Measuring BC and BrC with Aethalometers: non-linearities and information there-in

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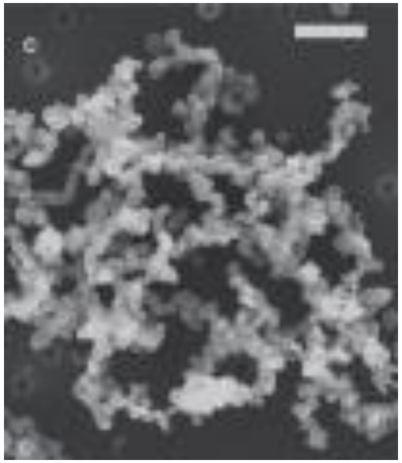
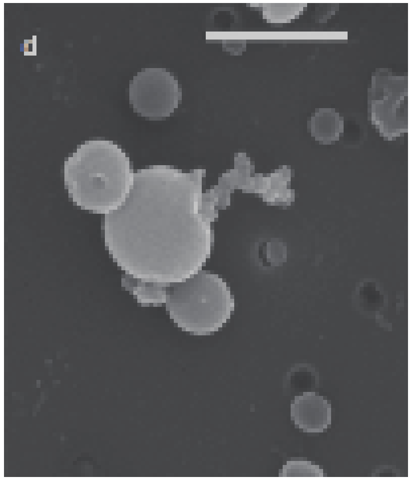
Training School on Black and Brown Carbon, 15-17 January 2018, Ljubljana

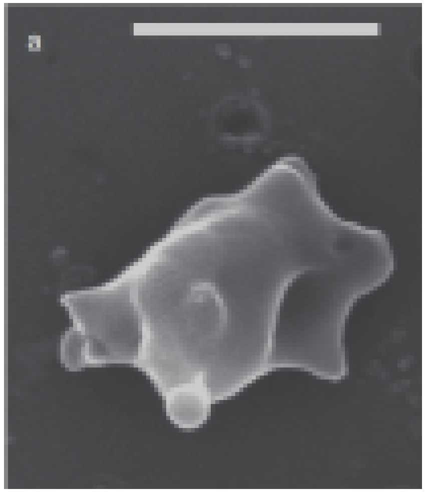
Overview

CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL

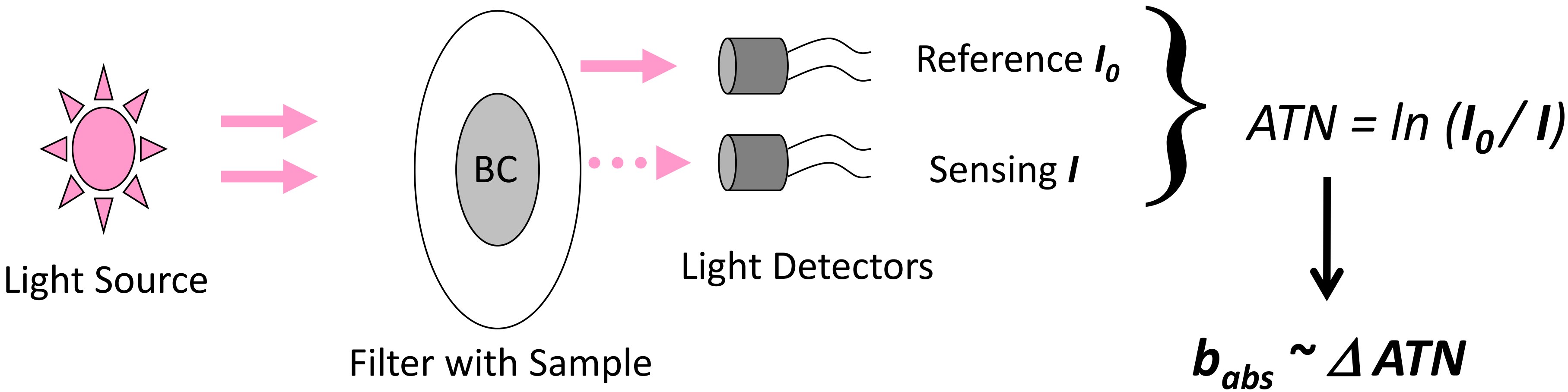
- Measurement of BC and source apportionment
- Filter loading effect
- Dual-spot compensation algorithm
- Investigation of filter loading parameter k
- Application of parameter k for aerosol characterisation







The method



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

$$BC(t) = b_{abs,880nm}(t) / \sigma_{880nm}$$

- Real-time data: **1 s/1 minute**

Source apportionment of BC

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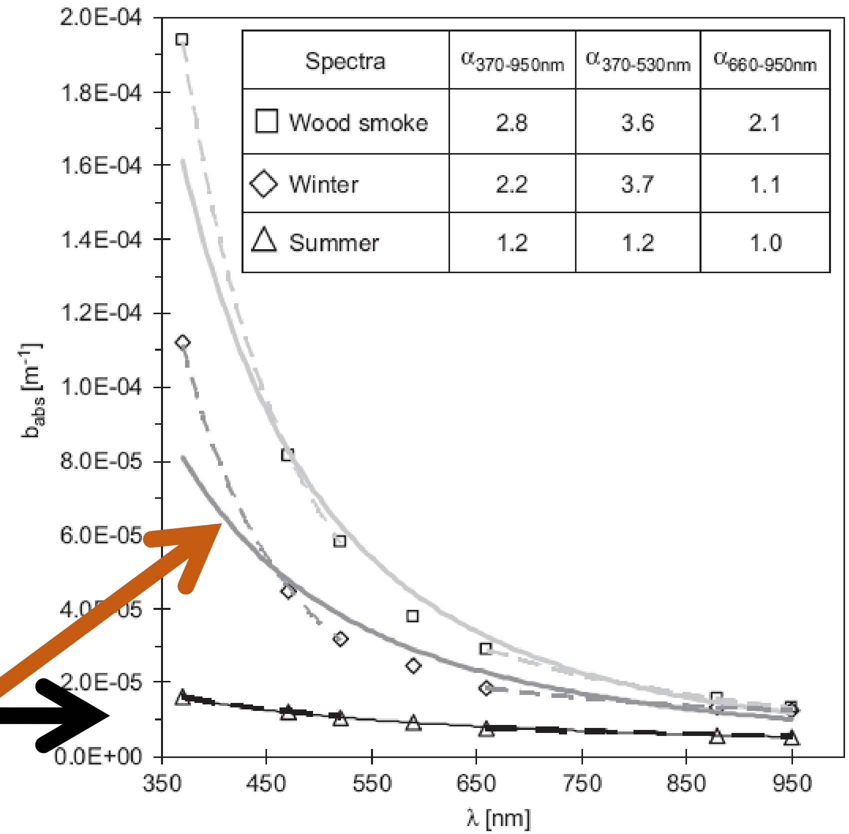
- measure attenuation with the Aethalometer
- absorption coefficient - b_{abs}
- for pure black carbon: $b_{abs} \sim 1/\lambda$
- generalize **Angstrom exponent**:

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

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

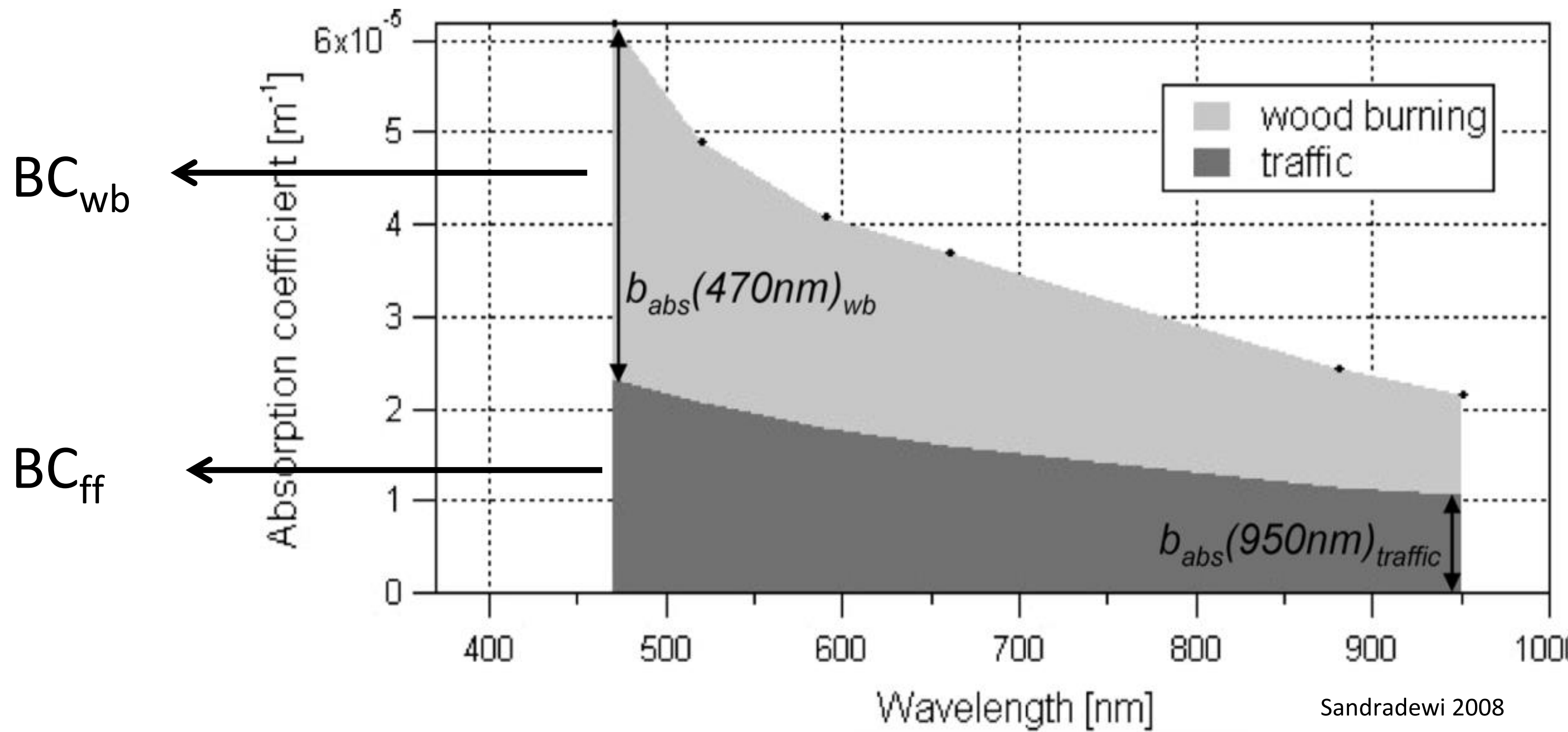
Source apportionment of BC

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

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

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

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

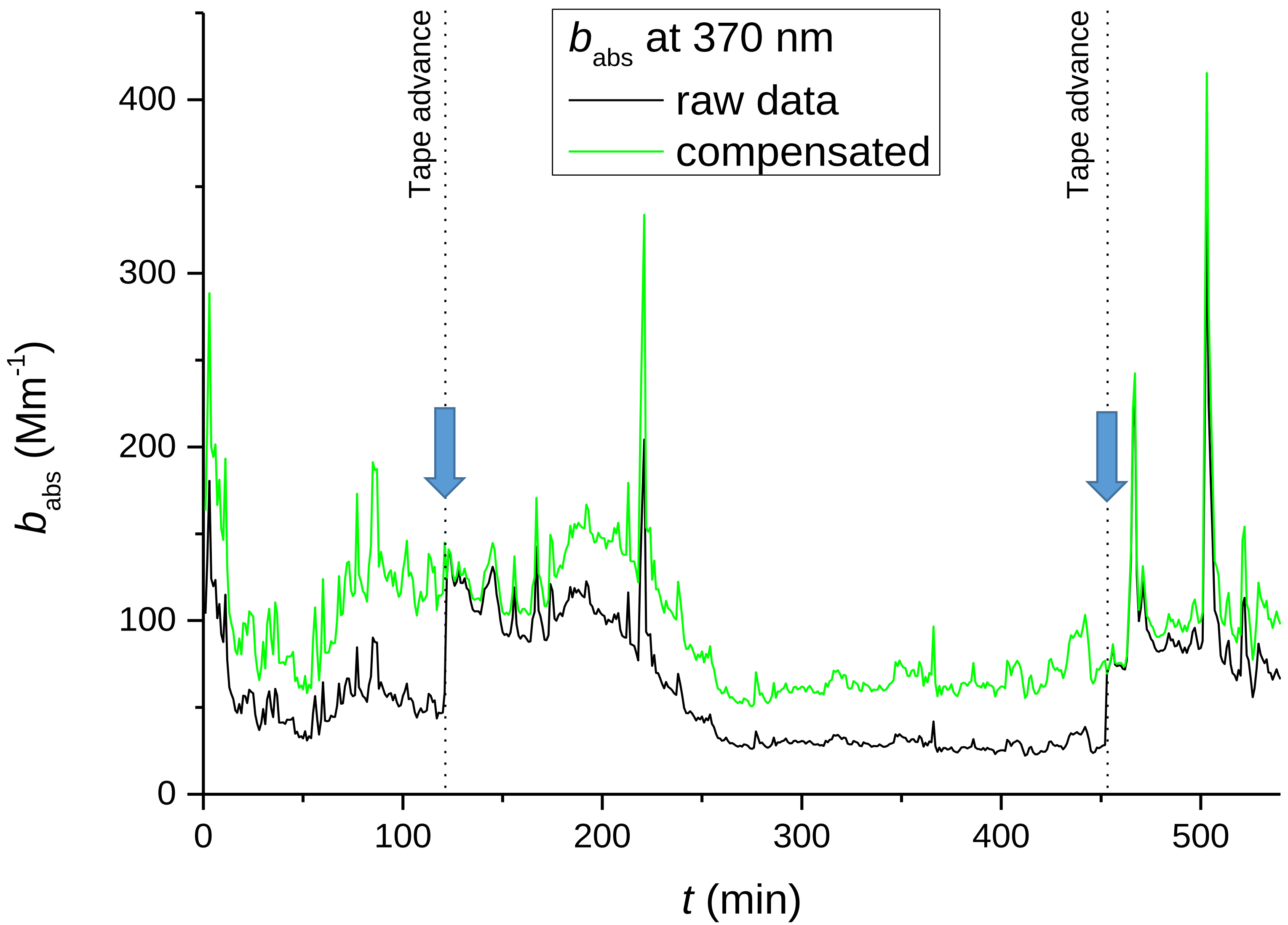


Sandradewi 2008

Filter loading effect

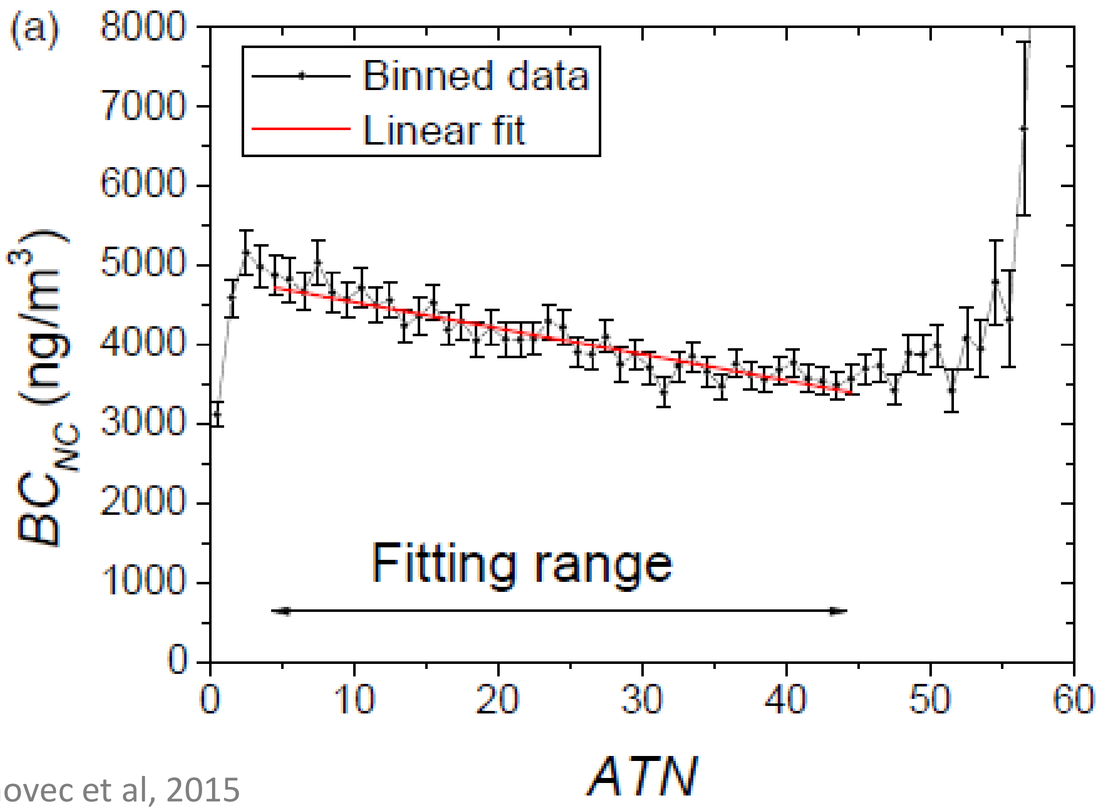
Jumps at tape advances

Drinovec et al, 2015



Filter loading effect

BC vs. ATN – reduction of the sensitivity
-> caused by change in light distribution in the loaded filter

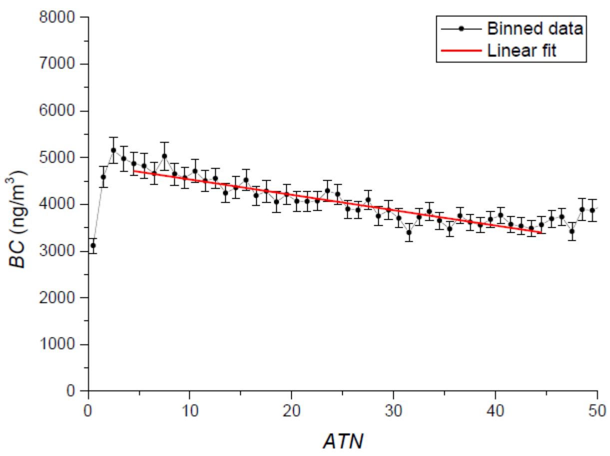


Drinovec et al, 2015

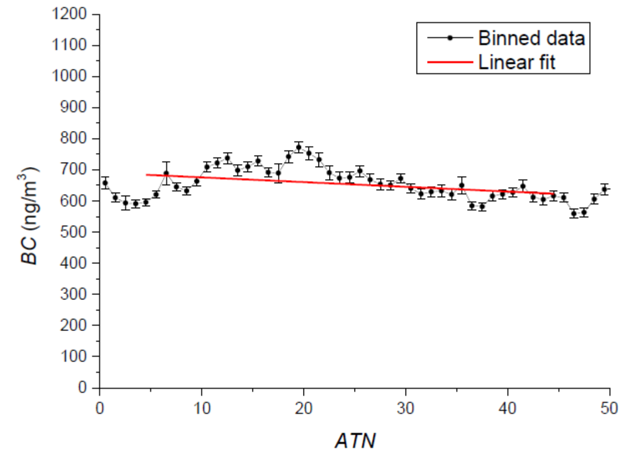
Filter loading effect

BC vs. ATN – FLE varies for different locations

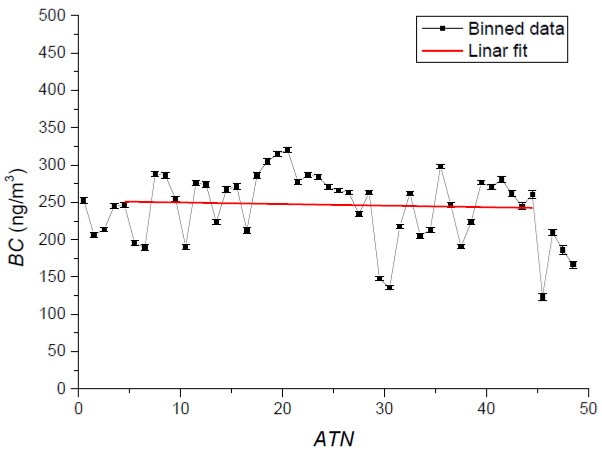
Drinovec et al, 2015



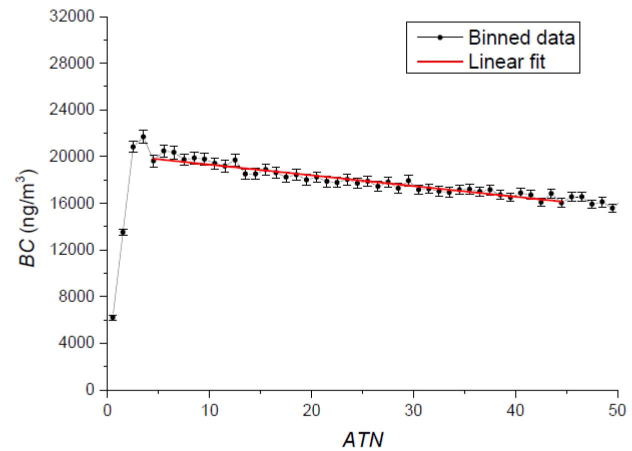
Klagenfurt (Austria) - roadsite



Anaheim (USA) – urban

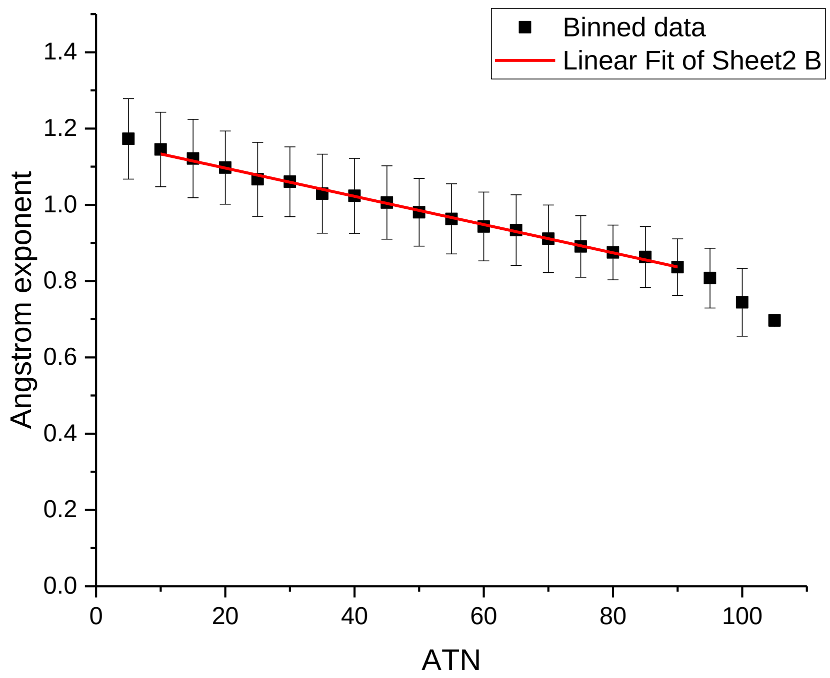


Sonnblick (Austria) – regional background



Kathmandu (Nepal) – urban

FLE infuences source apportionment

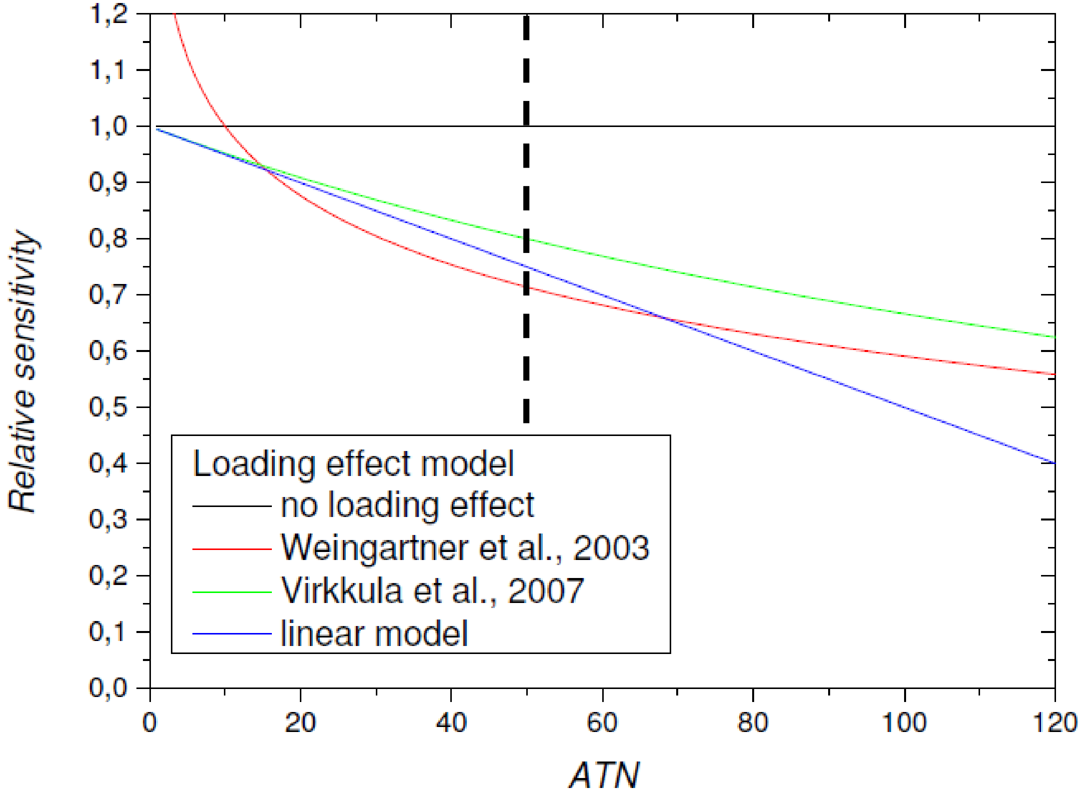


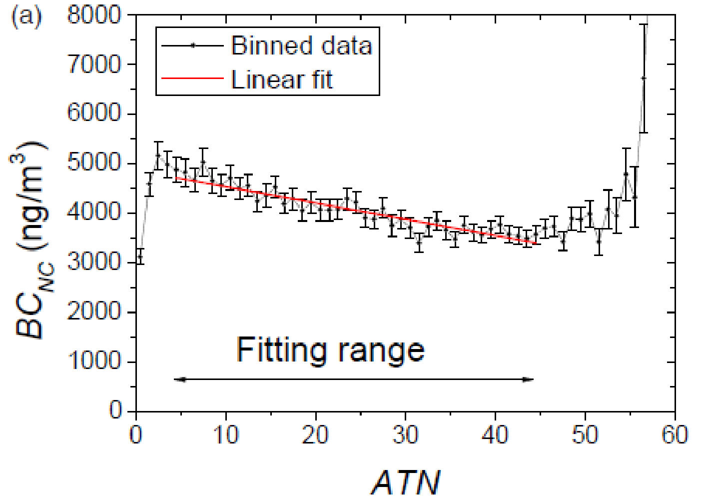
Observed Angstrom exponent is strongly impacted by FLE!

