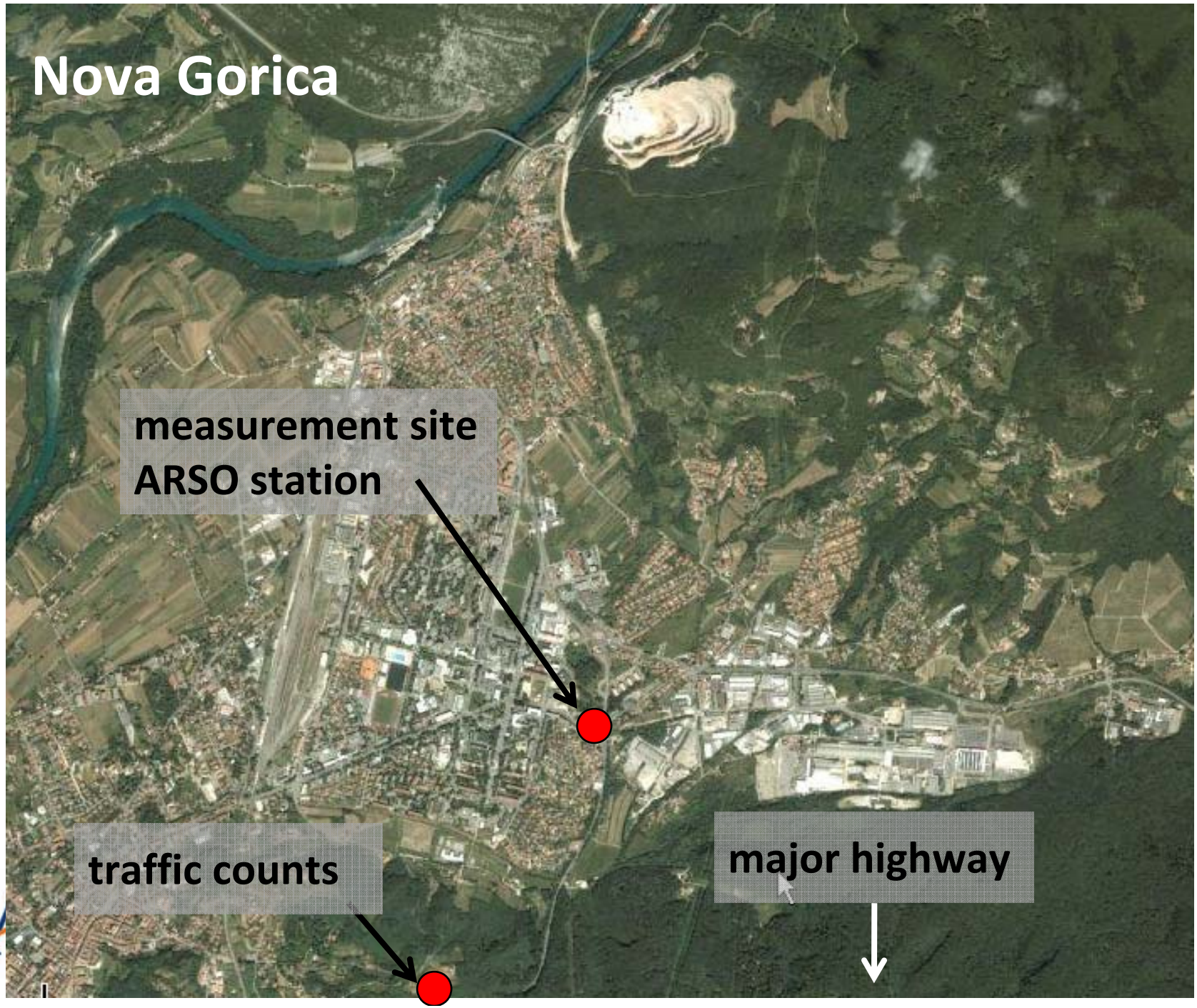


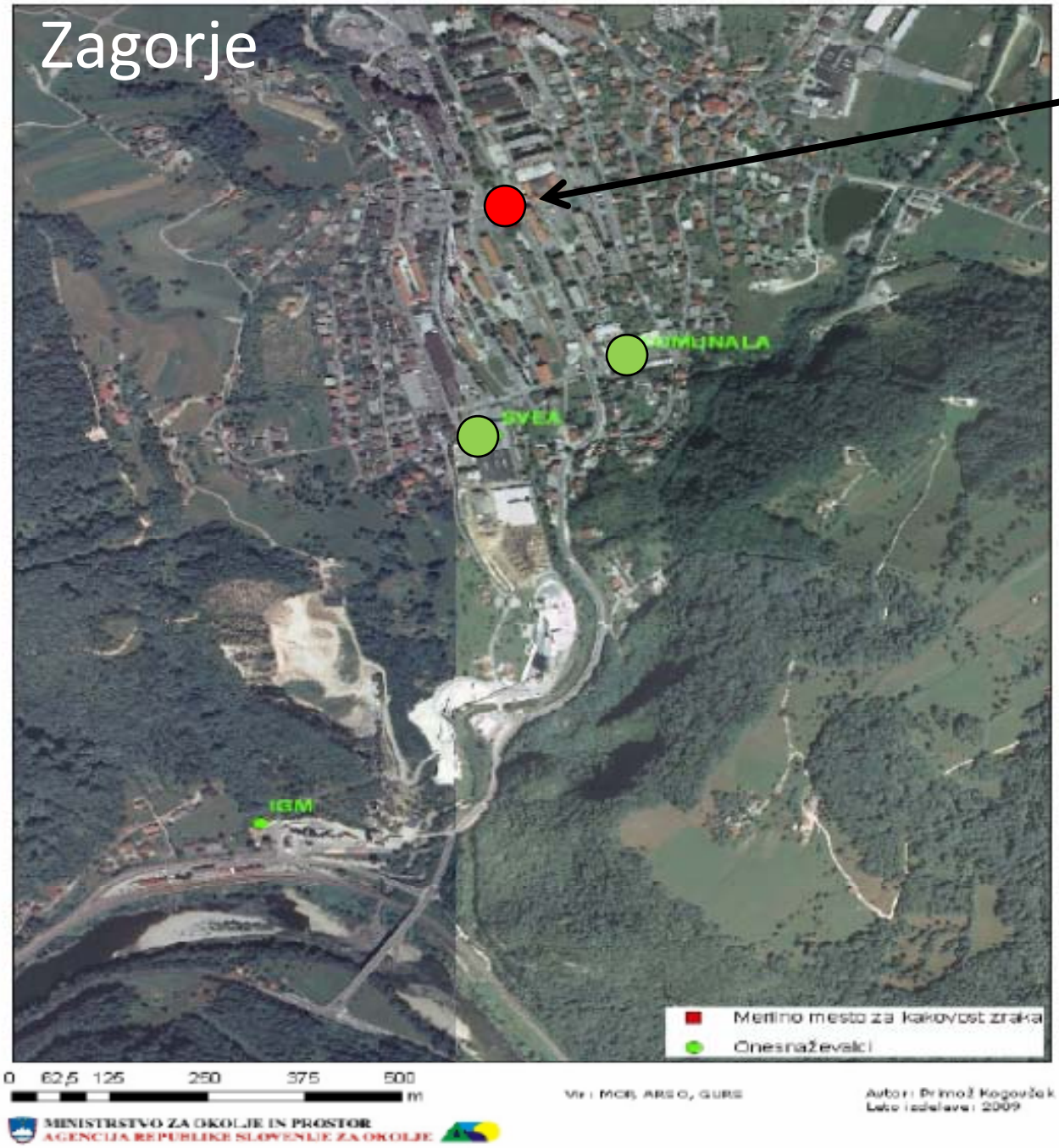
AE31 Spectrum – Ambient Air Quality Monitoring

- ✓ ***Seven wavelength (370, 470, 520, 590, 660, 880, and 950 nm)***
- ✓ ***Local source identification***
- ✓ ***Regional, Continental, Global Atmospheric studies***
- ✓ ***Particle size distribution, radiative transfer***
- ✓ ***Climate change, albedo, cloud modification***

Aerosol


Nova Gorica
Feb 2010
Zagorje
Nov 2009
Villach
Klagenfurt am Wörthersee
Maribor
Ljubljana
Kranj
Udine
Trieste
Rijeka
Koper
Pula
Novo Mesto
Celje
Jesenice
Tolmezzo
Monfalcone
Postojna
Kočevje
Karlovac
Ptuj
Pordenone


Nova Gorica
measurement site
ARSO station
traffic counts
major highway



measurement site
EARS station

thermal power plant
cement kiln

Site and instrumentation

Aerosol light absorption:
Aethalometer AE31-ER

- 7 wavelengths: 370, 470, 520, 590, 660, 880, 950 nm
- flow 4 LPM
- absorption coefficient b_{abs} - compensation for loading and scattering
- Angstrom exponent α from $b_{abs}(\lambda)$

5 min time resolution

OC / EC filter analysis:
Sunset T-O Carbon Aerosol analyzer

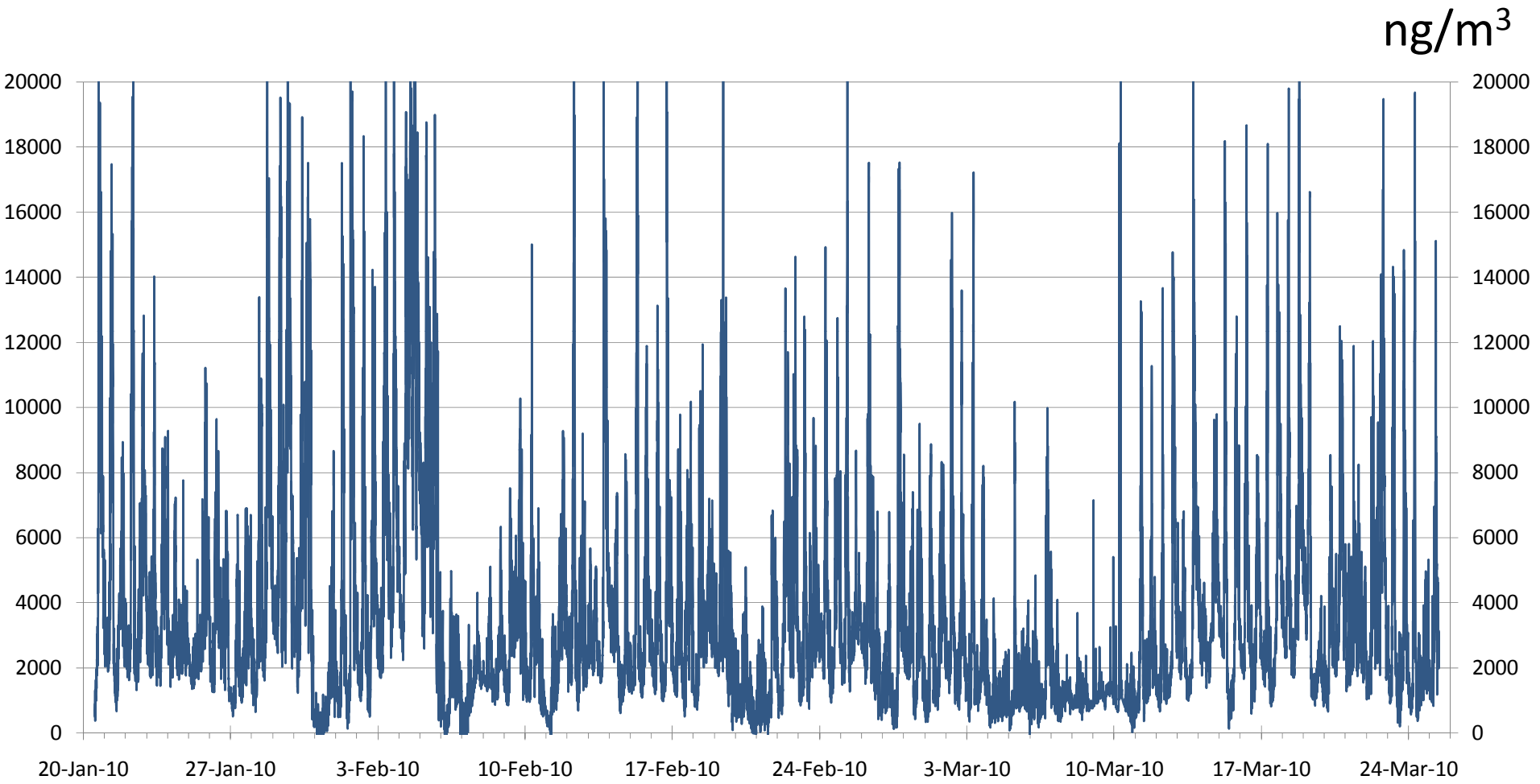
- 24 h quartz filters, 16,7 LPM
- EUSAAR-2 protocol

