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

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EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

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Black Carbon Source Apportionment

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Outline

- Introduction
- BC/EC Source Apportionment Methods
  - Source specific tracers and emission ratios
  - ^{14}C method
  - Aethalometer model
- Aethalometer model
  - Theory
  - Advantages and assumptions
  - α values
  - Examples
- Evaluation of the Aethalometer model
  - Introduction and Methods
  - MAC values
  - Best α pair and α_{WB} distribution
  - Other α combinations
  - High time resolution
  - Wavelength sensitivity
- Conclusion
- Recommendations

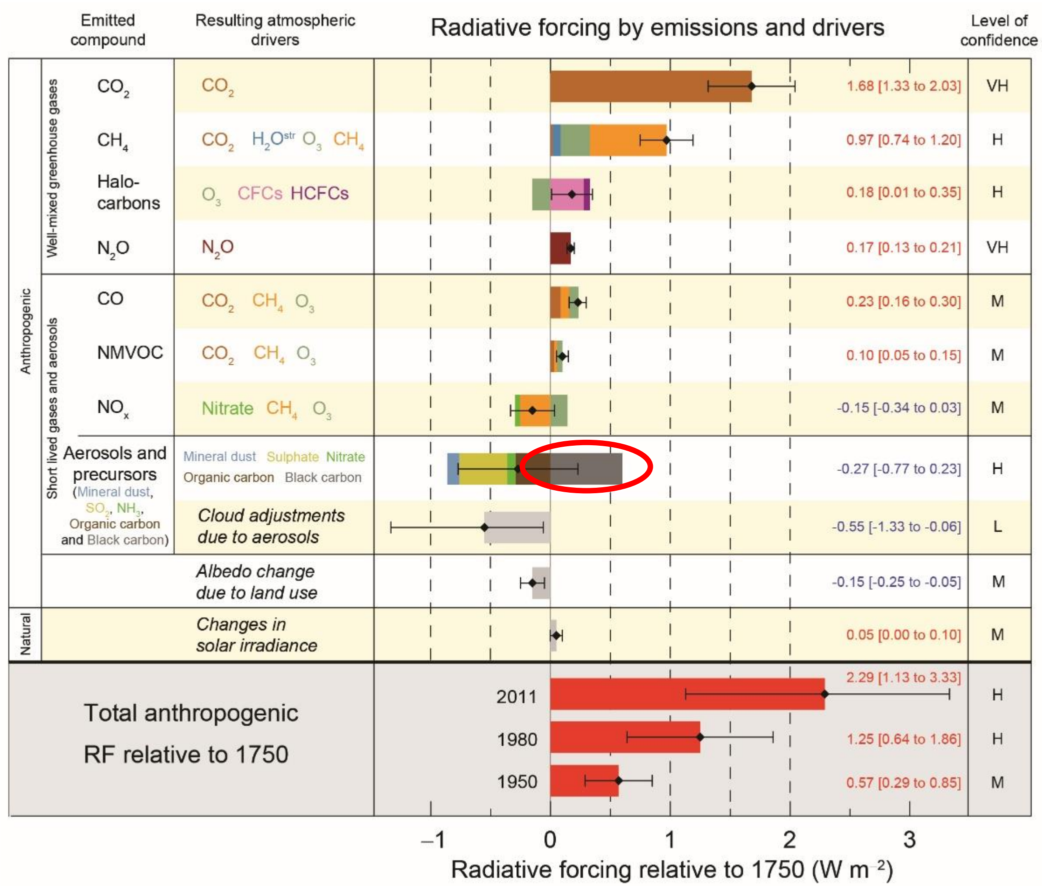
Introduction – General

Why is it important to measure BC and know its sources?