	Average Angstrom exponent	Biomass burning (%)
True value	1.2	14
FLE impacted	1	0

Aethalometer data needs to be compensated for FLE!

FLE - models





Weingartner model optimised for AE31
Linear model is used in AE33
Virkkula model is similar to the linear model

Drinovec et al, 2015

Filter loading effect - summary

FLE quantiffication
- Jumps at tape advances
- BC vs. ATN method

FLE influneces determination of BC and Angstrom exponent
-> compensation is needed

FLE varies between different locations (and times of year)
-> FLE must be measured

FLE models
- Weingartner et al., 2003
- Vitkkula et al., 2007
- Drinovec et al., 2015

Compensation methods
- AE31 -> offline compensation
- AE33 -> online compensation

Dual-spot compensation algorithm

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Because of variation of FLE it needs to be measured!!

Atmos. Meas. Tech., 8, 1965–1979, 2015
www.atmos-meas-tech.net/8/1965/2015/
doi:10.5194/amt-8-1965-2015
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Atmospheric Measurement Techniques
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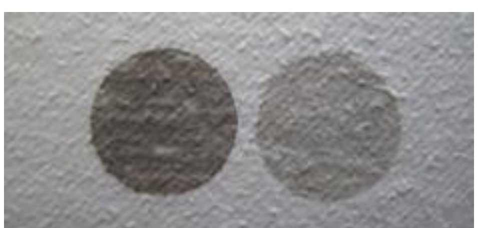
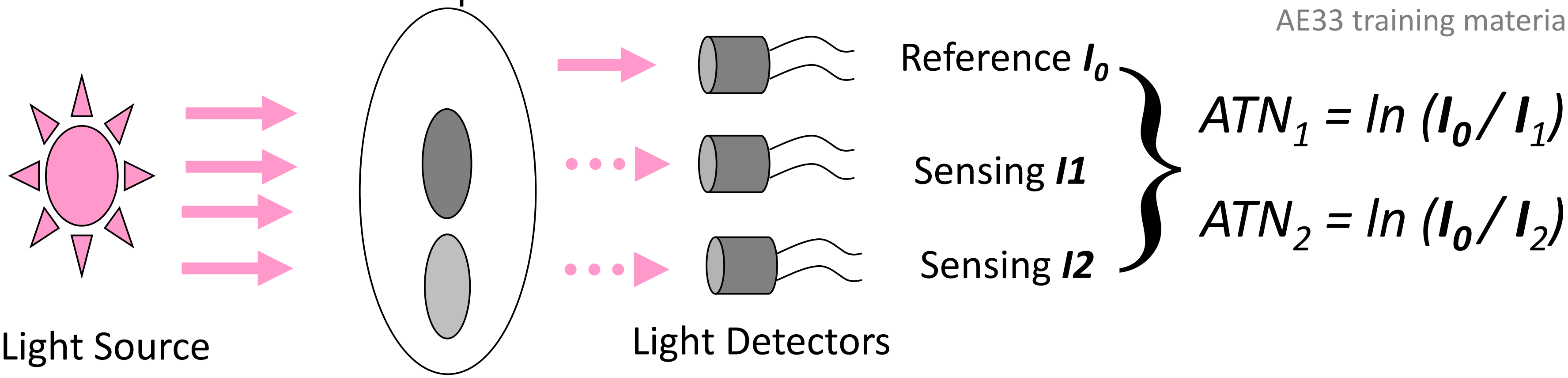
The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation

L. Drinovec[1], G. Močnik[1], P. Zotter[2,*], A. S. H. Prévôt[2], C. Ruckstuhl[3], E. Coz[4], M. Rupakheti[5], J. Sciare[6], T. Müller[7], A. Wiedensohler[7], and A. D. A. Hansen[1,8]



Determination of compensation parameter k

AE33 training materials

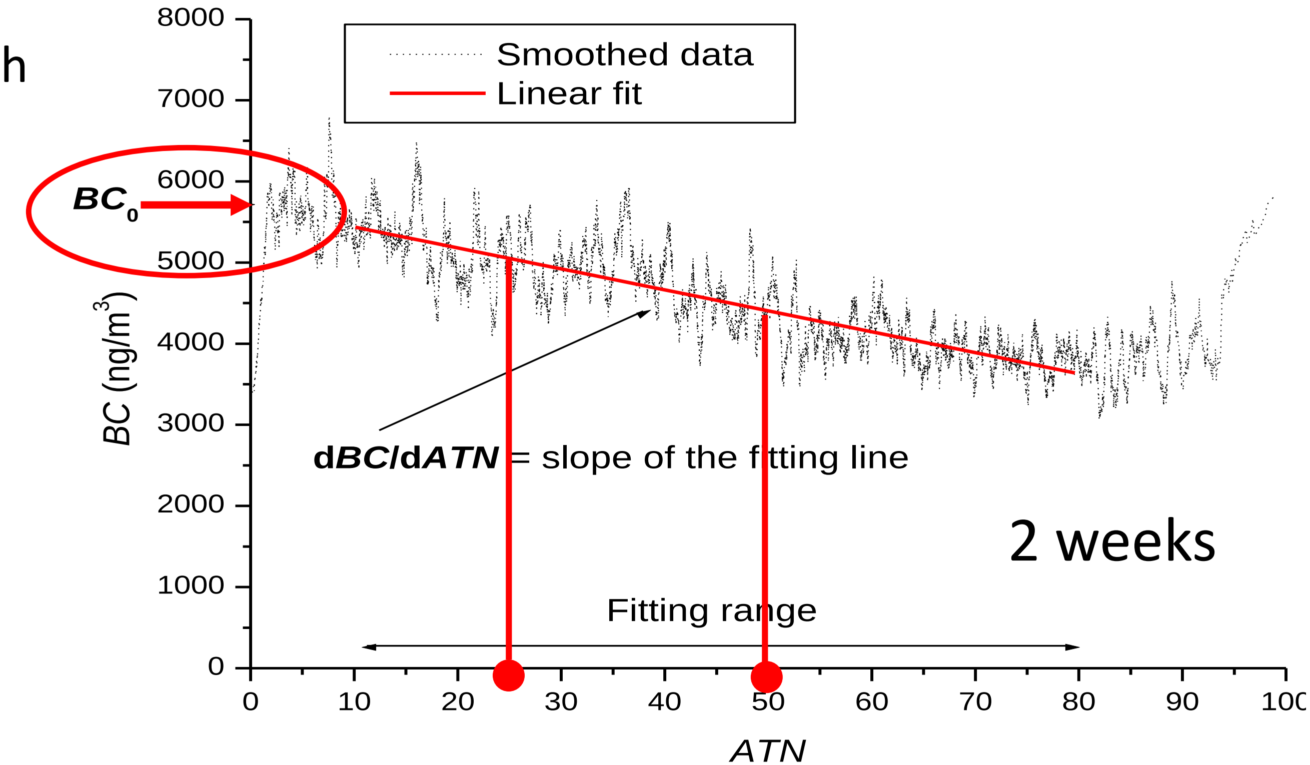


Two parallel spots with different flow, therefore

different loading and attenuation.

Calculate loading compensated **BC** and ***slope***!

$BC = BC_1/(1 - k*ATN_1)$



Dual-spot compensation algorithm

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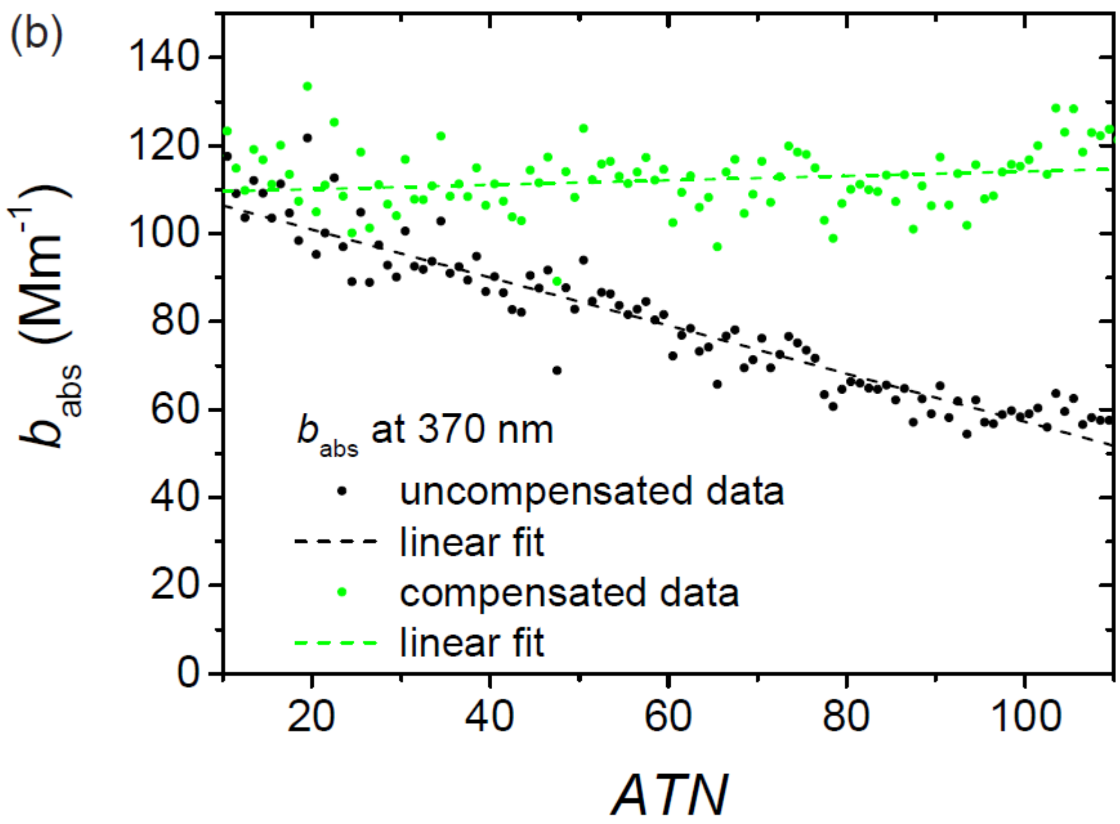
1. Determination of compensation parameter $k(\lambda)$
2. Calculation of compensated *BC*: $BC = BC_1/(1 - k*ATN_1)$



Dual-spot compensation algorithm

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Compensation minimises the slope of BC(ATN) and α(ATN)

(a)

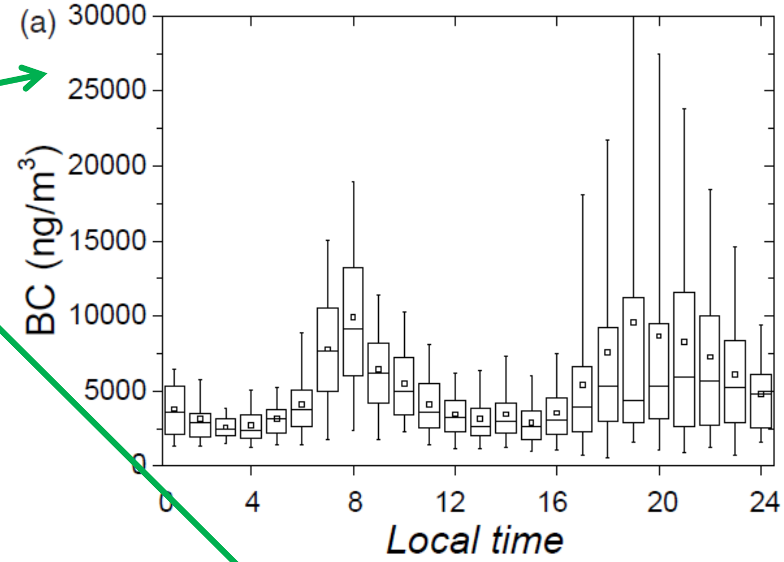
Instrument	BC_0 – nc. ($ng\,m^{-3}$)	$\overline{BC}$ – nc. ($ng\,m^{-3}$)	$\overline{BC}$ – comp. ($ng\,m^{-3}$)	Relative slope BC(ATN) – nc.	Relative slope BC(ATN) – comp.
AE31	4905 ± 193	4459	4831	-0.0051 ± 0.0017	-0.0006 ± 0.0018
AE33 quartz	4909 ± 86	4379	5015	-0.0053 ± 0.0008	0.0003 ± 0.0008
AE33 TFE	4888 ± 89	4059	4960	-0.0069 ± 0.0007	-0.0003 ± 0.0008