PM10:
EN 12341
reference gravimetric method

1 day time resolution

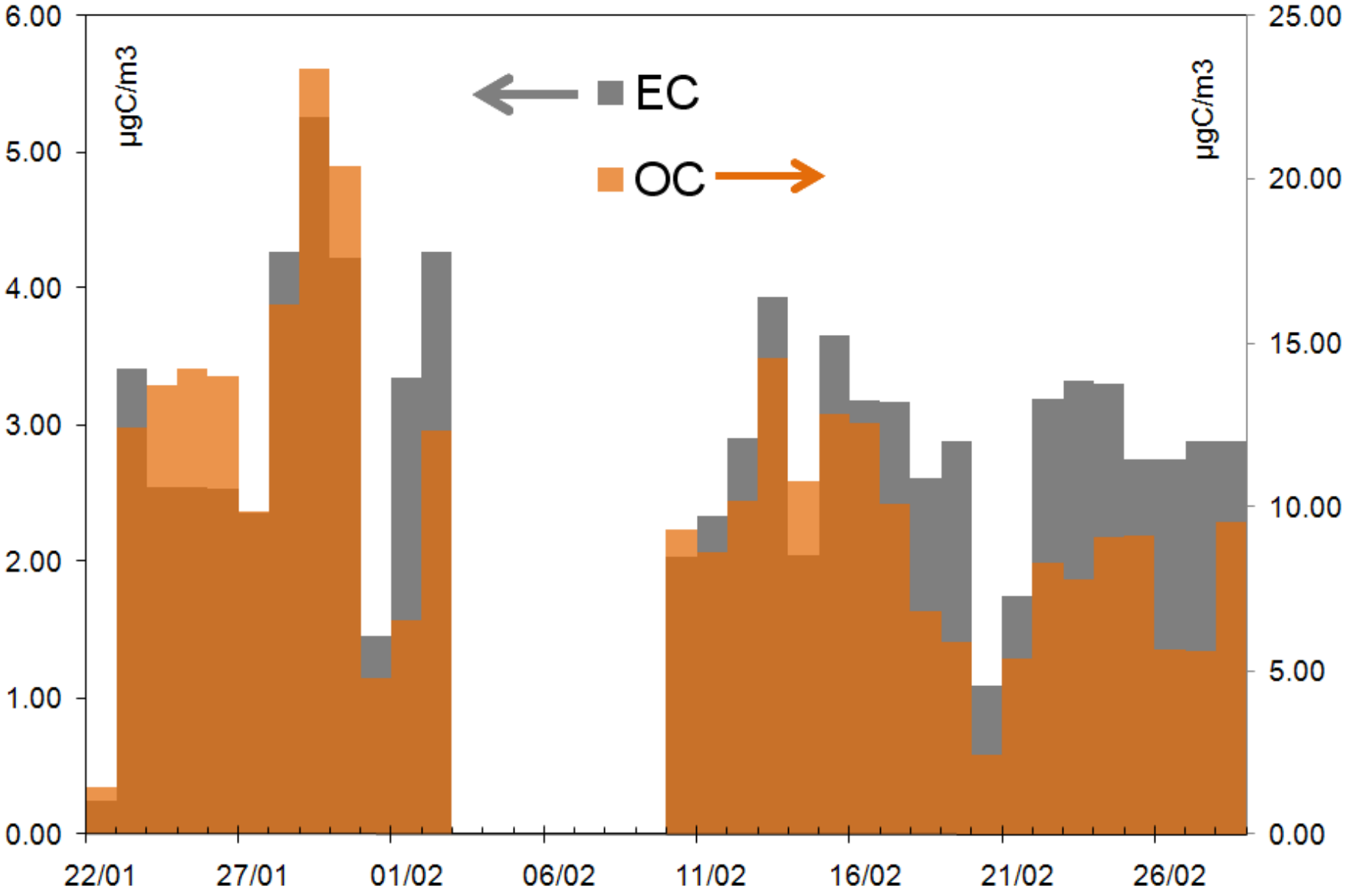
Aerosol

BC time-series, Nova Gorica

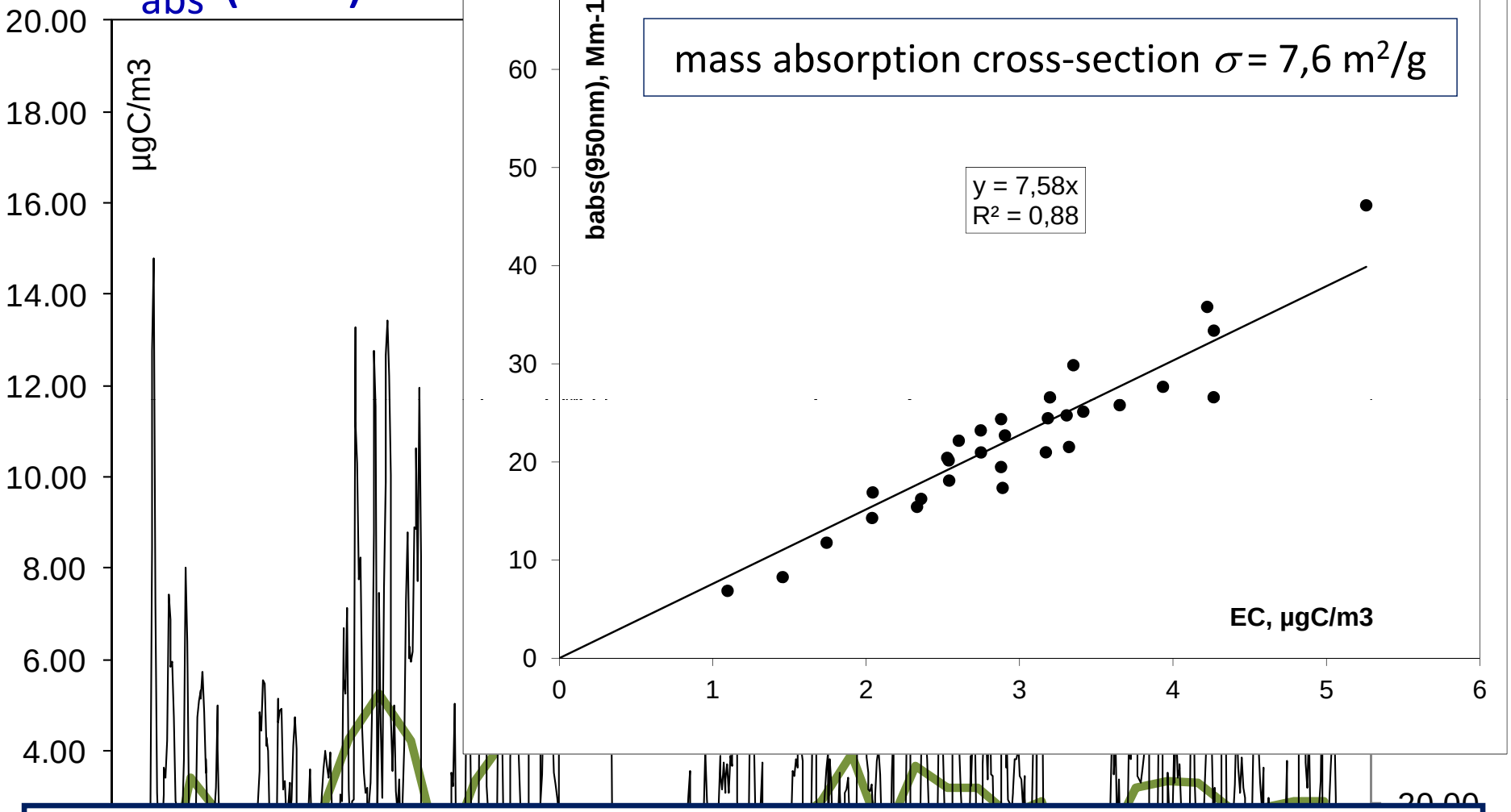


Aerosol

OC, EC time-series, Nova Gorica

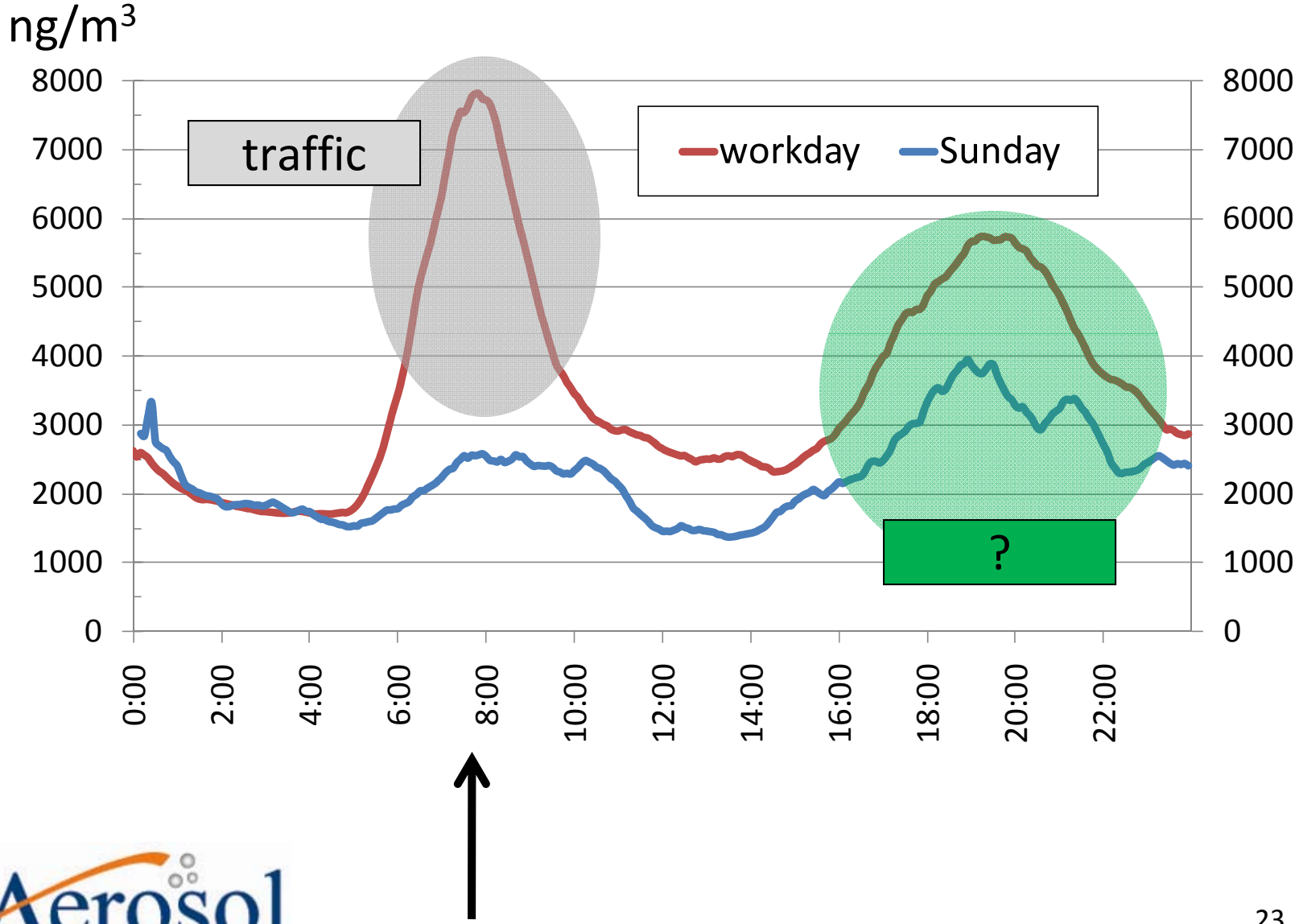


b_{abs} (950) ~ B



Good agreement between thermal EC and optical BC!