- BC negatively influences human health
- BC influences the climate
  - 3rd strongest contribution to global warming
  - But has a short atmospheric lifetime (few days to max. a couple of weeks)

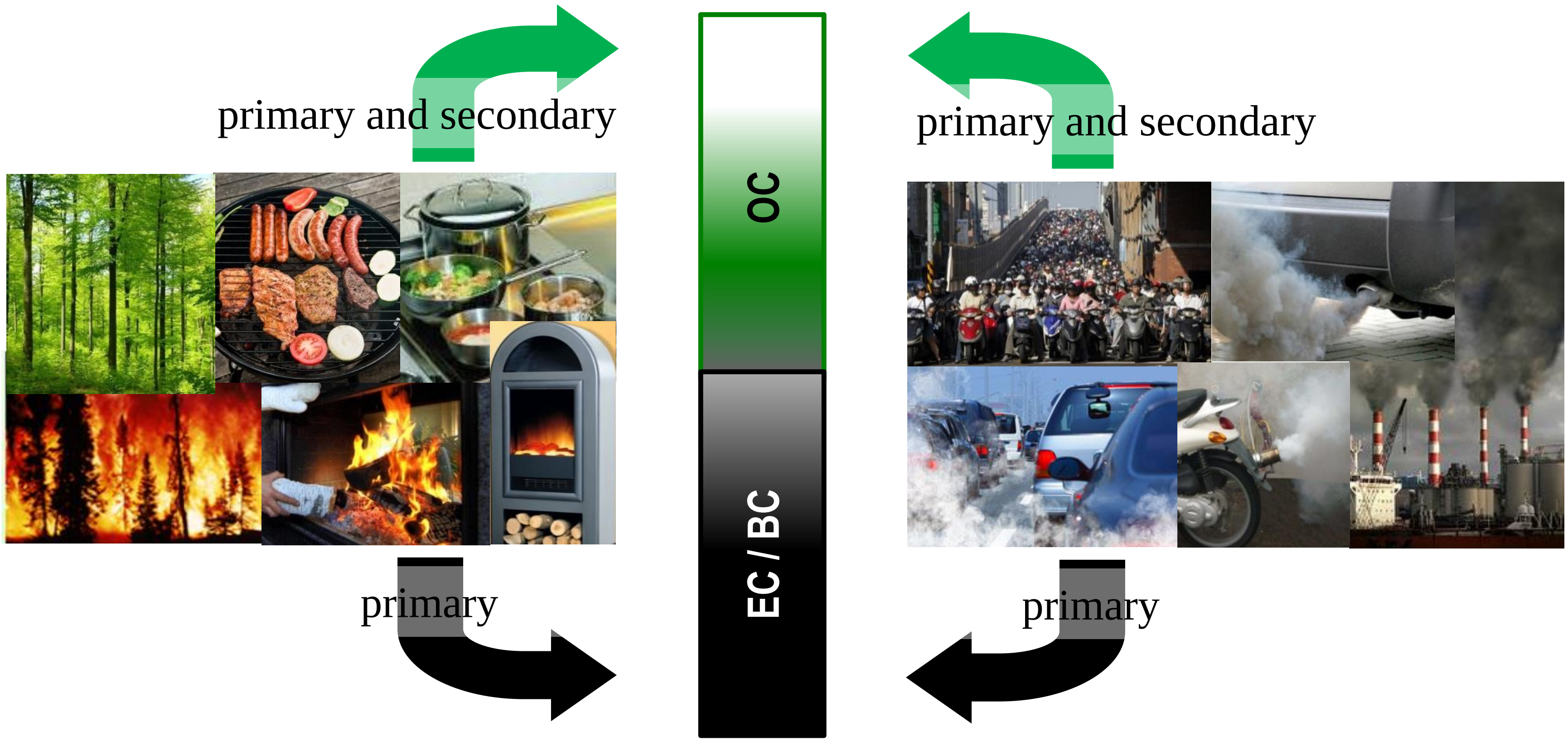
→ Reducing BC emissions is important

→ But for effective mitigation strategies BC sources must be identified and quantified



Introduction – BC Sources

- Carbonaceous aerosols are a major fraction of fine aerosols
  - Especially in Alpine regions during winter time (up to 90%)
- Sources:



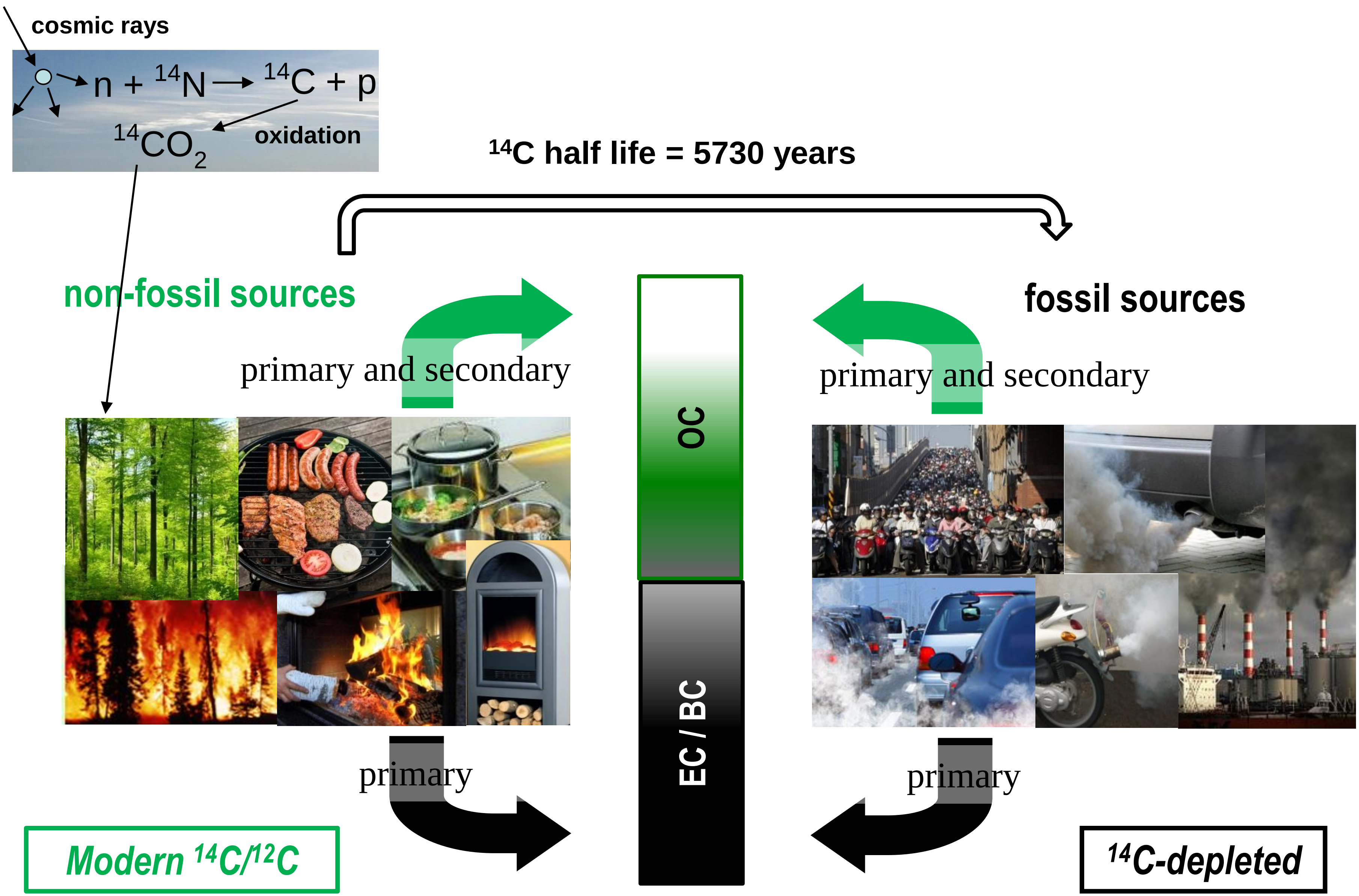
BC/EC Source Apportionment Methods

- Source specific tracers and emission ratios
- ^{14}C Method
- Aethalometer model