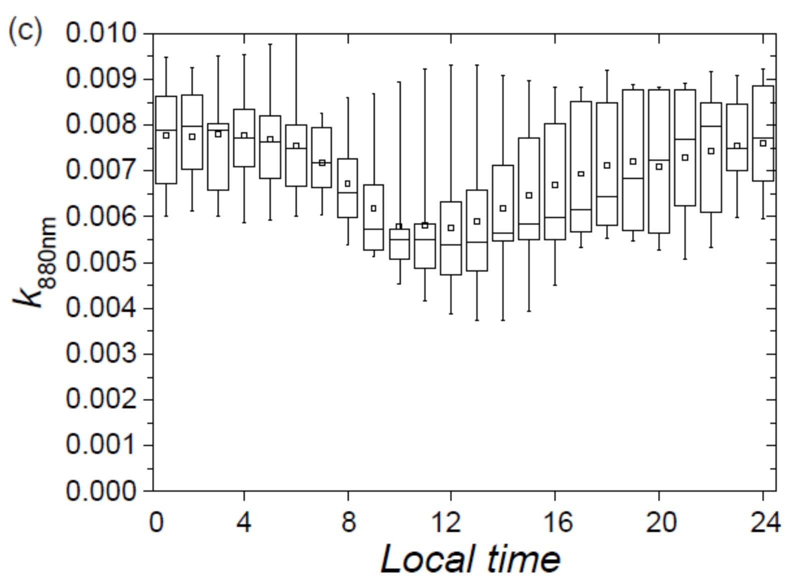
(b)

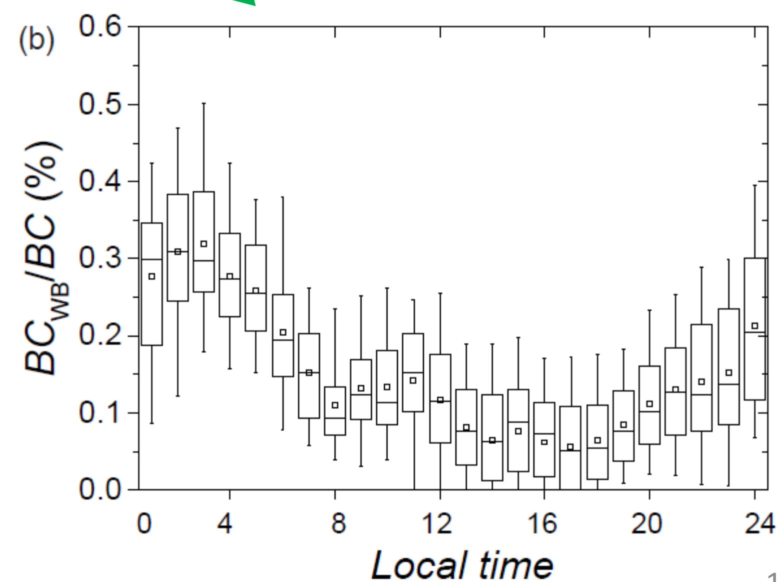
Instrument	α_0 – nc.	$\overline{\alpha}$ – nc.	$\overline{\alpha}$ – comp.	Relative slope α vs. ATN – nc.	Relative slope α vs. ATN – comp.
AE31	1.22 ± 0.01	1.07	1.29	-0.0025 ± 0.0002	-0.0010 ± 0.0002
AE33 quartz	1.26 ± 0.03	1.09	1.23	-0.0026 ± 0.0001	-0.0002 ± 0.0001
AE33 TFE	1.18 ± 0.02	0.97	1.21	-0.0033 ± 0.0003	0.0009 ± 0.0001

Compensated data

- Correct BC
- Correct BC source apportionement
- Compensation parameter k





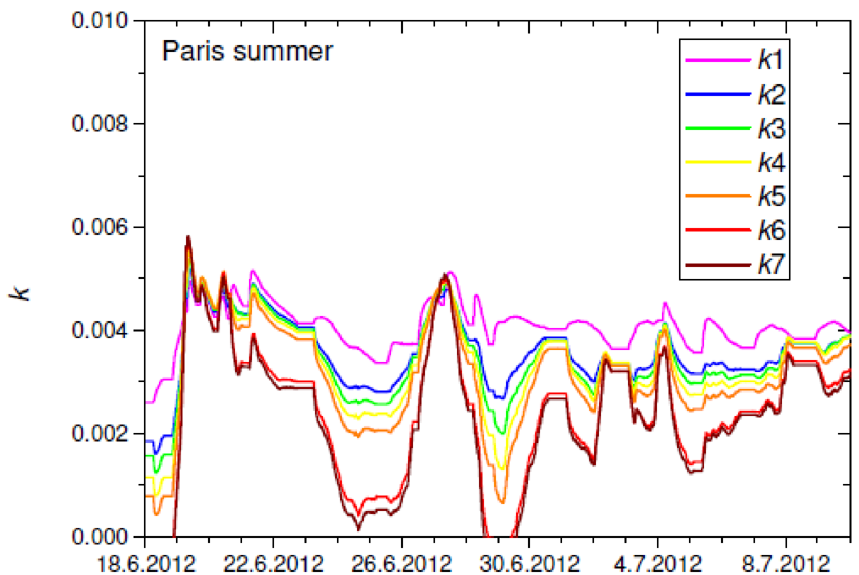


Dual-spot compensation algorithm - summary

- Dual-spot algorithm allows for online compensation for FLE
- In practice the effects of FLE are significantly reduced.
- Online compensation allows for real-time source apportionment of BC
- Dual-spot algorithm is sensitive to perturbations

  - Instruments should be well maintained

  - Data needs to be checked for correct compensation
- Compensation parameter k represents an additional parameter for characterisation of aerosols.



Drinovec et al, 2017

Investigation on parameter k

Atmos. Meas. Tech., 10, 1043–1059, 2017
www.atmos-meas-tech.net/10/1043/2017/
doi:10.5194/amt-10-1043-2017
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Atmospheric Measurement Techniques
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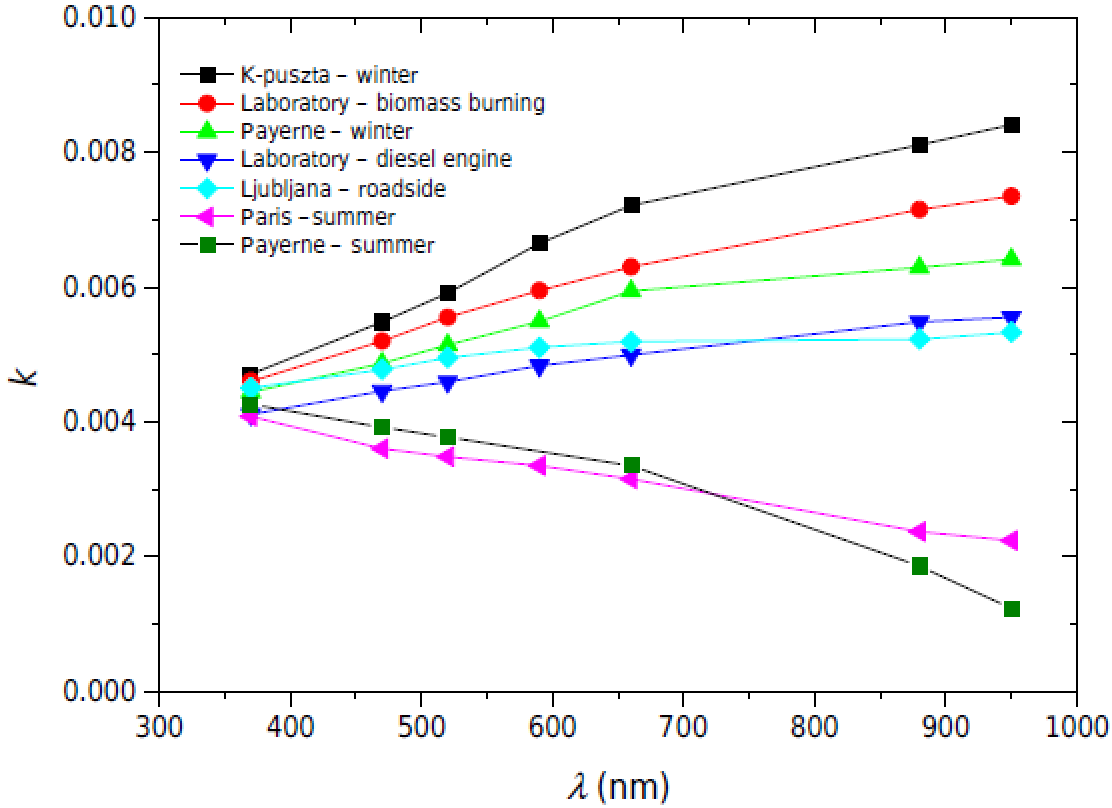
The filter-loading effect by ambient aerosols in filter absorption photometers depends on the coating of the sampled particles

Luka Drinovec[1,2], Asta Gregorič[3], Peter Zotter[4,a], Robert Wolf[4], Emily Anne Bruns[4], André S. H. Prévôt[4], Jean-Eudes Petit[5,6,b], Olivier Favez[5], Jean Sciare[6,7], Ian J. Arnold[8,c], Rajan K. Chakrabarty[8,d], Hans Moosmüller[8], Agnes Filep[9], and Griša Močnik[1,2]

Parameter k – spectral fingerprint



Ambient - winter

Biomass burning

Diesel exhaust, roadside

Ambient - summer

- Big variability of parameter k in the infra-red

One year time series of parameter k

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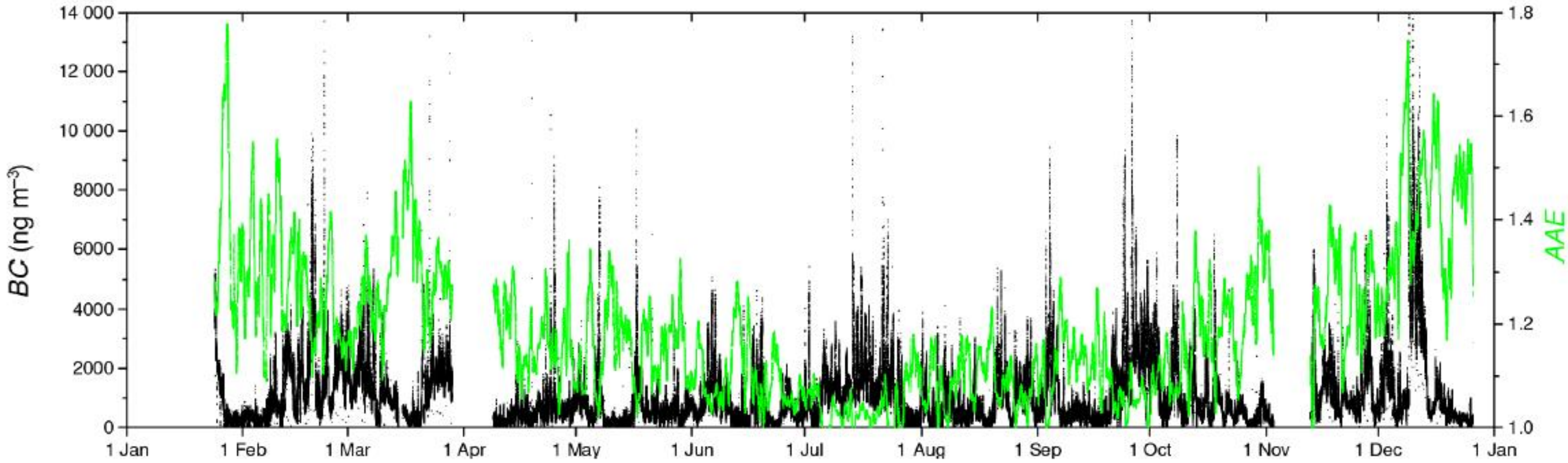


Figure 2. Black carbon mass concentration and AAE measured at the Paris urban background site (SIRTA observatory) during 2013.