BC in Nova Gorica – diurnal variation



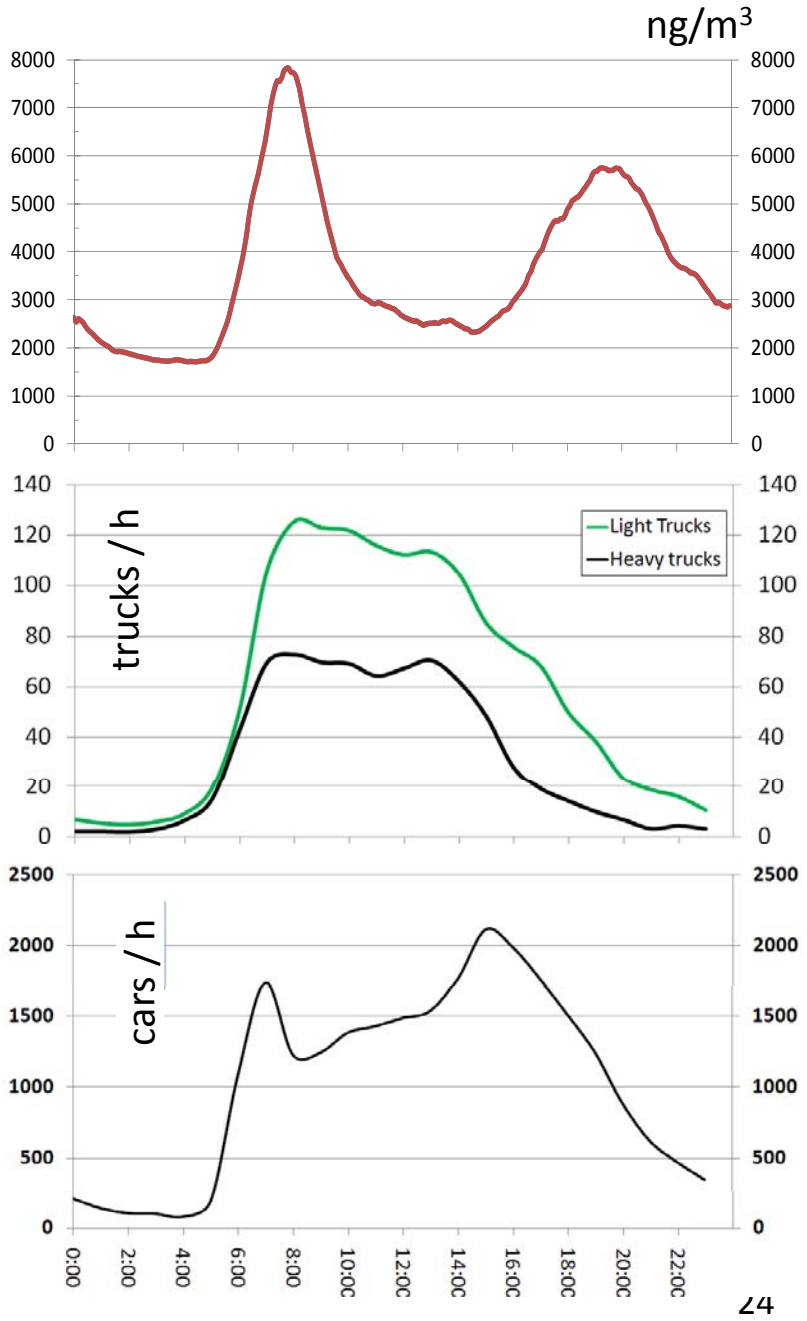
Traffic

Does traffic diurnal pattern match the BC pattern?

Trucks are all diesel and emit more than other vechicles.

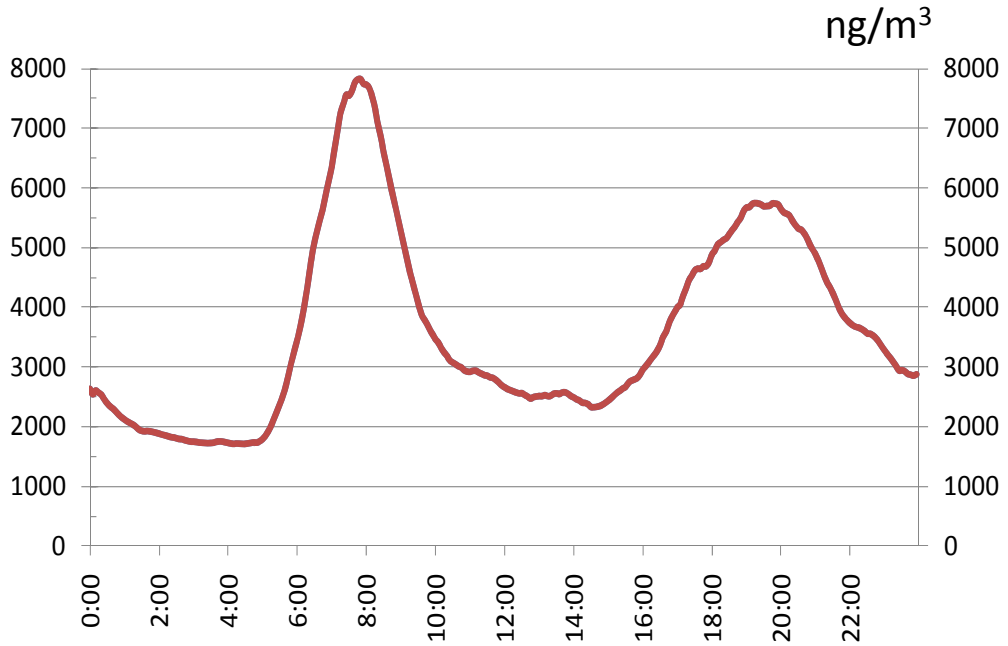
What about cars?

Note the change in scale!

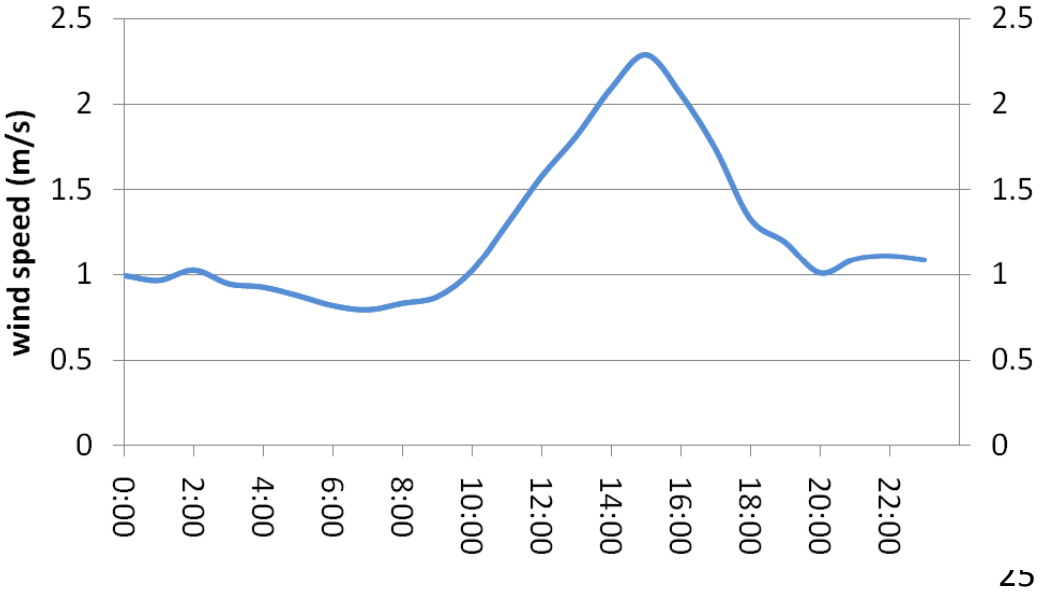


Wind

Does the wind diurnal pattern influence the BC pattern?



Wind does disperse the primary air pollution!



Aerosol

From Black&White to Color

Wood-smoke vs. diesel

- measure attenuation with the Aethalometer: UV-IR
- calculate absorption coefficient $b_{abs}(\lambda)$
- for completely **black sample**: $b_{abs} \sim 1/\lambda$
- woodsmoke contains aromatic substances – increased absorption: more at **lower wavelengths**!

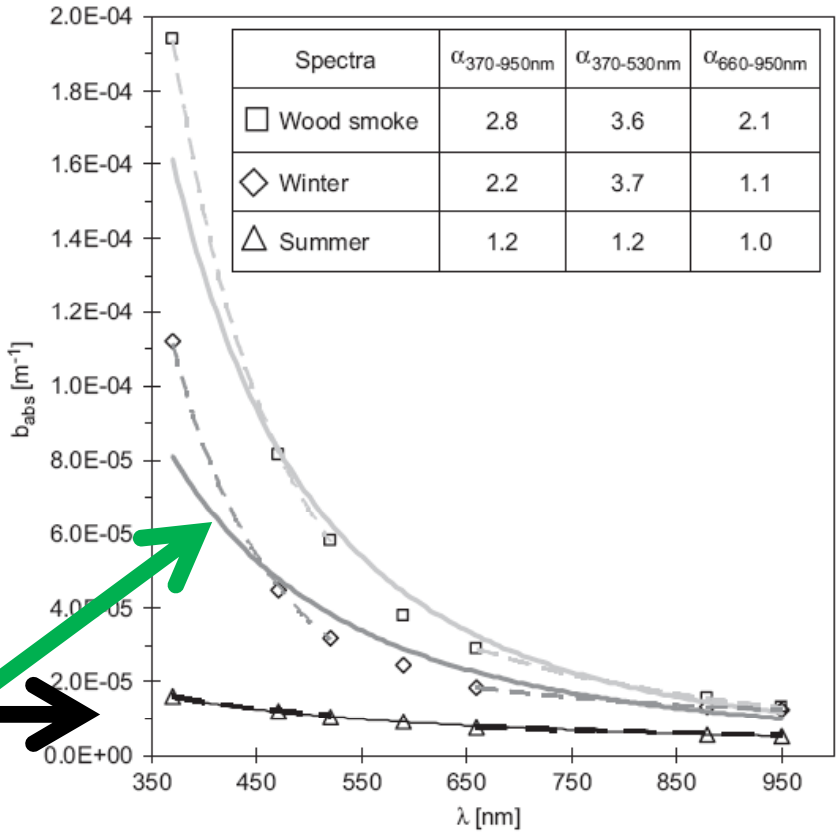
Wood-smoke vs. diesel - 7λ

- measure attenuation with the Aethalometer
- absorption coefficient - b_{abs}
- for pure black carbon: $b_{abs} \sim 1/\lambda$
- generalize **Angstrom exponent**:

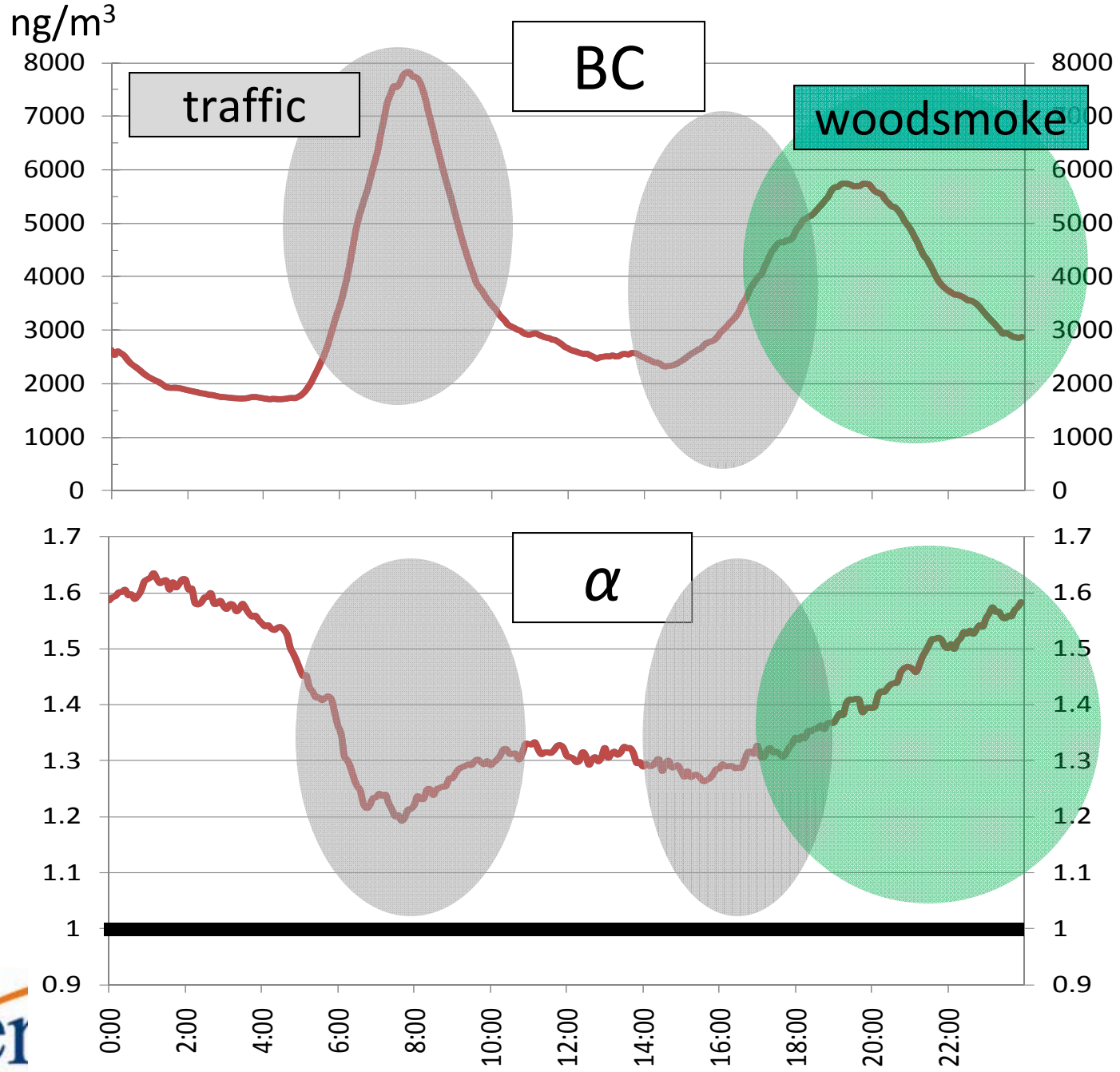
$$b_{abs} \sim 1/\lambda^{\alpha}$$

diesel: $\alpha \approx 1$

wood-smoke: $\alpha \approx 2$ and higher



J. Sandradewi et al., A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength Aethalometer, Atmospheric Environment (2008) 101–112


ng/m3
BC
traffic
woodsmoke
8000
7000
6000
5000
4000
3000
2000
1000
0
α
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0:00
2:00
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00

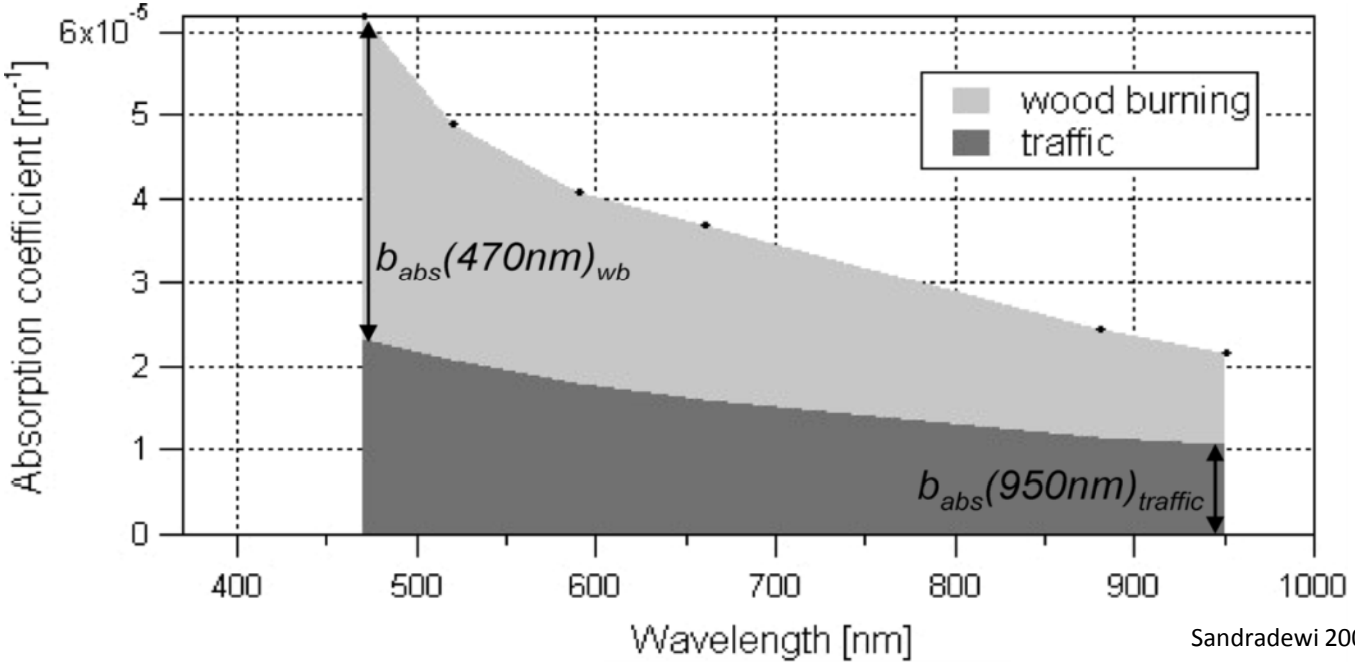
Quantification

$b(\lambda) = b_{wb}(\lambda,\text{wood}) + b_{ff}(\lambda,\text{fossil})$ λ = 470 nm, 950 nm

$b_i(470\text{ nm}) / b_i(950\text{ nm}) = (470\text{ nm} / 950\text{ nm})^{-\alpha}$

$\alpha = 1,0 \pm 0,1$ (fossil) Bond & Bergstrom 2004 .

$\alpha = 2,0$ -0,5/+1,0 (wood) Kirchstetter 2004, Day 2006, Lewis 2008



Sandradewi 2008

Quantification

$$b(\lambda) = b_{wb}(\lambda,\text{wood}) + b_{ff}(\lambda,\text{fossil}) \qquad \lambda = 470\ nm,\ 950\ nm$$

$$b_i(470\ nm) / b_i(950\ nm) = (470\ nm / 950\ nm)^{-\alpha}$$

$\alpha = 1{,}0 \pm 0{,}1$ *(fossil)* Bond & Bergstrom 2004 .

$\alpha = 2{,}0\ -0{,}5/+1{,}0$ *(wood)* Kirchstetter 2004, Day 2006, Lewis 2008

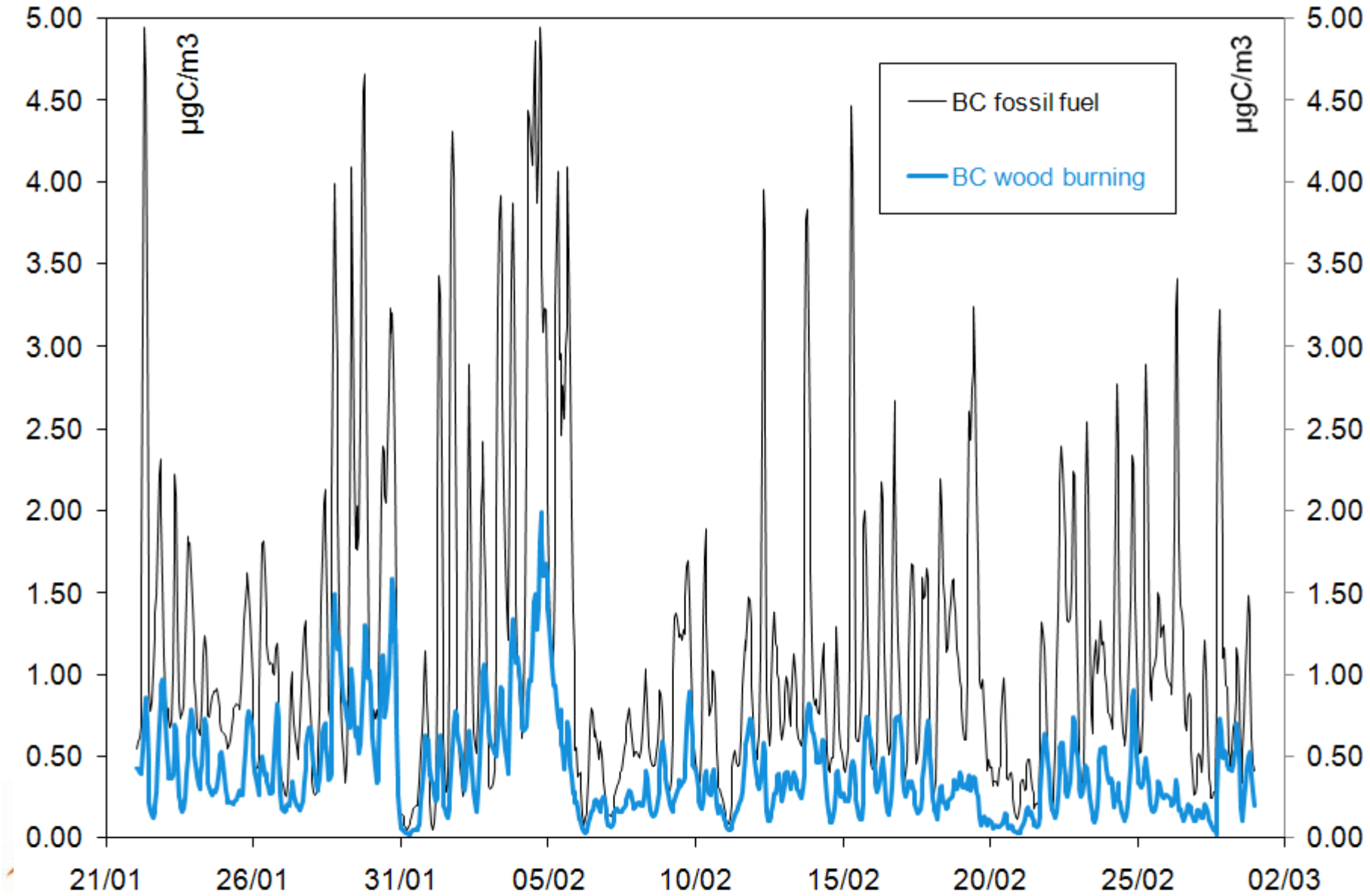
$$BC_{ff} = BC\ b_{ff}(950\ nm) / b(950\ nm)$$