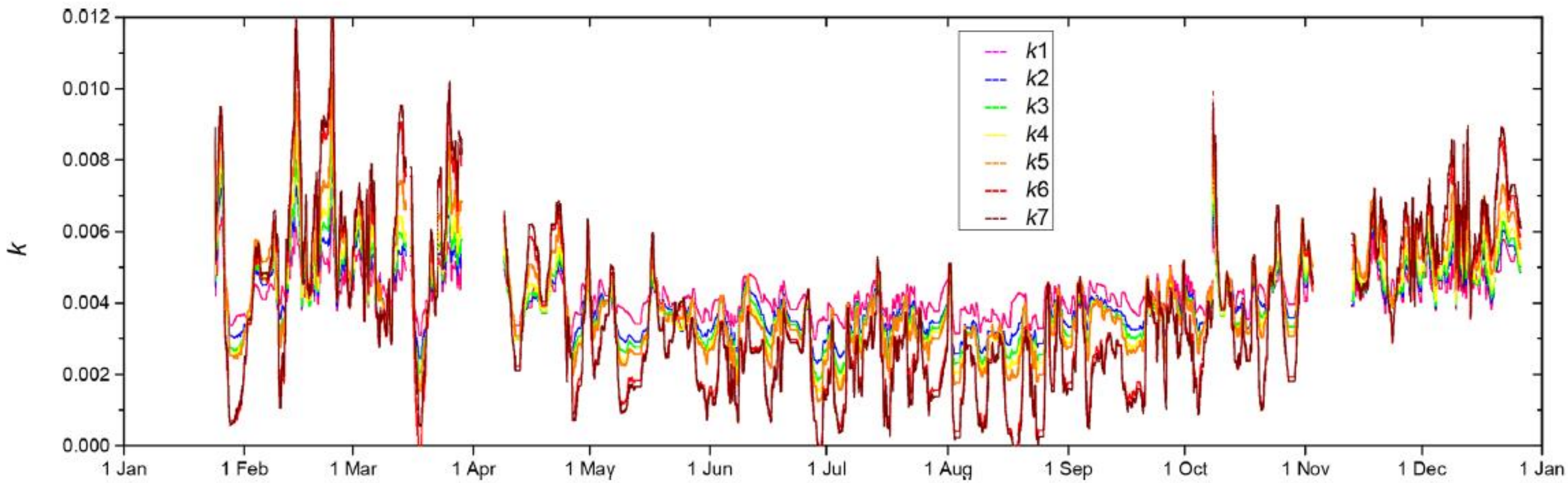
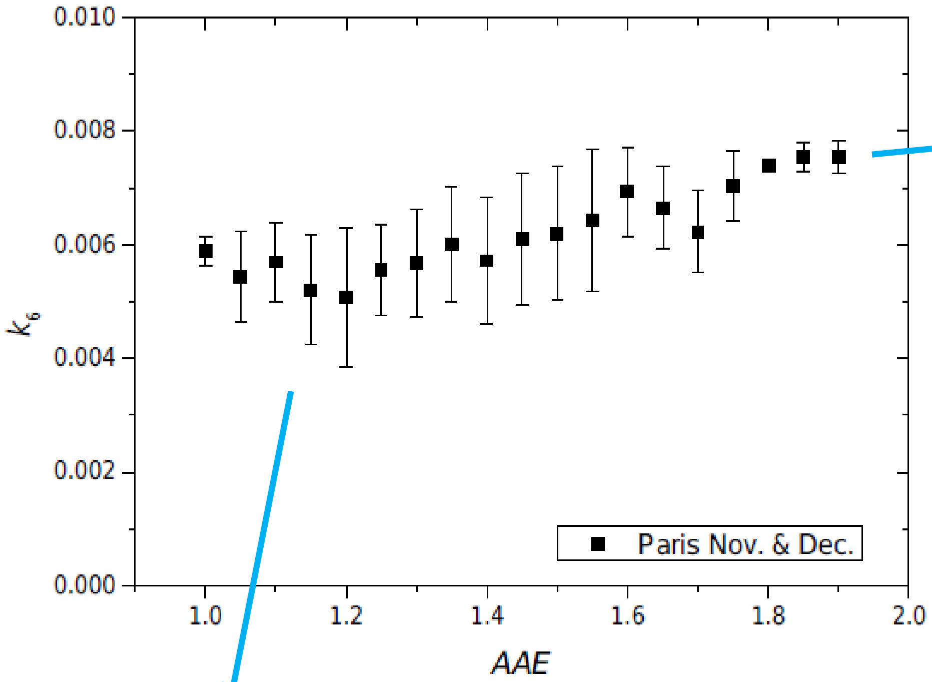
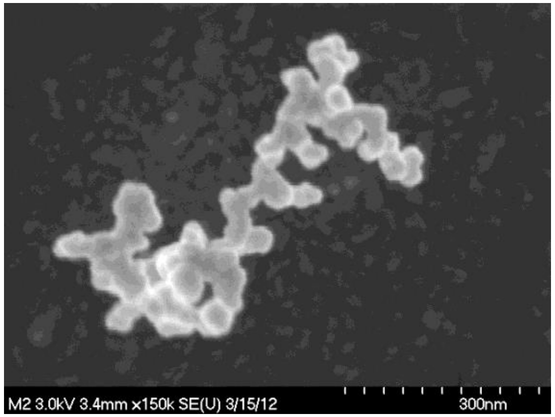


Figure 3. Filter-loading parameter *k* measured at the Paris urban background site (SIRTA observatory) in 2013.

Variability of k_6 during winter

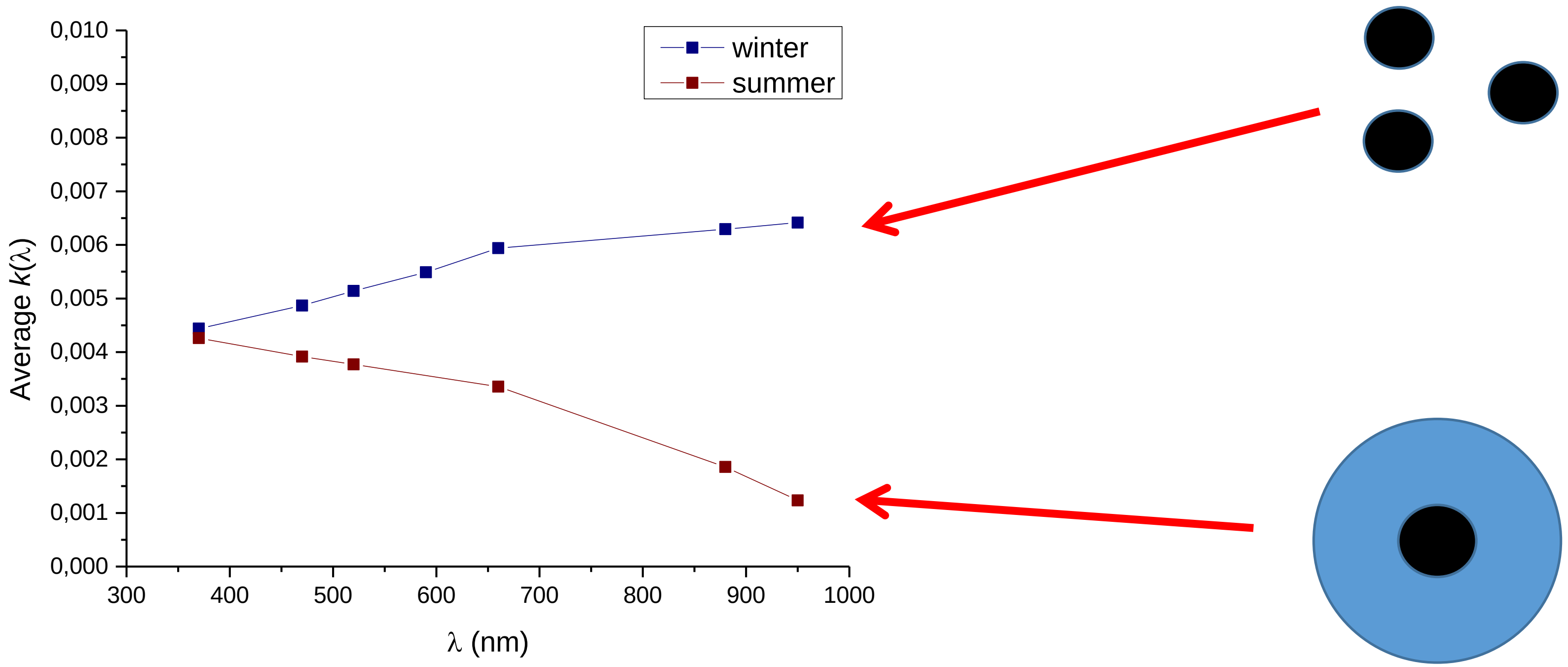




Biomass burning -> big BC particles

Diesel exhaust -> small BC particles

Summer-winter variabilitiy of k

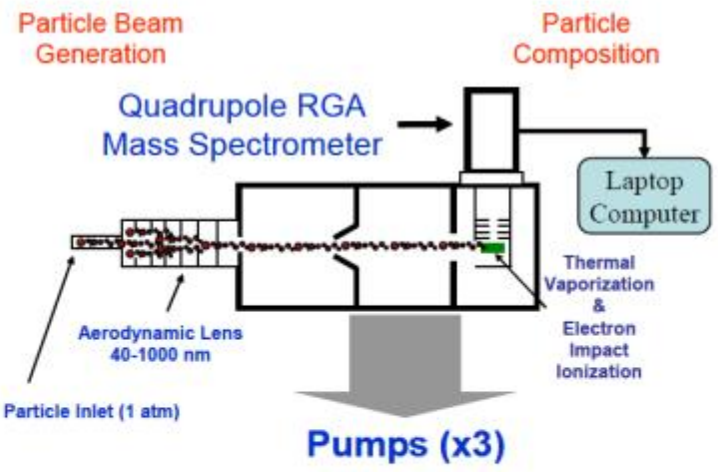


Is it the particle coating responsible for this variability?

Coating factor

Coating factor (*CF*) – ratio between the sum of nonrefractory aerosol mass to *BC*:

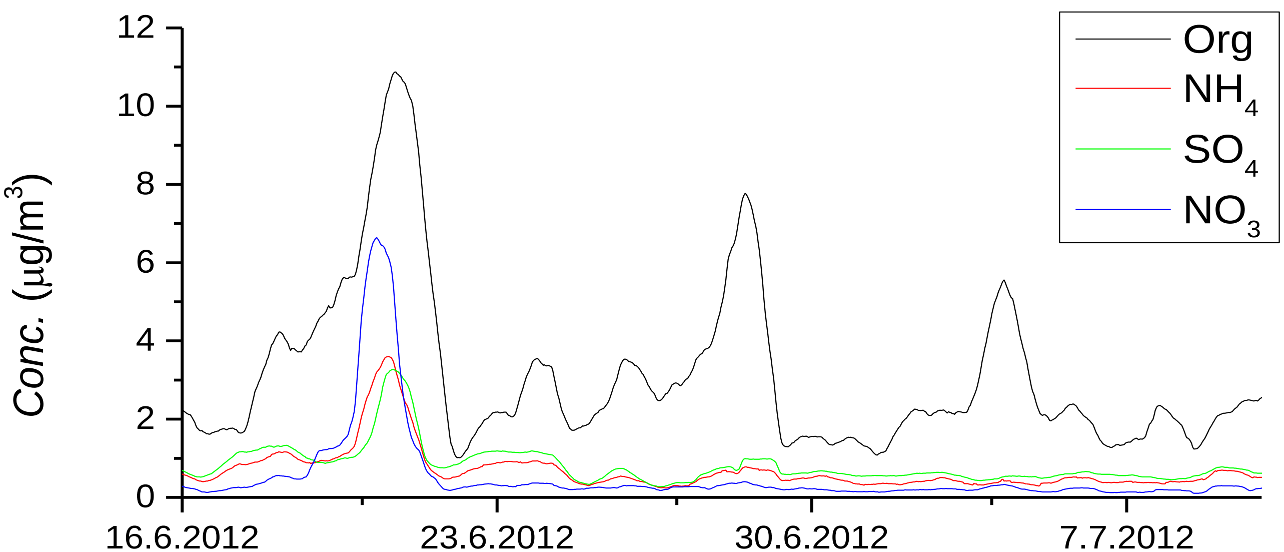
$$CF = (Org + NH_4 + SO_4 + NO_3)/BC$$



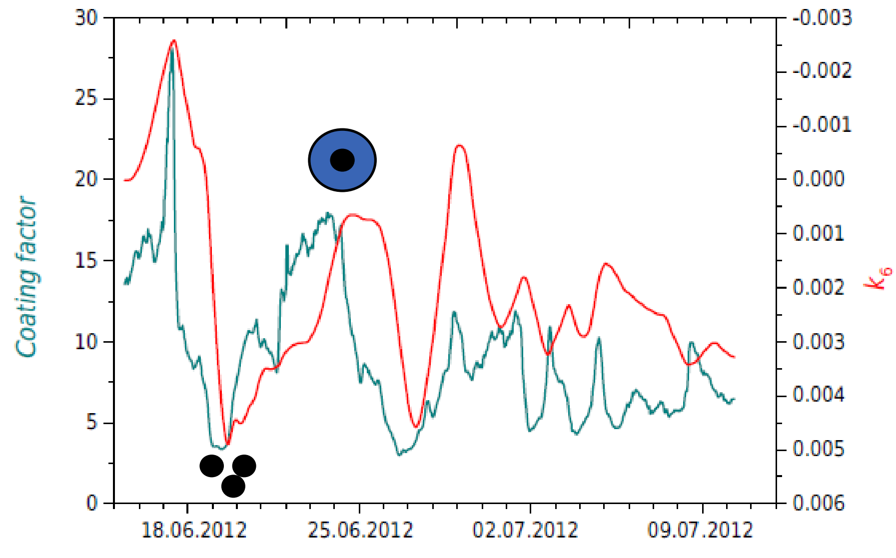
Aerosol mass spectrometers:

ACSM & AMS (Aerodyne)

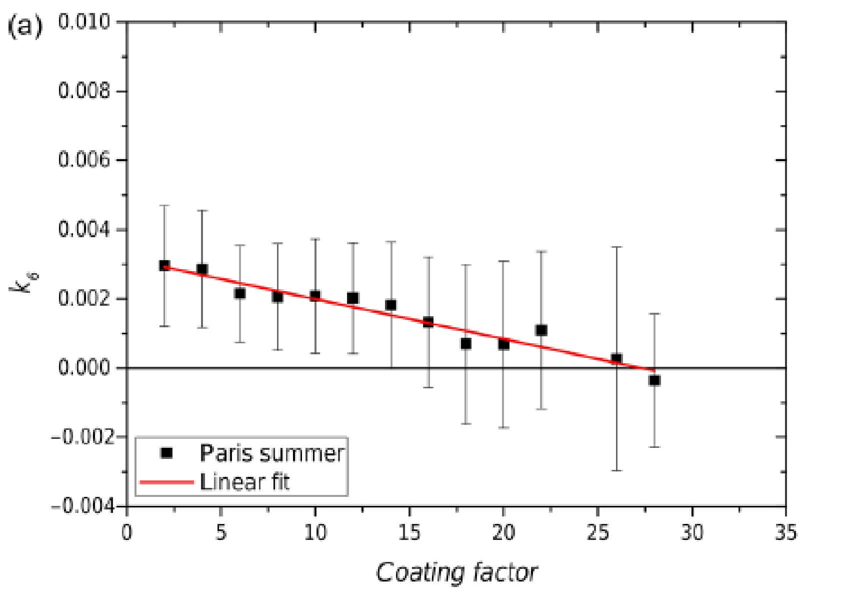
-> Aerosol chemical composition is obtained



Coating factor – Paris summer



Coating factor represents a material potentially available for coating of black carbon cores

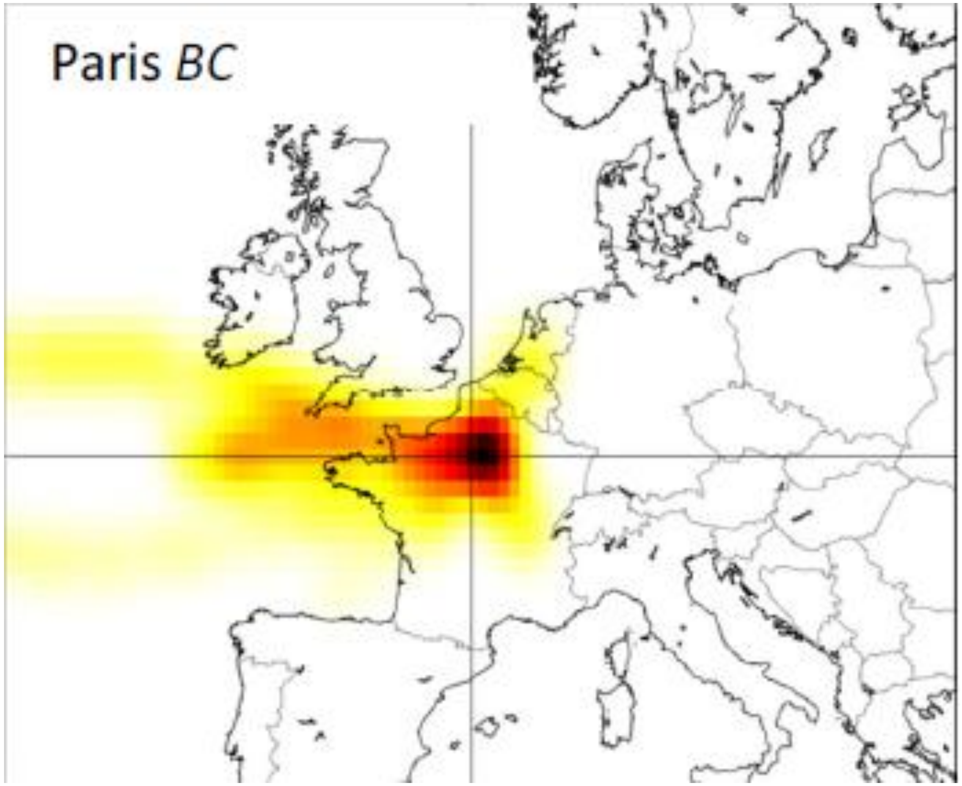


During summer parameter k_6 is well correlated with the coating factor

Backtrajectory analysis

PSCF = Potential Source Contribution Function

- Probability for an air parcel to be responsible for high concentration at the measurement site
- Calculated using 72h HYSPLIT backtrajectories that at Sirta, 500 m a.g.l.



Most of BC comes from local sources north-east from the station.

There is also some regional transport.

Backtrajectory analysis

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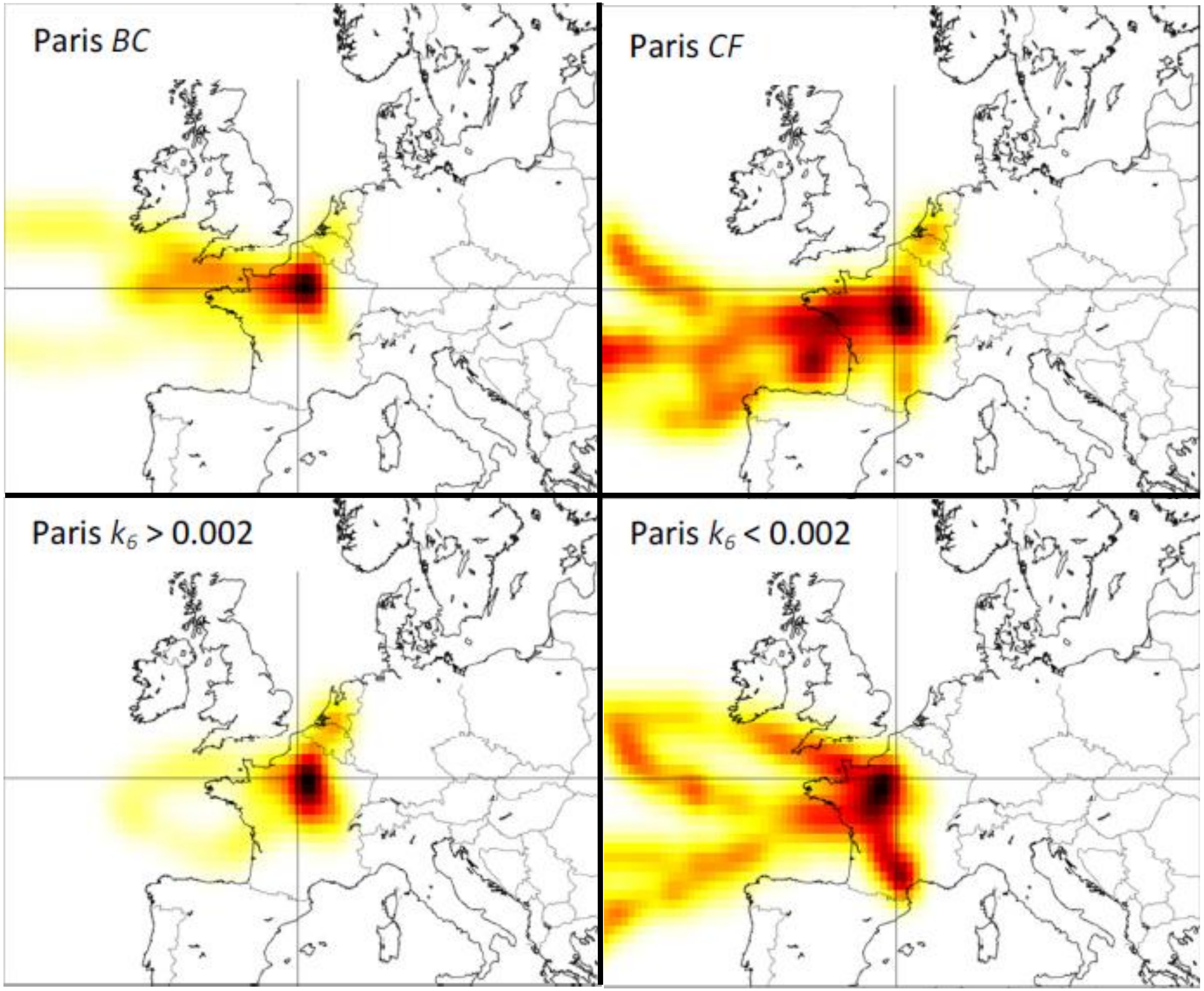
PSCF (Potential Source Contribution Function)



Fresh aerosol

Aged aerosol

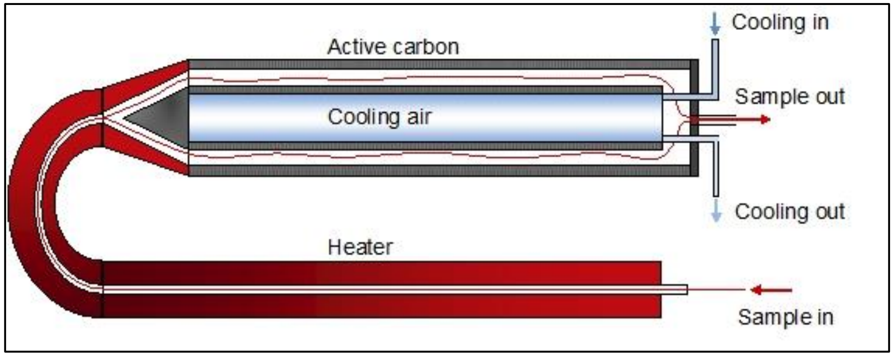
Parameter k discriminates between local and transported aerosol

The “de-coating” experiment

Investigate influence of coating during summer ambient campaign

-> Remove coating with drier and/or thermo-denuder

Aerosol inlet dryer (Magee Scientific)
Dew point reduction: 12 °C



Thermodenuder (Dekati)
T=300 deg. C

The “de-coating” experiment

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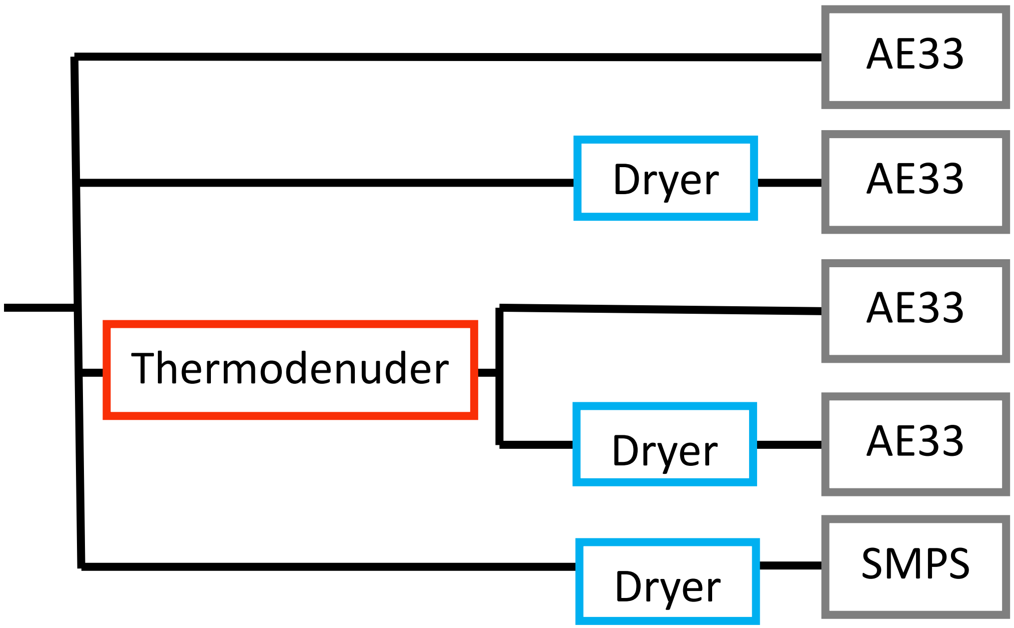
Rural site close to Ljubljana, Slovenia.
Some local pollution. 600 m from the highway
Summer: 6 Aug – 15 Sept 2014