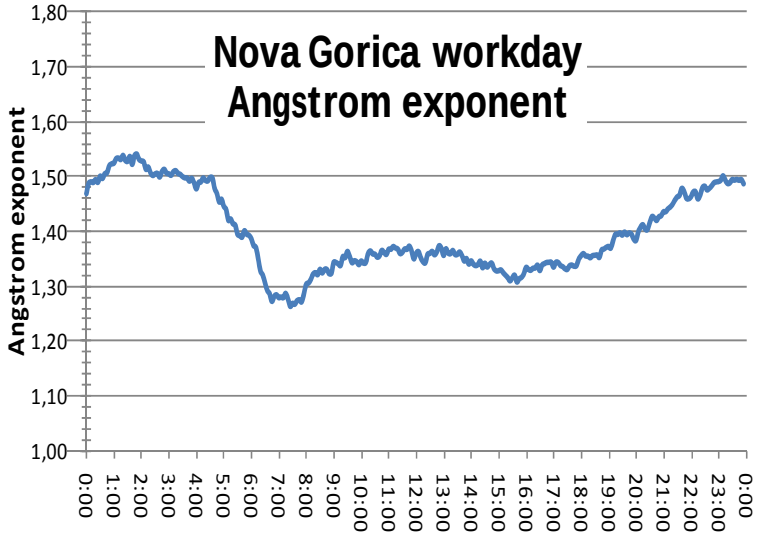
$$BC_{wb} = BC - BC_{ff}$$

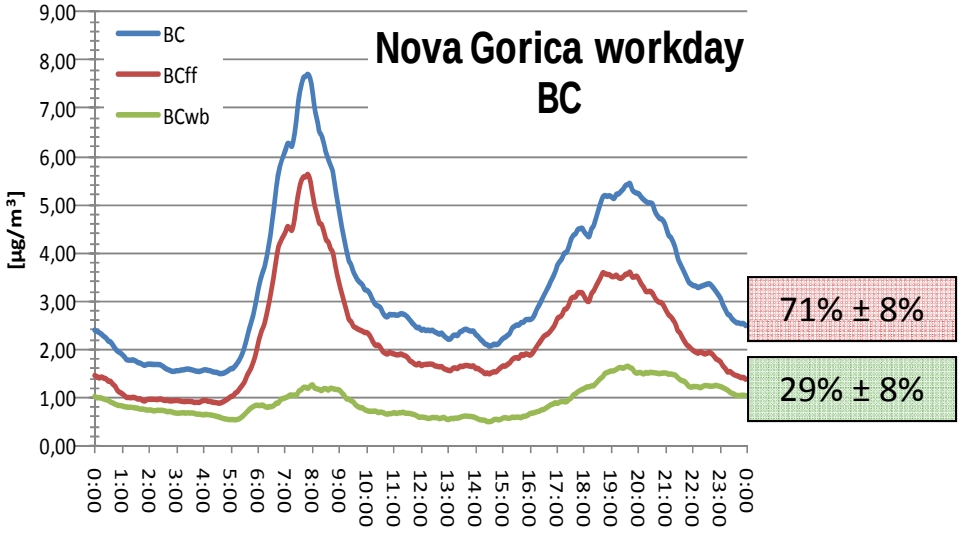
Sandradewi 2008

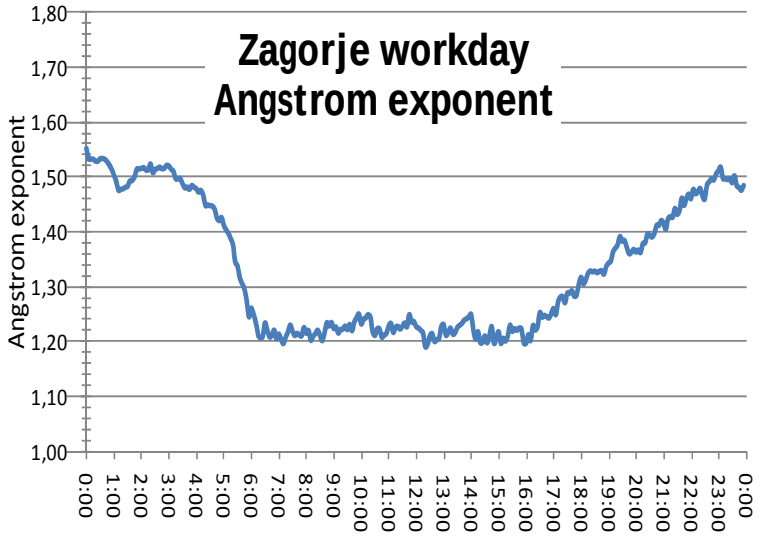
Aerosol

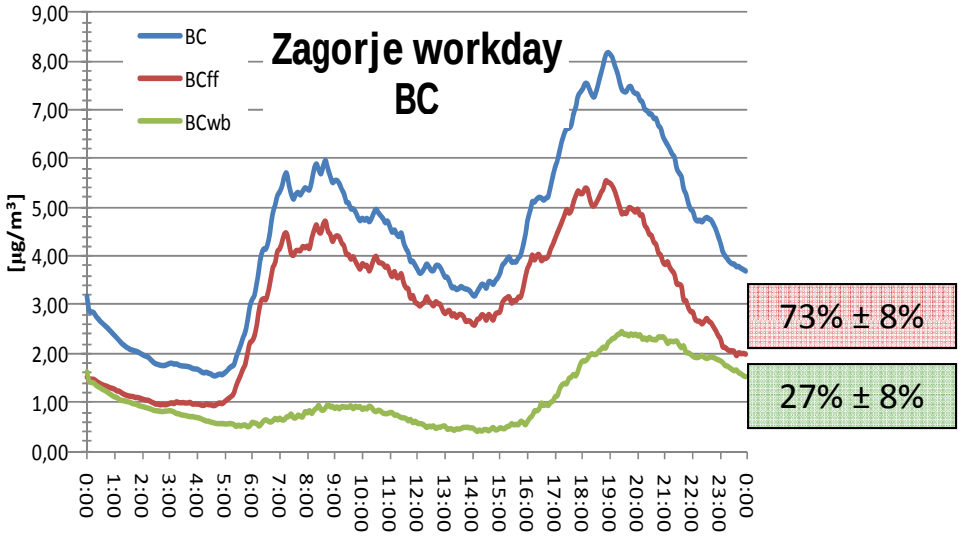
BC_{ff}, BC_{wb} time series, Nova Gorica




Nova Gorica workday
Angstrom exponent
Angstrom exponent
1,80
1,70
1,60
1,50
1,40
1,30
1,20
1,10
1,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00


Nova Gorica workday
BC
BC
BCff
BCwb
[µg/m³]
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00
71% ± 8%
29% ± 8%


Zagorje workday
Angstrom exponent
Angstrom exponent
1,80
1,70
1,60
1,50
1,40
1,30
1,20
1,10
1,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00

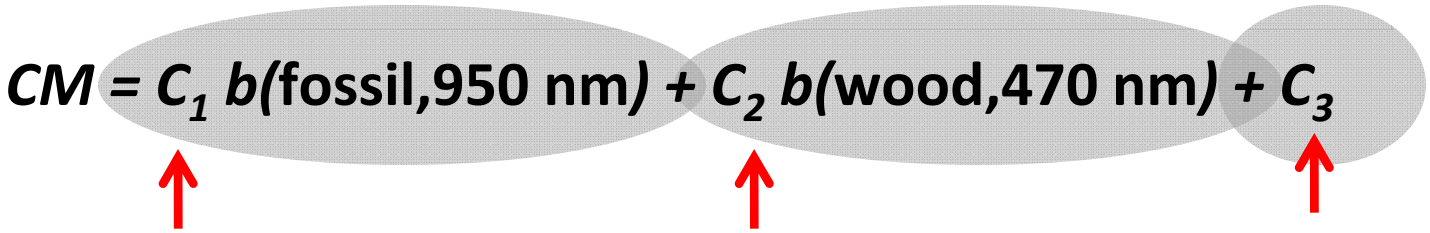

Zagorje workday
BC
BC
BCff
BCwb
[µg/m³]
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00
73% ± 8%
27% ± 8%

Aerosol

Carbonaceous matter

measure Total Carbon – 24 h resolution

TC = OC + EC → *carbonaceous matter CM*



fossil fuel combustion

BrC containing – wood combustion

non-combustion sources

CM = BC + OM

C_1, C_2, C_3 determination – some hand-waving

- C_1 is less variable than C_2 and C_3 and fixed to 290.000
- C_2 and C_3 determined from (CM-CM_{ff}) vs. CM
- determine CM_{ff} from

$$\boldsymbol{CM_{ff} = BC_{ff} + OM_{ff}}$$

$$\boldsymbol{BC_{ff} / OC_{ff} = 1}$$

$$\boldsymbol{OM_{ff} = 1{,}8\ OC_{ff}}$$

} supported by ambient and emission studies, WSOC measured

Sandradewi 2008, Favez 2010

Aerosol

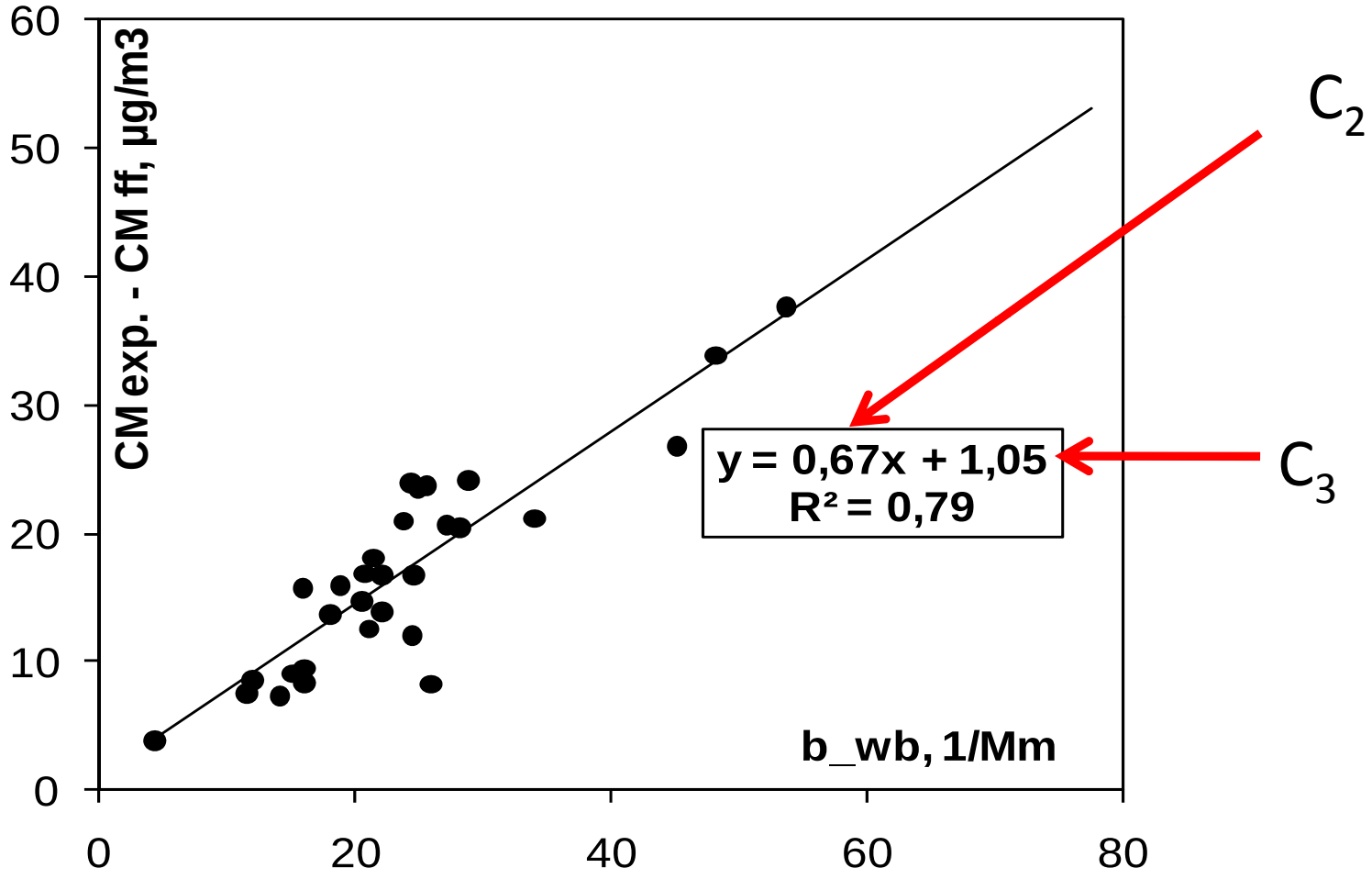
C_2, C_3 determination (2) – Nova Gorica

$$CM = C_1\, b(\text{ff},950\text{ nm}) + C_2\, b(\text{wb},470\text{ nm}) + C_3$$

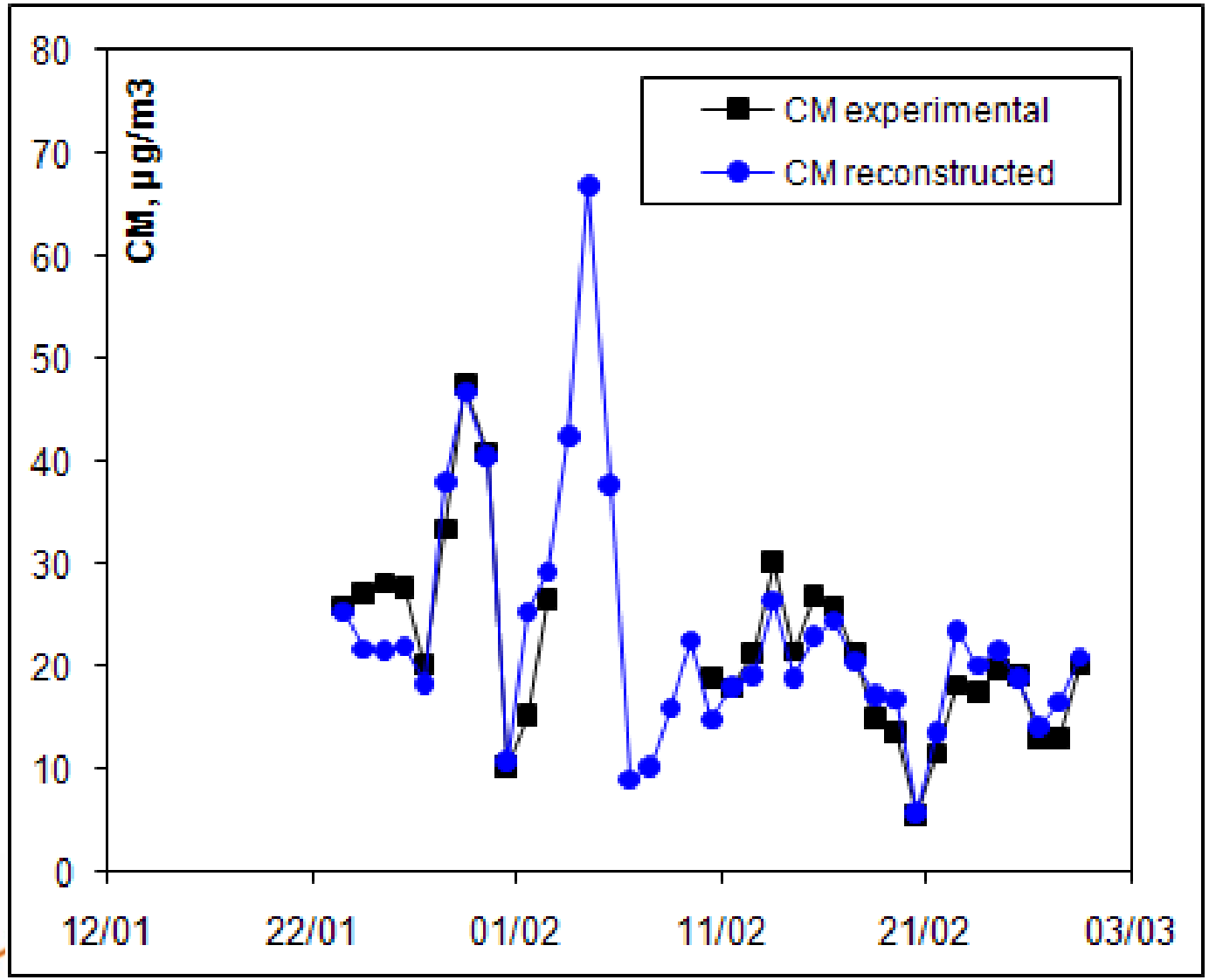
$$CM - C_1\, b(\text{ff},950\text{ nm}) = C_2\, b(\text{wb},470\text{ nm}) + C_3$$

Aerosol

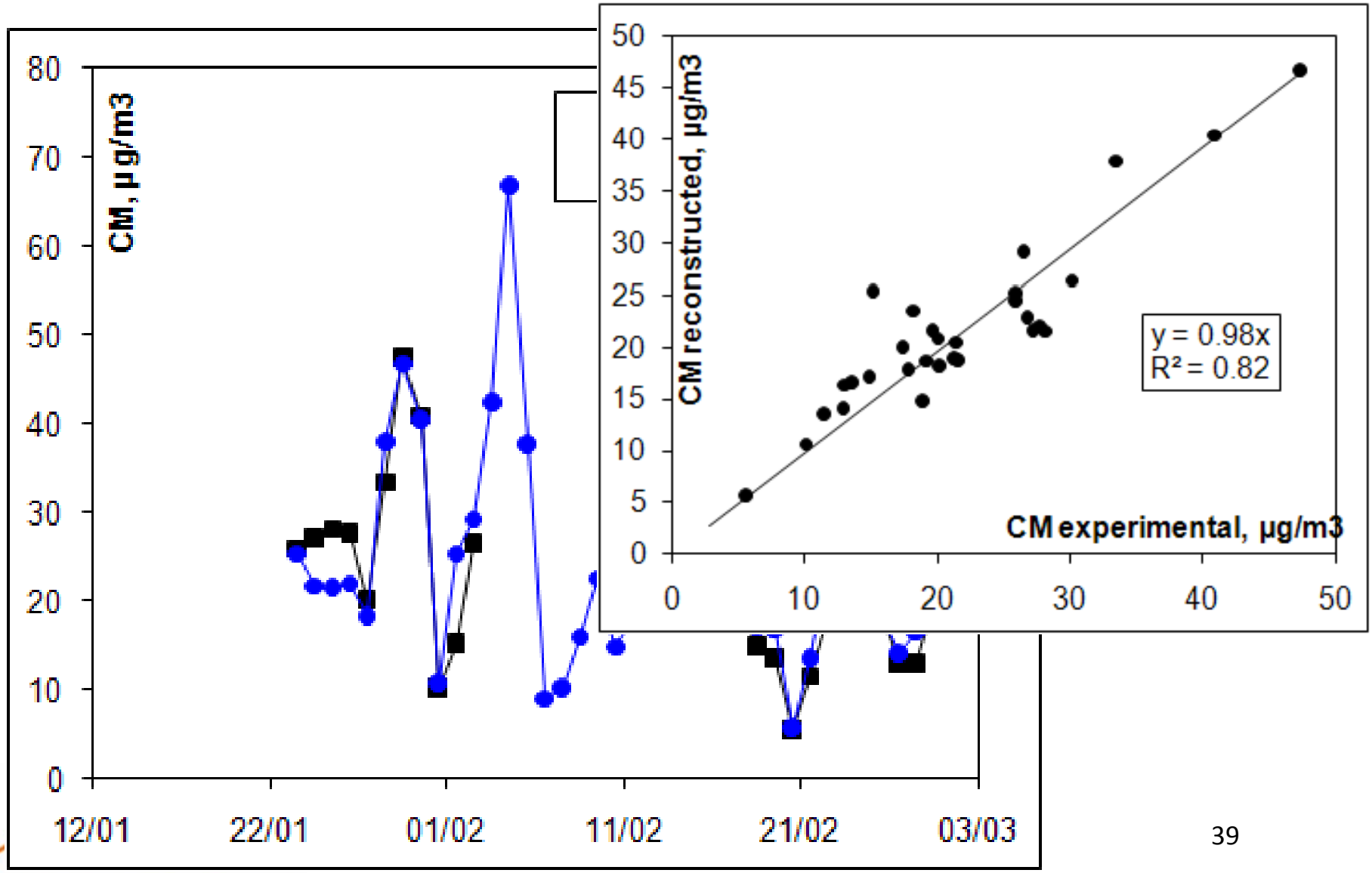
C_2, C_3 determination (2) – Nova Gorica

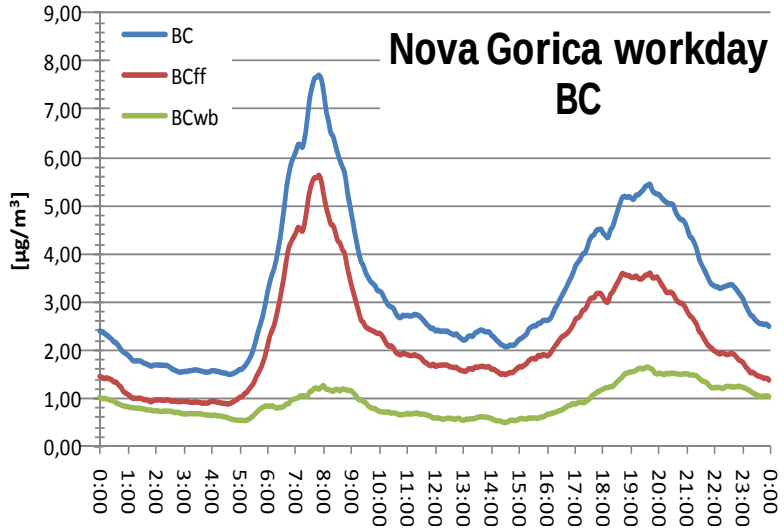


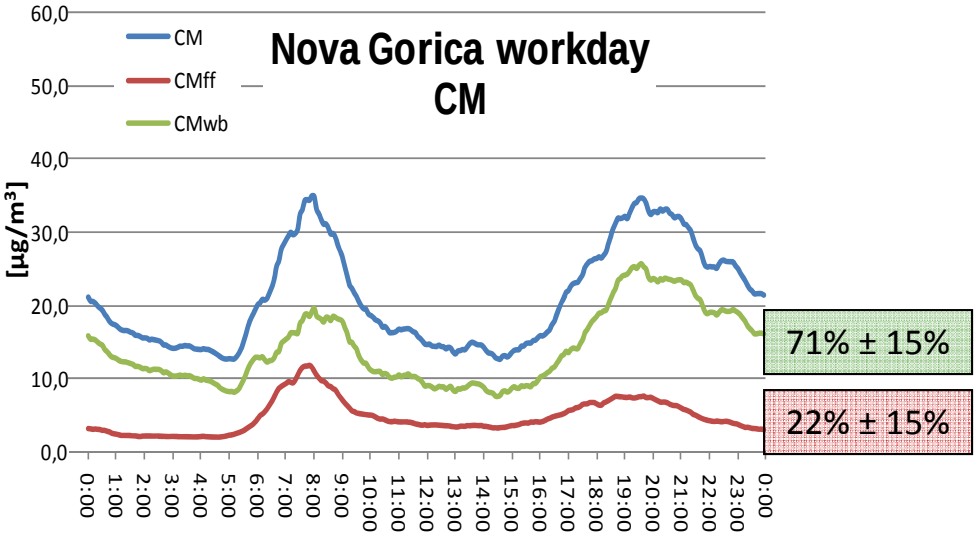
CM reconstruction using C_i – Nova Gorica

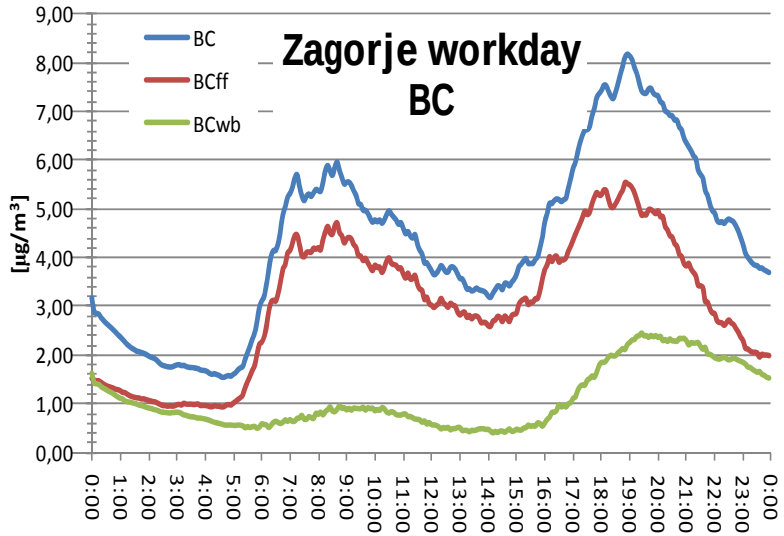


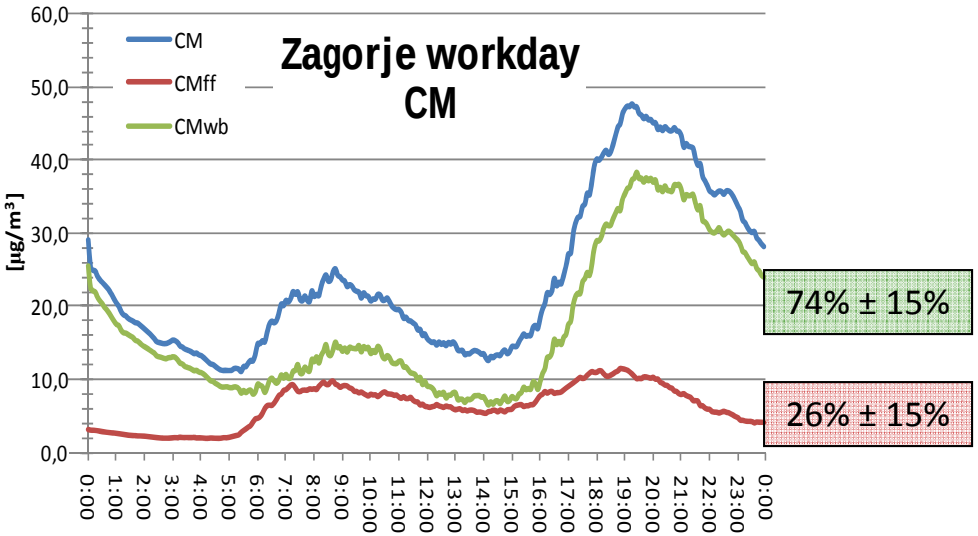
CM reconstruction using C_i – Nova Gorica




Nova Gorica workday
BC
BC
BCff
BCwb
[µg/m³]
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00


Nova Gorica workday
CM
CM
CMff
CMwb
[µg/m³]
60,0
50,0
40,0
30,0
20,0
10,0
0,0
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00
71% ± 15%
22% ± 15%