The "de-coating" experiment

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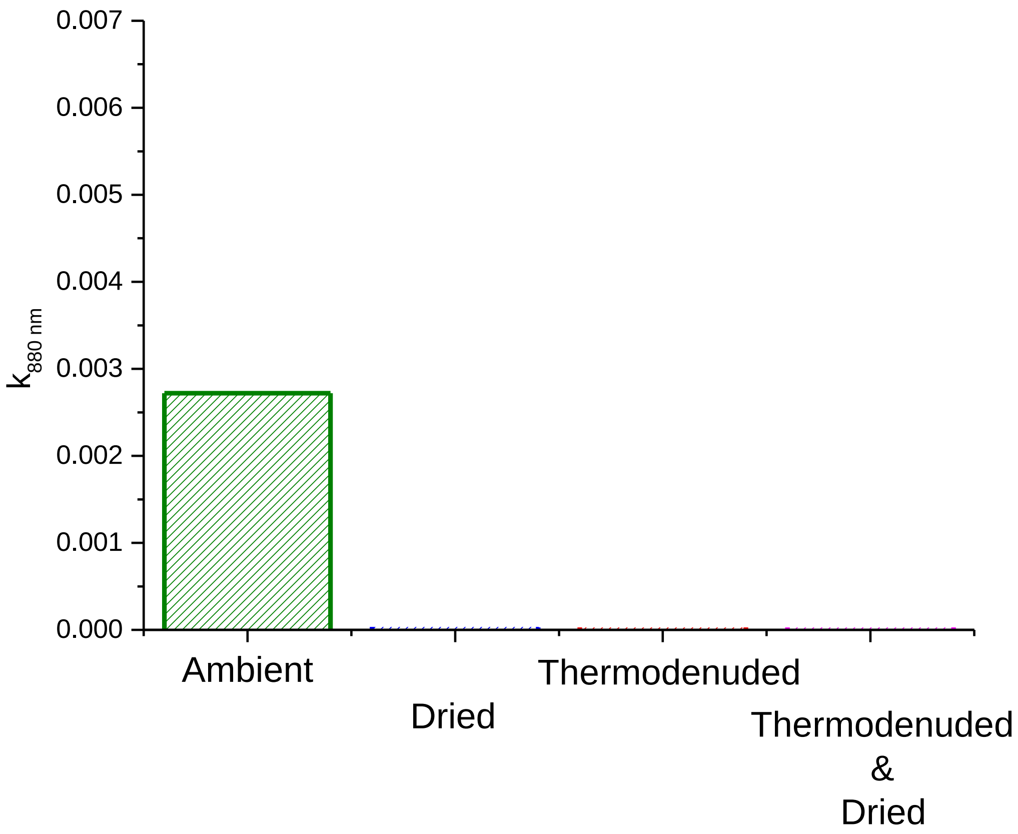
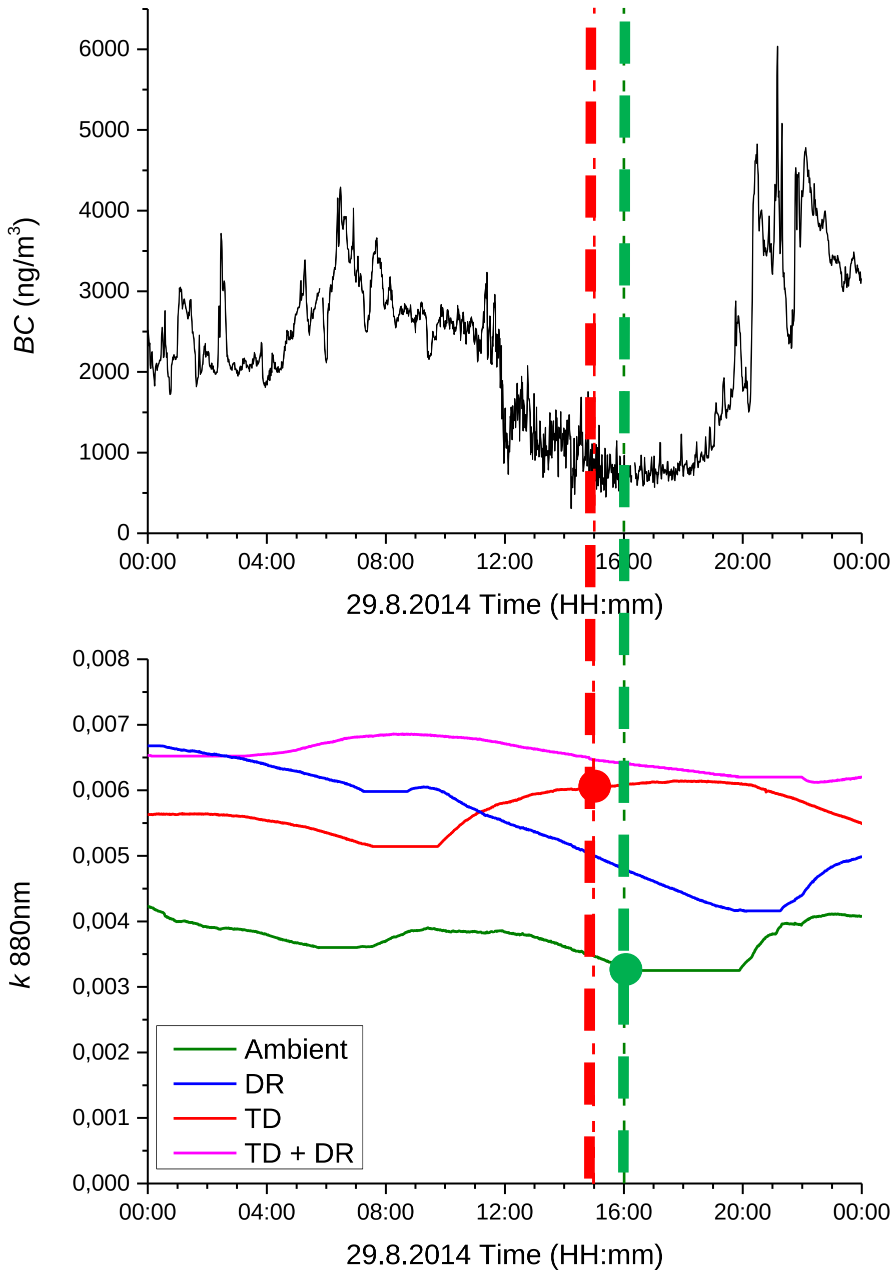


- Placing the drier and/or thermodenuder at the sample inlet caused an increase of the parameter *k* at λ= 880 nm
- Effect of aerosol drying implies the presence of hygroscopic coating material

The "de-coating" experiment – SEM



Typical campaign day

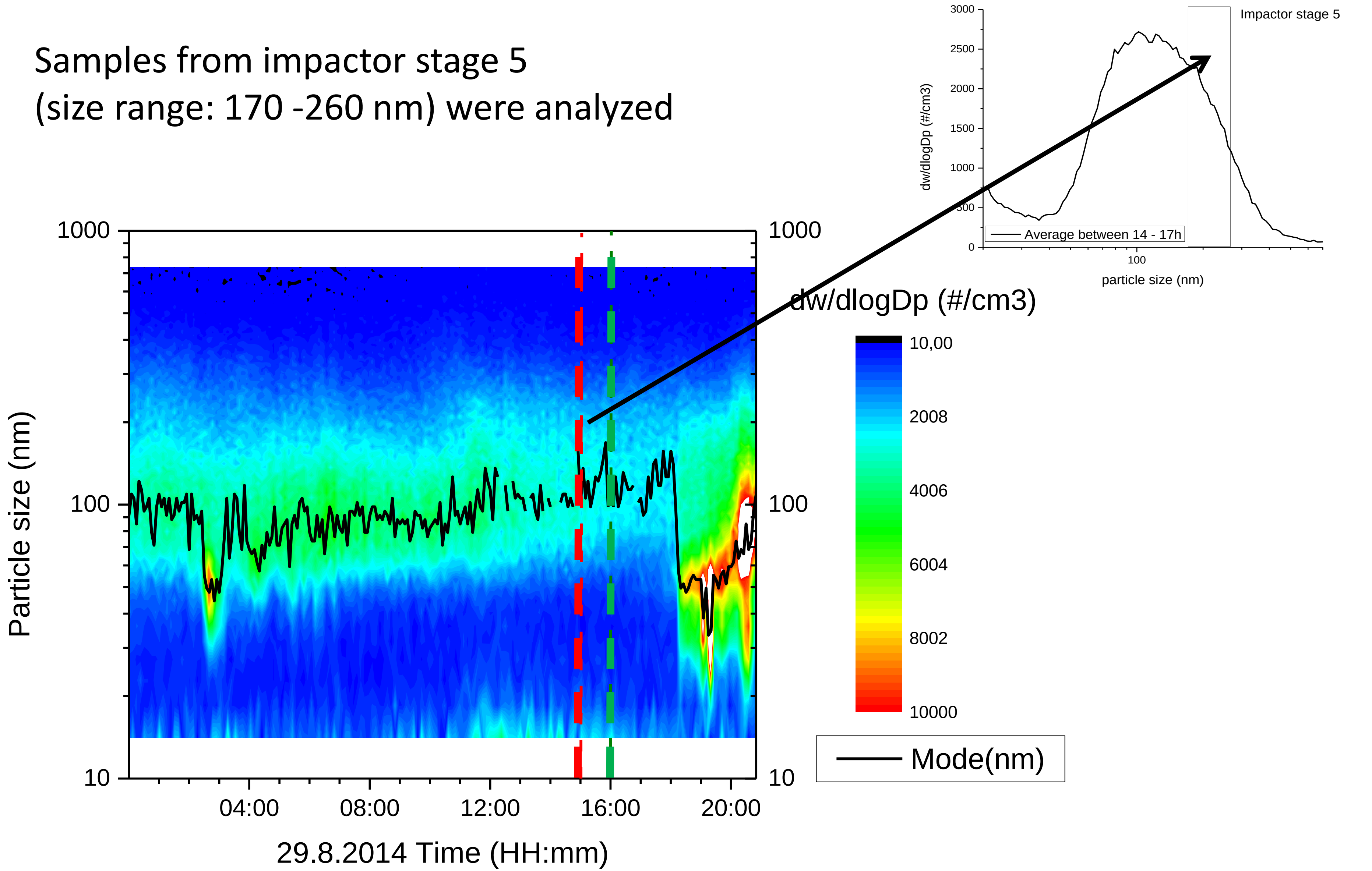
Impactor SEM samples were taken in the middle of the day with strong vertical mixing