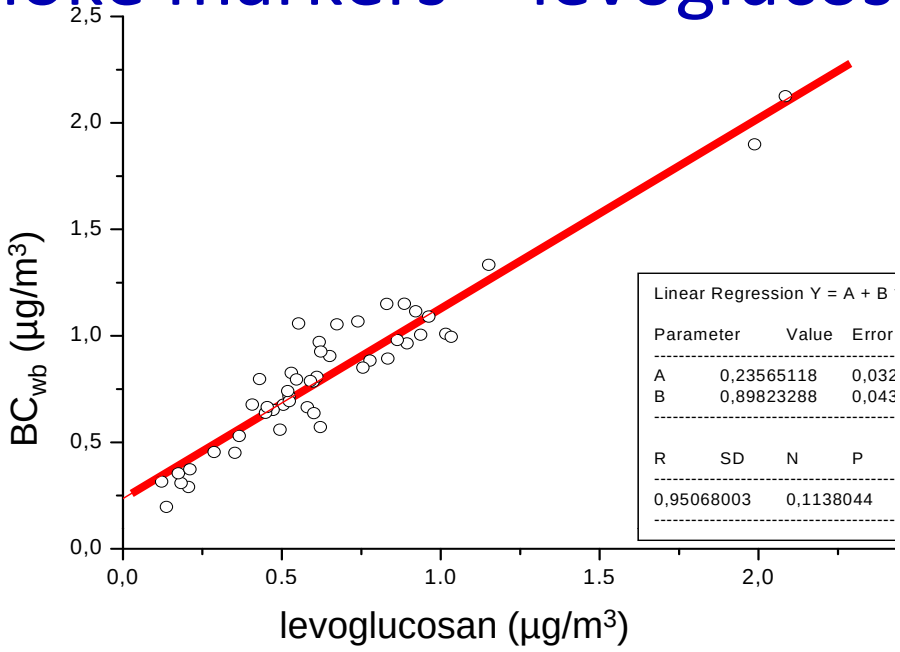

Zagorje workday
BC
BC
BCff
BCwb
[µg/m³]
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00


Zagorje workday
CM
CM
CMff
CMwb
[µg/m³]
60,0
50,0
40,0
30,0
20,0
10,0
0,0
0:00 1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 0:00
74% ± 15%
26% ± 15%

Aerosol

Wood-smoke markers – levoglucosan

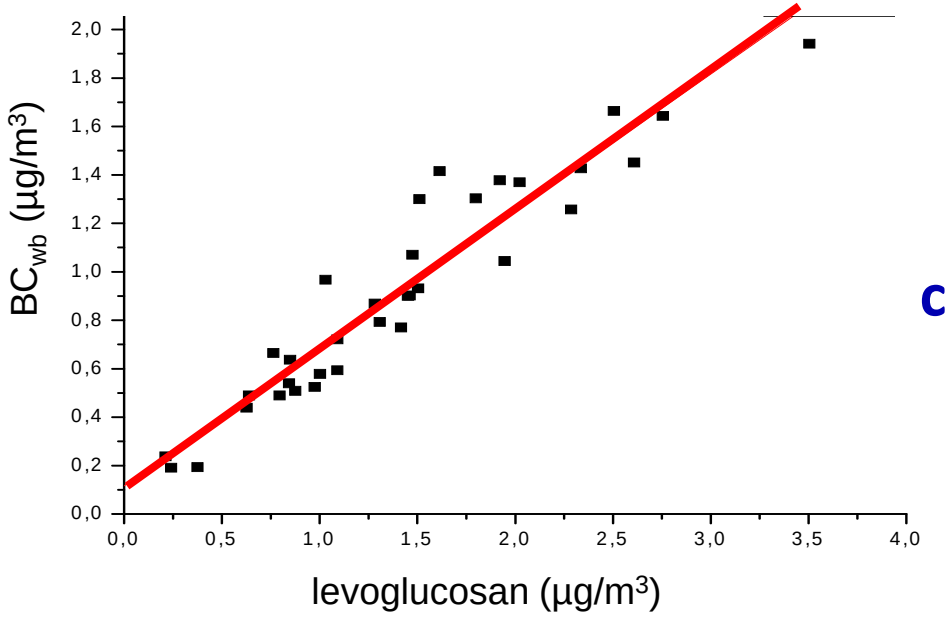
Nova Gorica



beech logwood

Different slopes (=emission factors) can be explained by different biomass fuels!