Thermodenuded

Ambient

The “uncoating” experiment - SEM

Samples from impactor stage 5
(size range: 170 -260 nm) were analyzed



SEM – ambient sample

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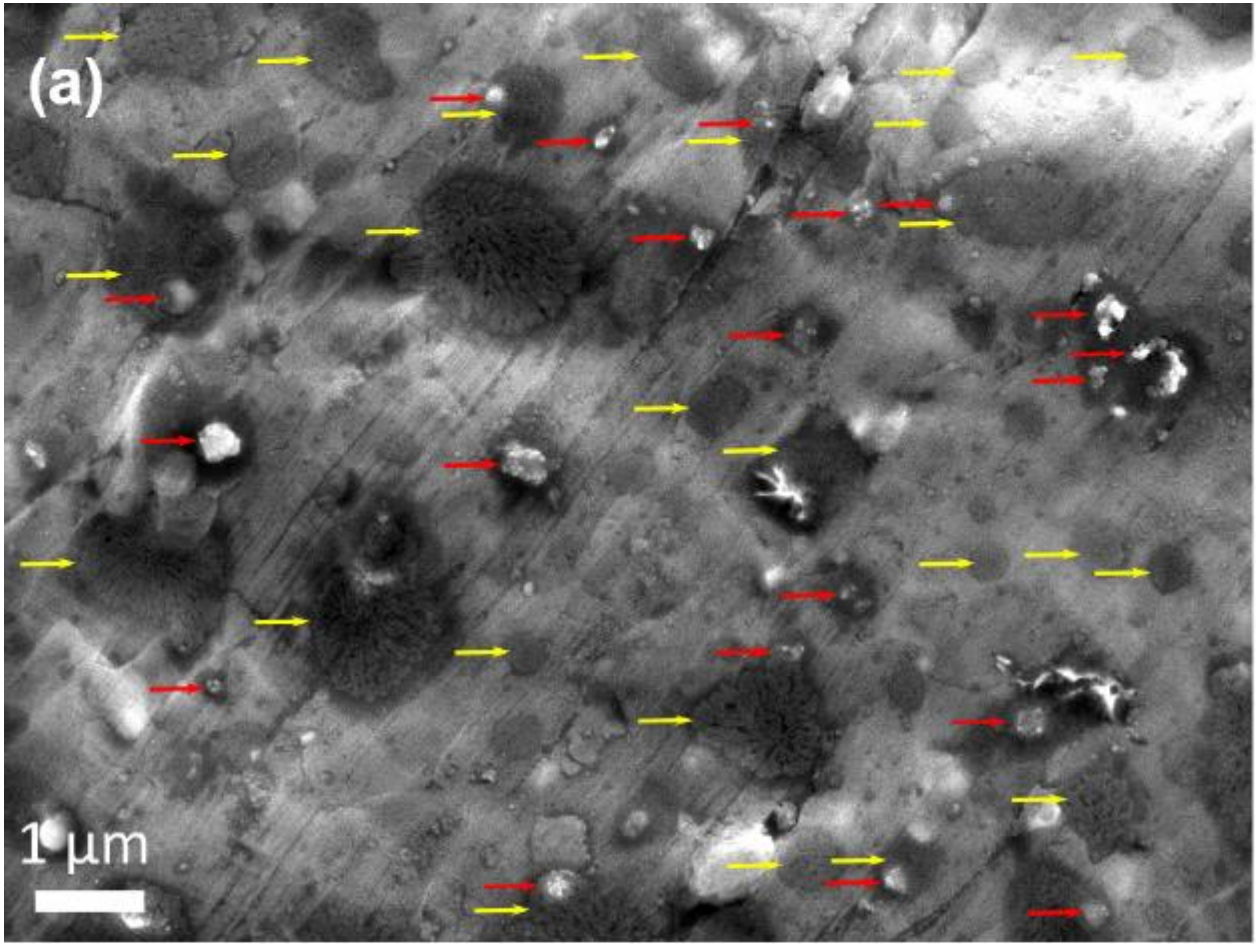
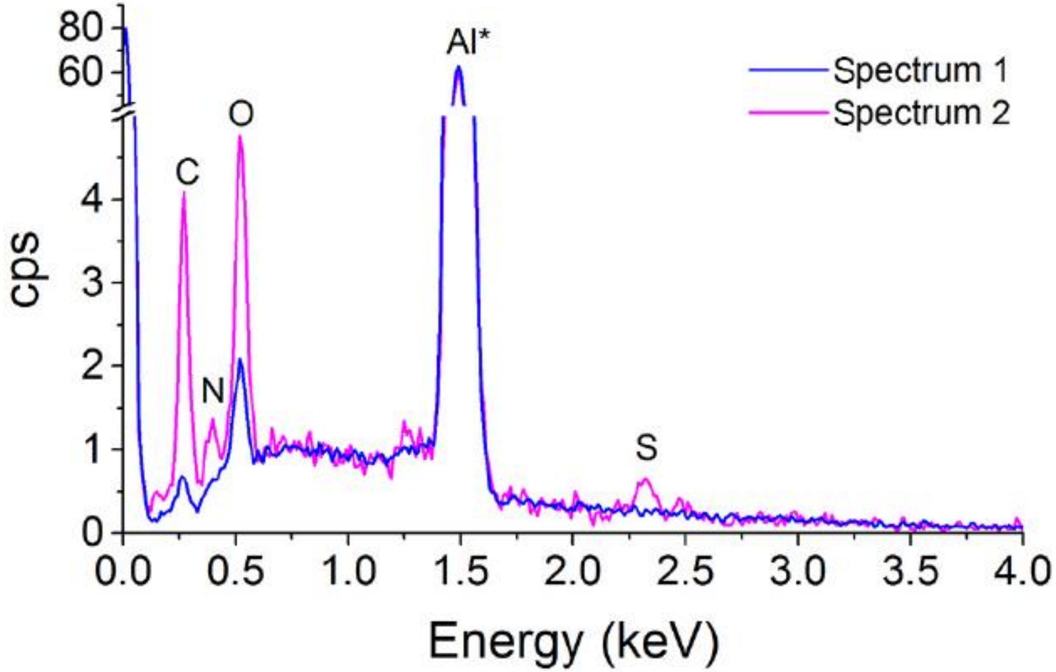
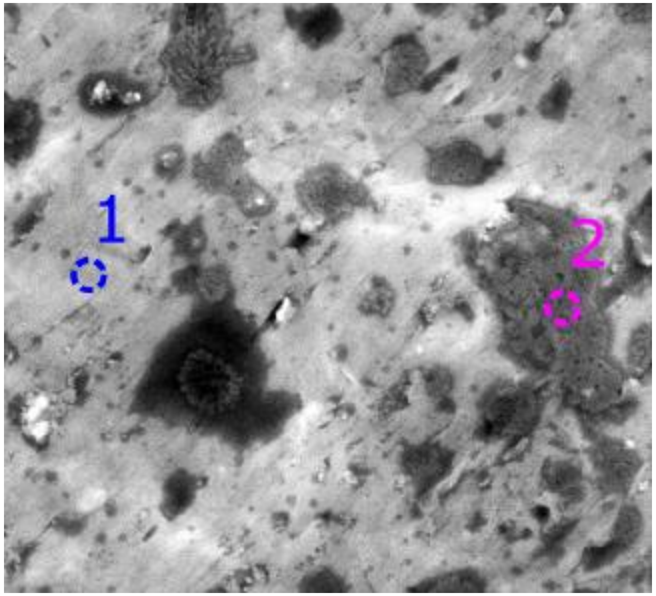


→ BC particles
→ Brain-shaped dendritic residues

SEM – Energy-dispersive X-ray spectra



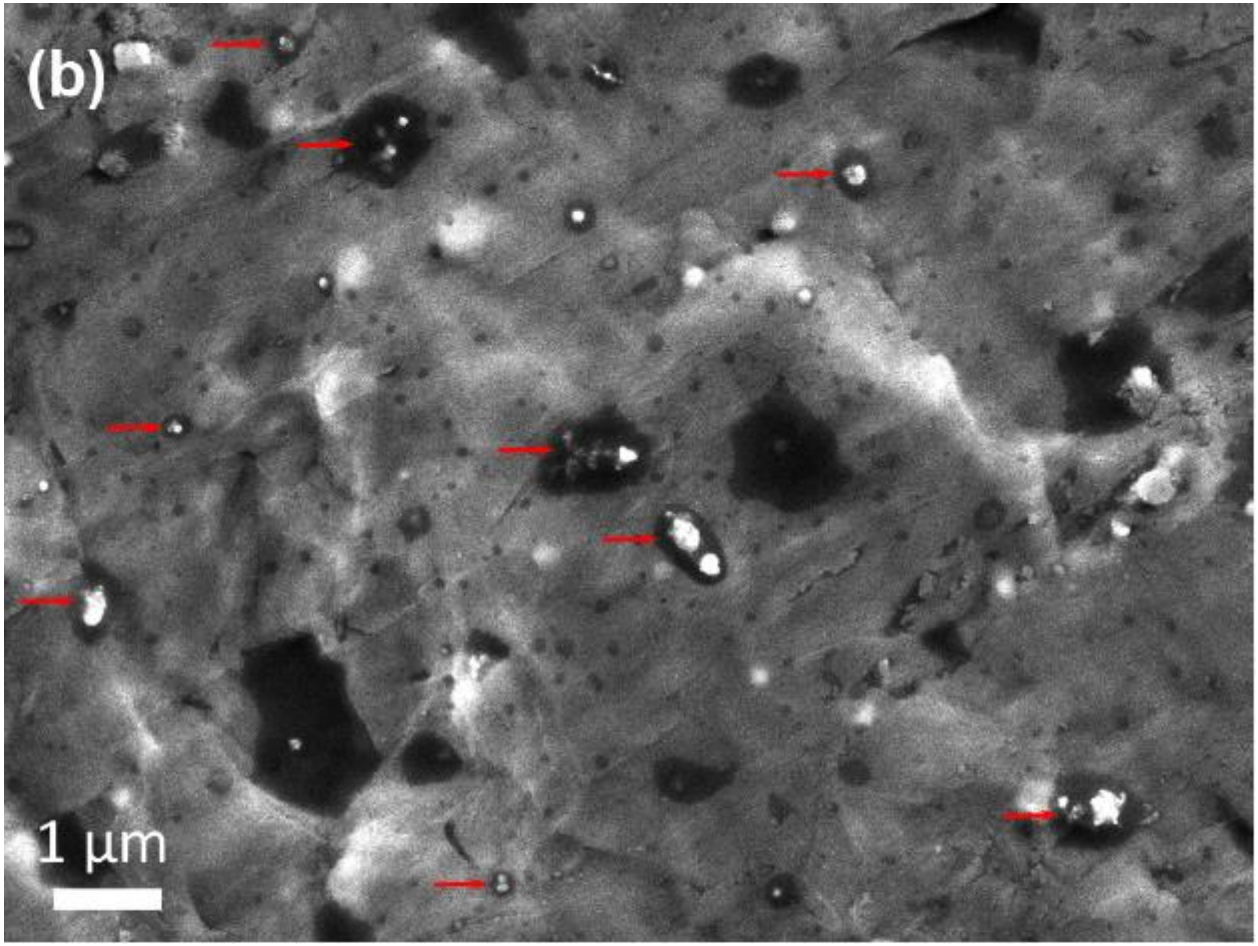


Spectrum 1: Background = Al foil

Spectrum 2: Residue contains elements: S, N and C:

- Ammonia, sulphate, nitrate
- Organics

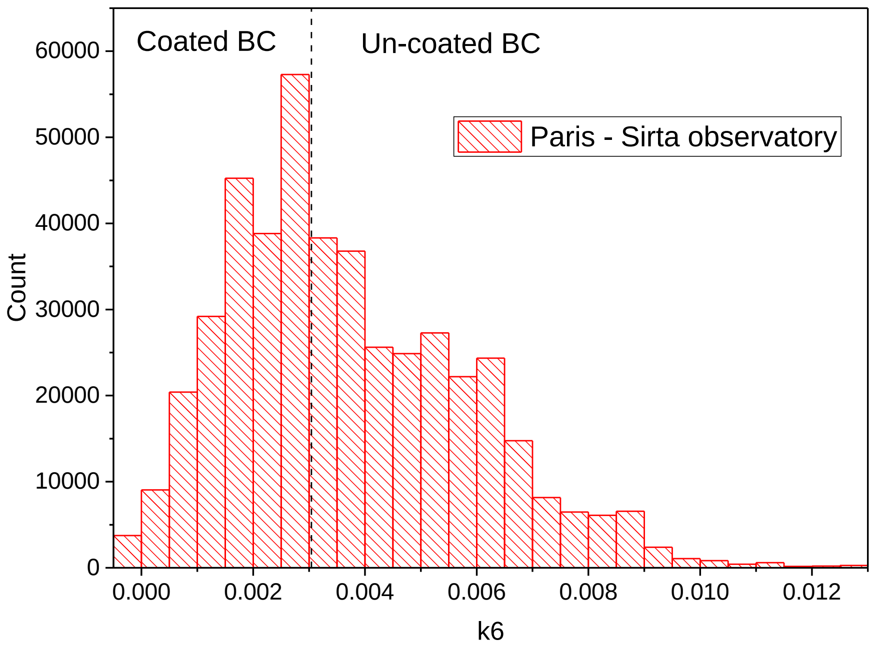
SEM – thermodenuded sample

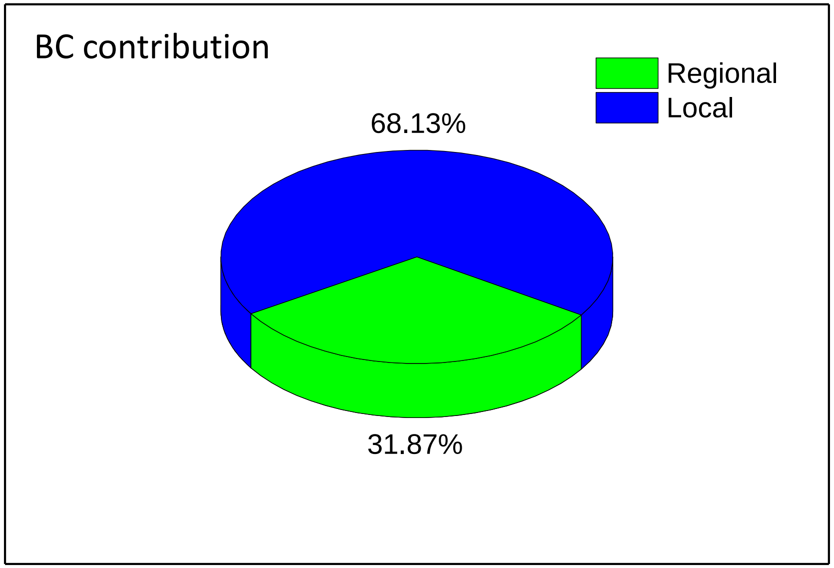


No residues present -> Nitrates and sulphates decompose above 280 ^{o}C
Some of the organics are still present -> LV-OOA

Discrimination of local vs. regional pollution

We can distinguish local(uncoated) and regional(coated) BC using parameter k_6





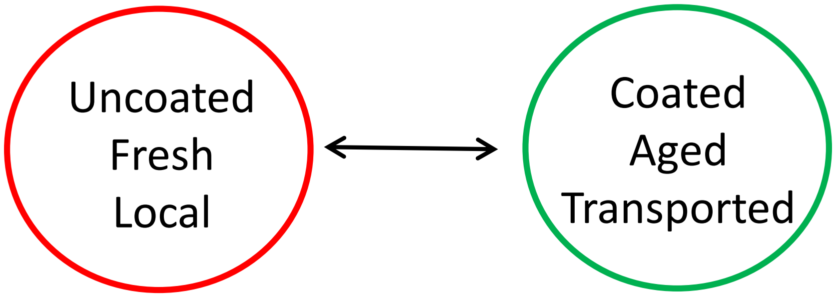
There is about one third of regional contribution to BC measured at SIRTA

Parameter k & aerosol properies - summary

- High variability of parameter k in the infra-red

- Parameter k increases with BC core size
- Parameter k decreases with particle coating

- Parameter k can be used to discriminate:



It is possible to assess the influence of regional transport on local air quality!

Acknowledgements

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