Zagorje

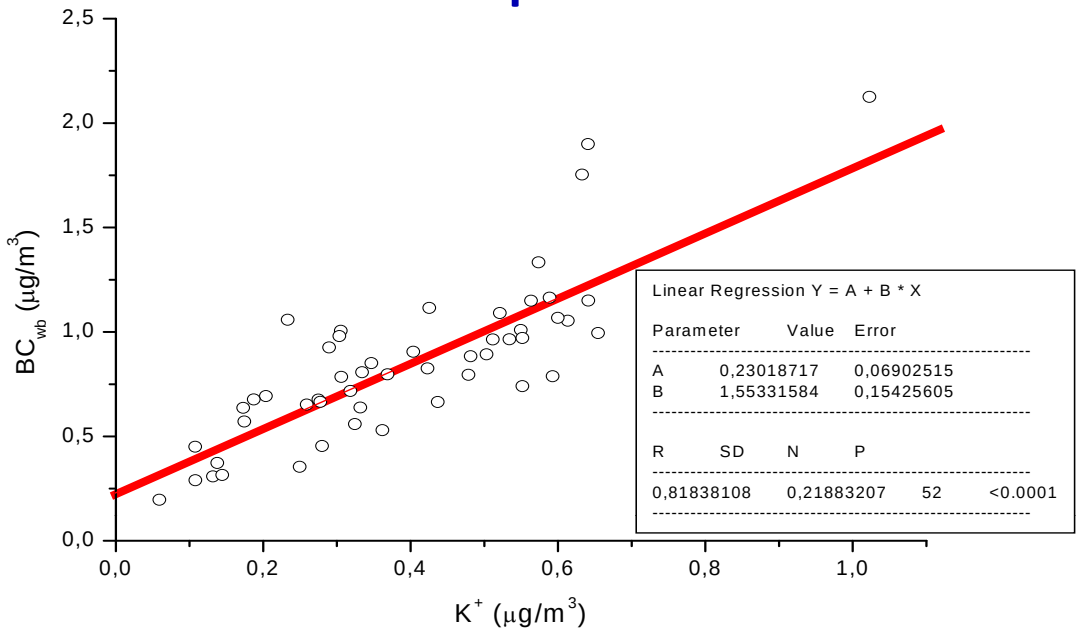


chips, pellets

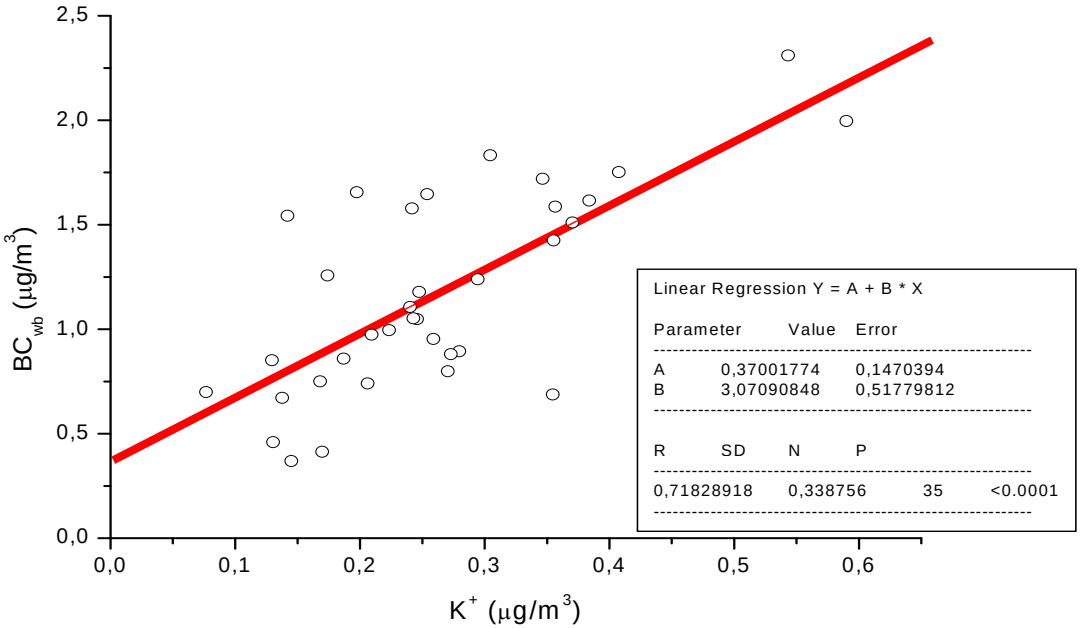
Levoglucosan - ion chromat. EARS

Wood-smoke markers – potassium

Nova Gorica



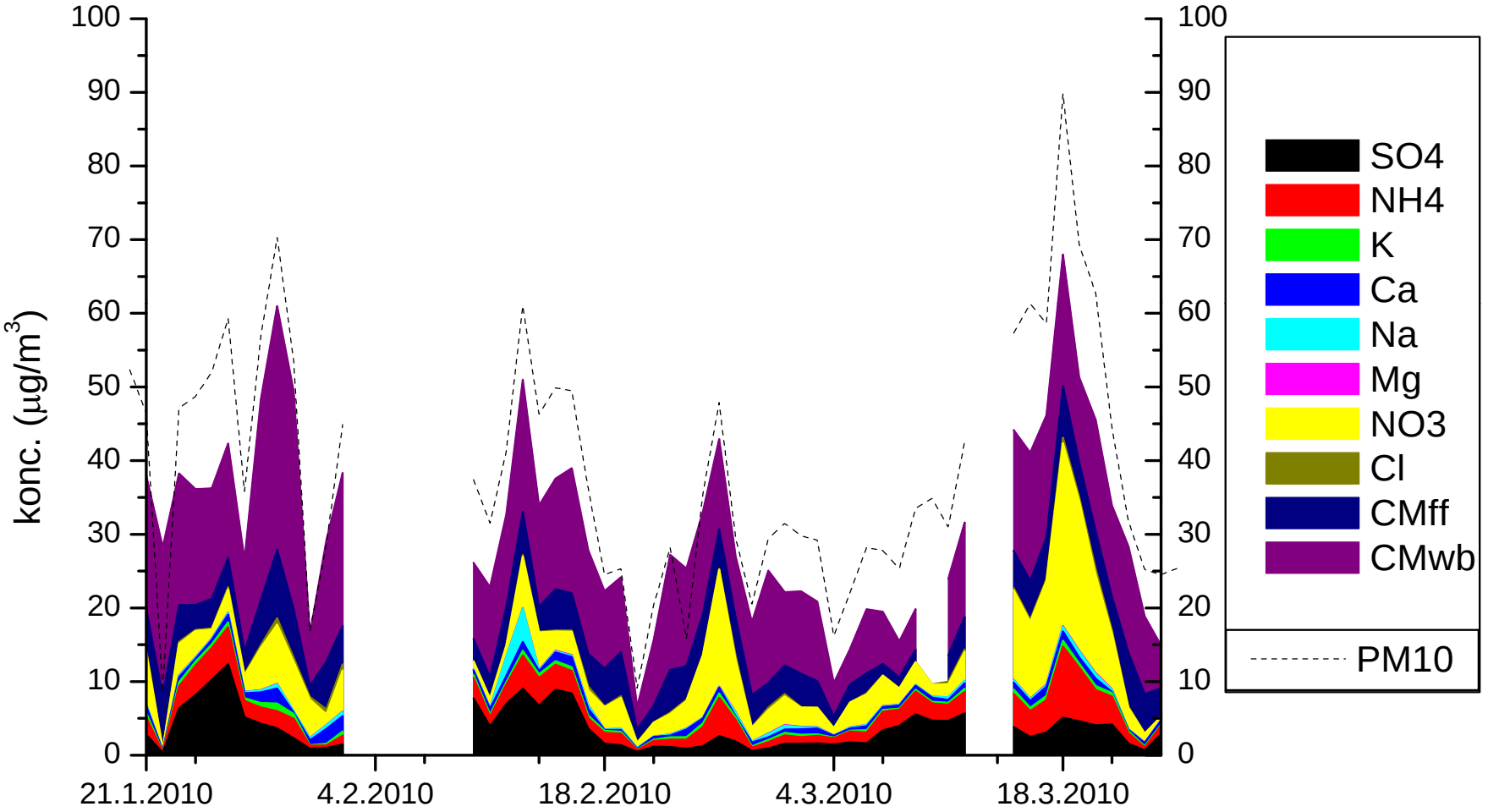
Zagorje



K$^+$ - ion chromat. ARSO

Mass closure – Nova Gorica

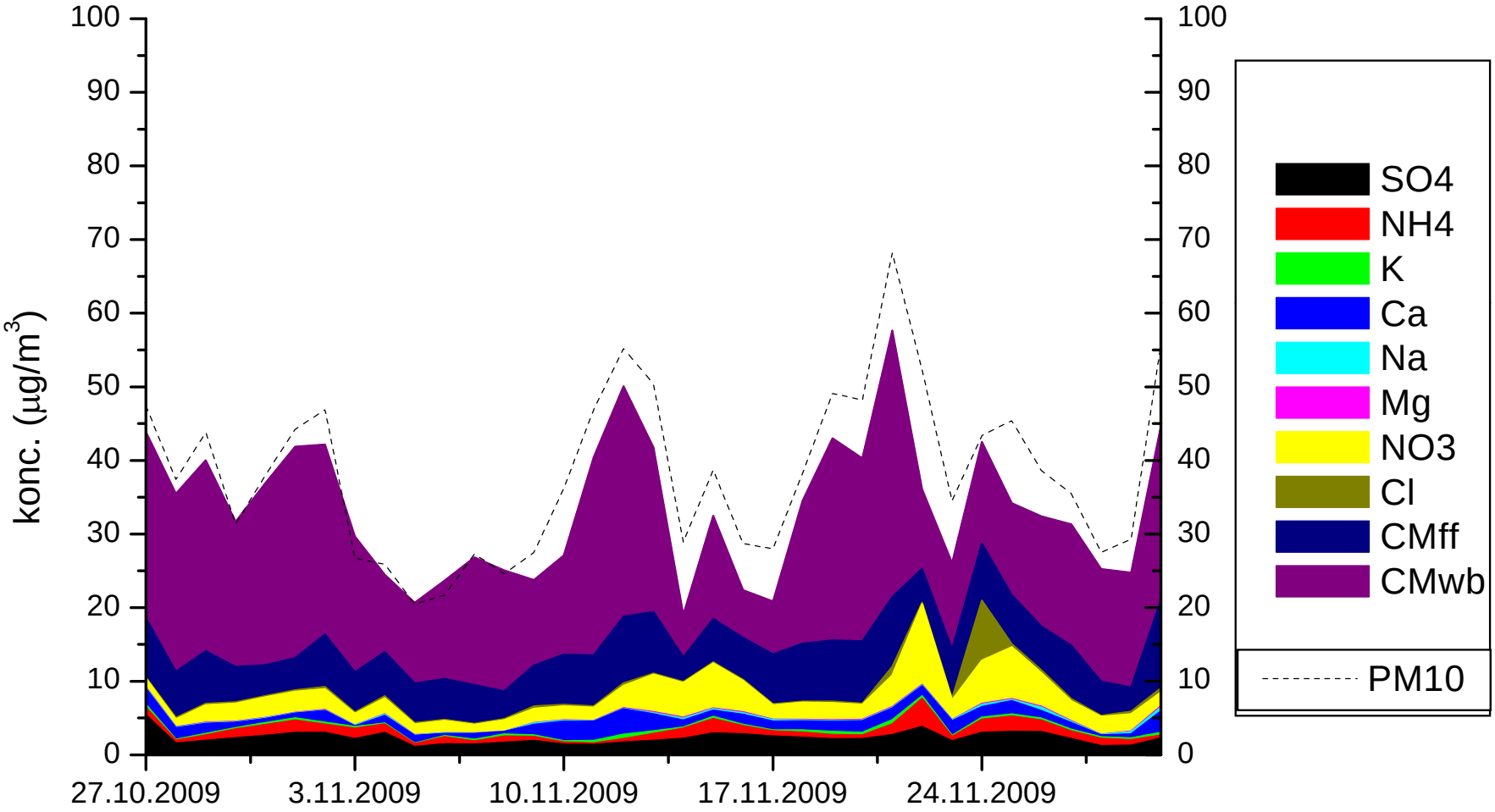
Filter chemical analysis- EARS



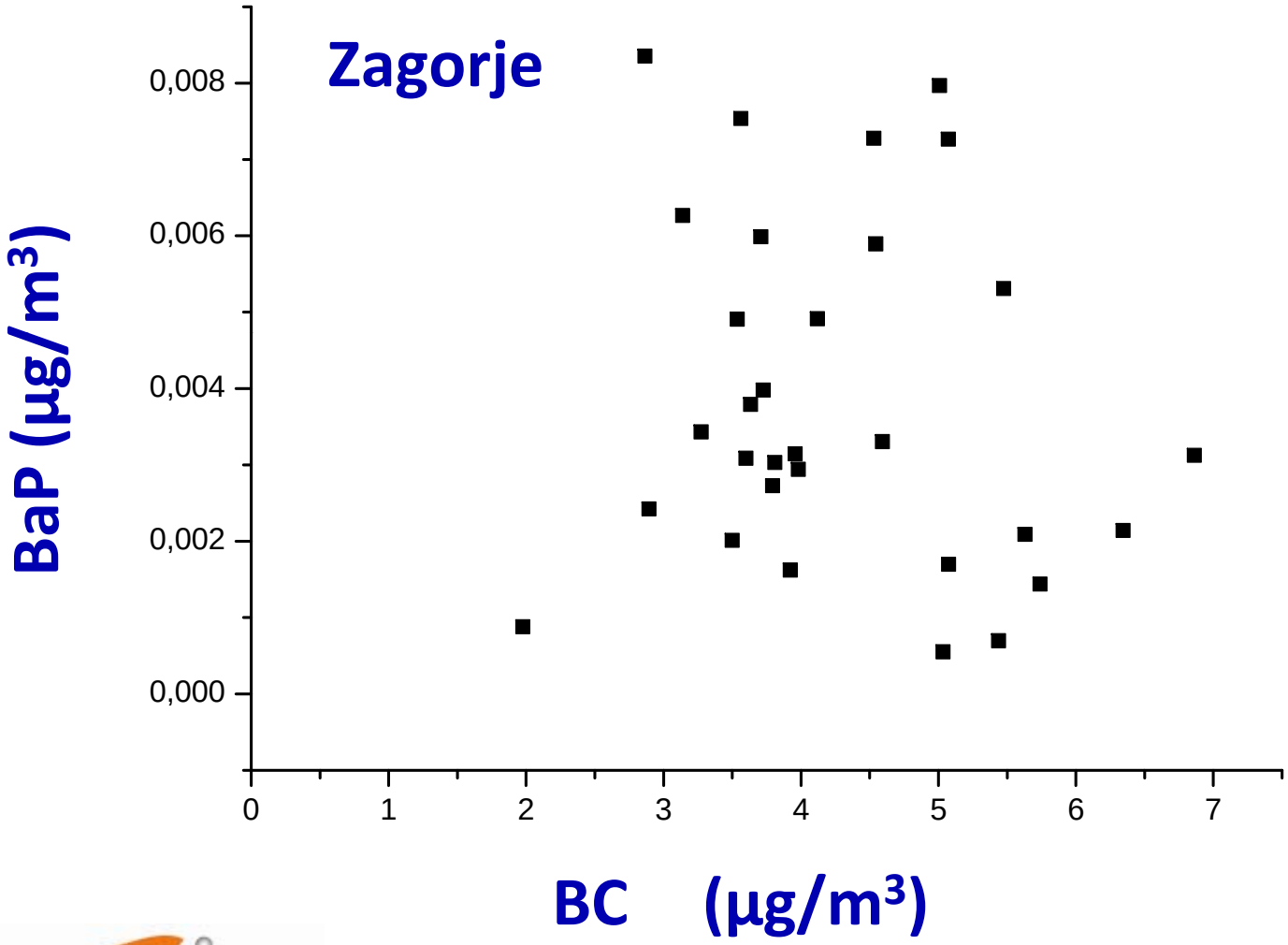
Aerosol

Mass closure - Zagorje

Filter chemical analysis- EARS



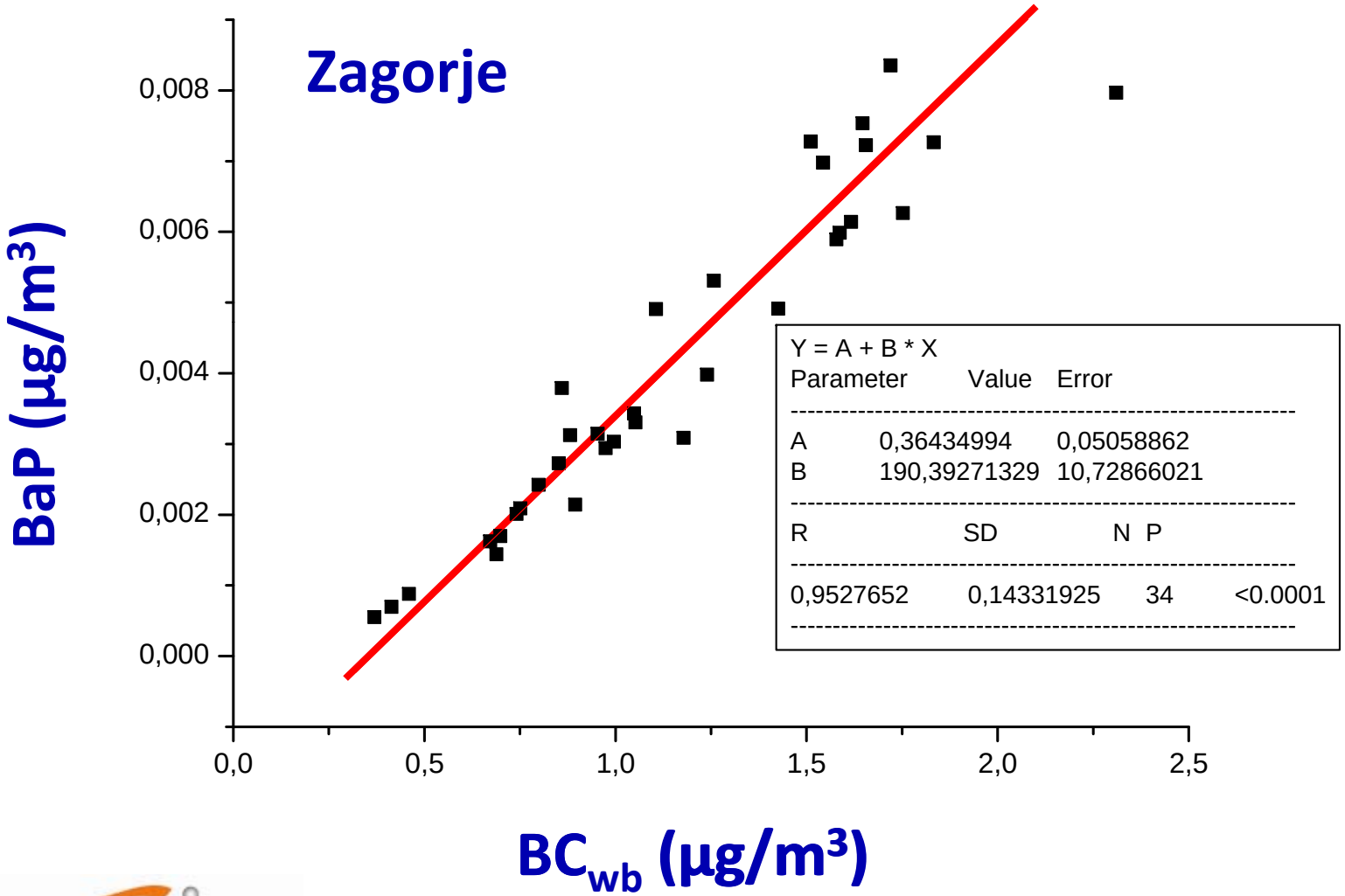
PAH – what is the source?



Aerosol

BaP by GC-MS - EARS

PAH – what is the source?



Aerosol

BaP by GC-MS - EARS

Conclusions

- we can measure **Fossil Fuel** and **Wood-Smoke Black Carbon** with the Aethalometer: less BC from wb than ff
- time resolution is **5 min**
- we can investigate **time evolution** of BC and WS during the day, excellent correlation with markers, PAH source
- **quantitative Wood-Smoke determination** – 24 h TC, yet still high time resolution (15-30 min): more carbonaceous aerosol from wb than ff!

Aerosol

Conclusions (2)

- all this and more - automatically in AE-33 and TC module, under development

AE-33	+	TC
1 min		~ 20 min

Thank you for your attention!
Questions?

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