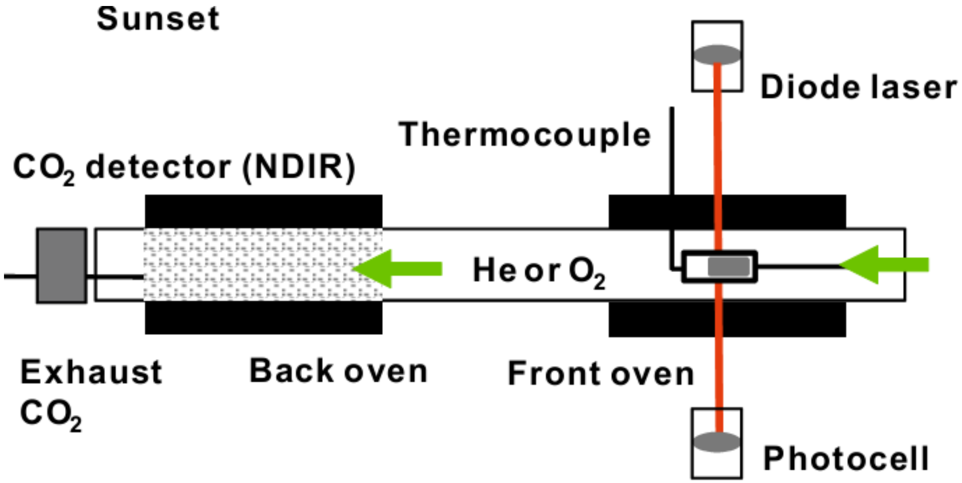
Source specific tracers and emission ratios

- Measurement of e.g. OC, EC and source specific tracers
  - For biomass burning e.g. levoglucosan, potassium
- Applying emissions ratios and/or source profiles (for CMB, PMF) from literature
  - E.g. OC_{bb}/EC_{bb}, levoglucosan/OC_{bb}, OC_{tr}/EC_{tr}
- *<u>Limitation:</u>*
  - Assumption of constant emission ratios and/or source profiles
  - Emission ratios are dependent on the combustion conditions and fuel type
  - Wide range of emission ratios have been previously reported
    - OM_{bb}/EC_{bb}:
      - 3 – 63 (Schauer et al., 2001; Fine et al., 2001, 2002, 2004a, 2004b; Schmidl et al., 2008)
    - OM_{tr}/EC_{tr}:
      - 0.25 – 0.45 for Europe (El Haddad et al. 2013)
      - 0.9 – 1.4 for the US (Zhang et al., 2005; Sun et al., 2012; Stroud et al., 2012)
  - Offline analysis necessary
  - Limited time resolution

^{14}C Method - Introduction



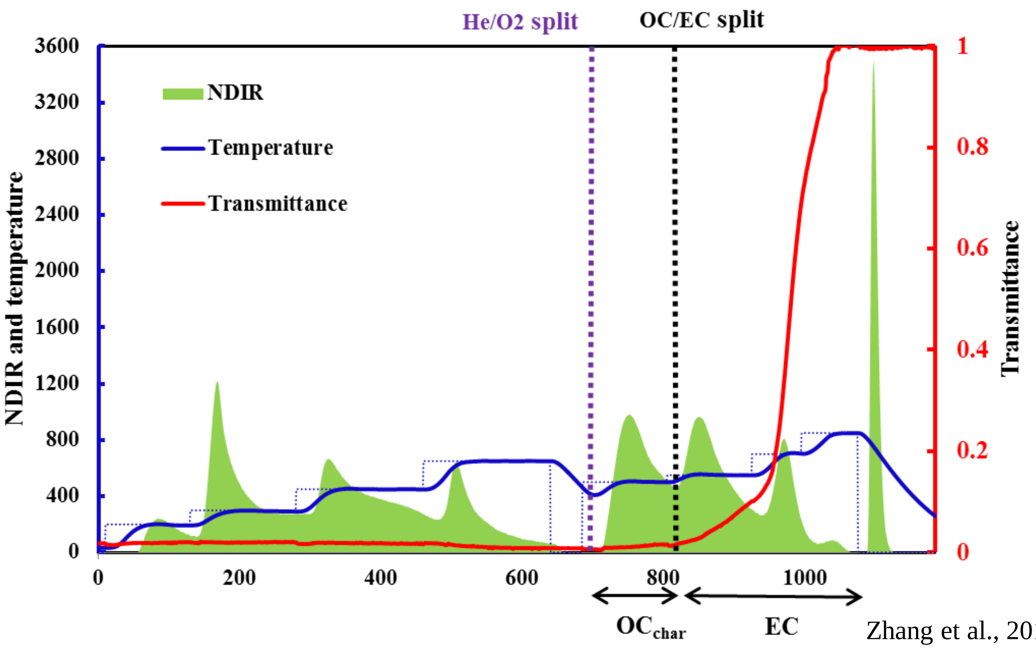
OC/EC measurement using the Sunset analyzer



Sunset lab instrument:

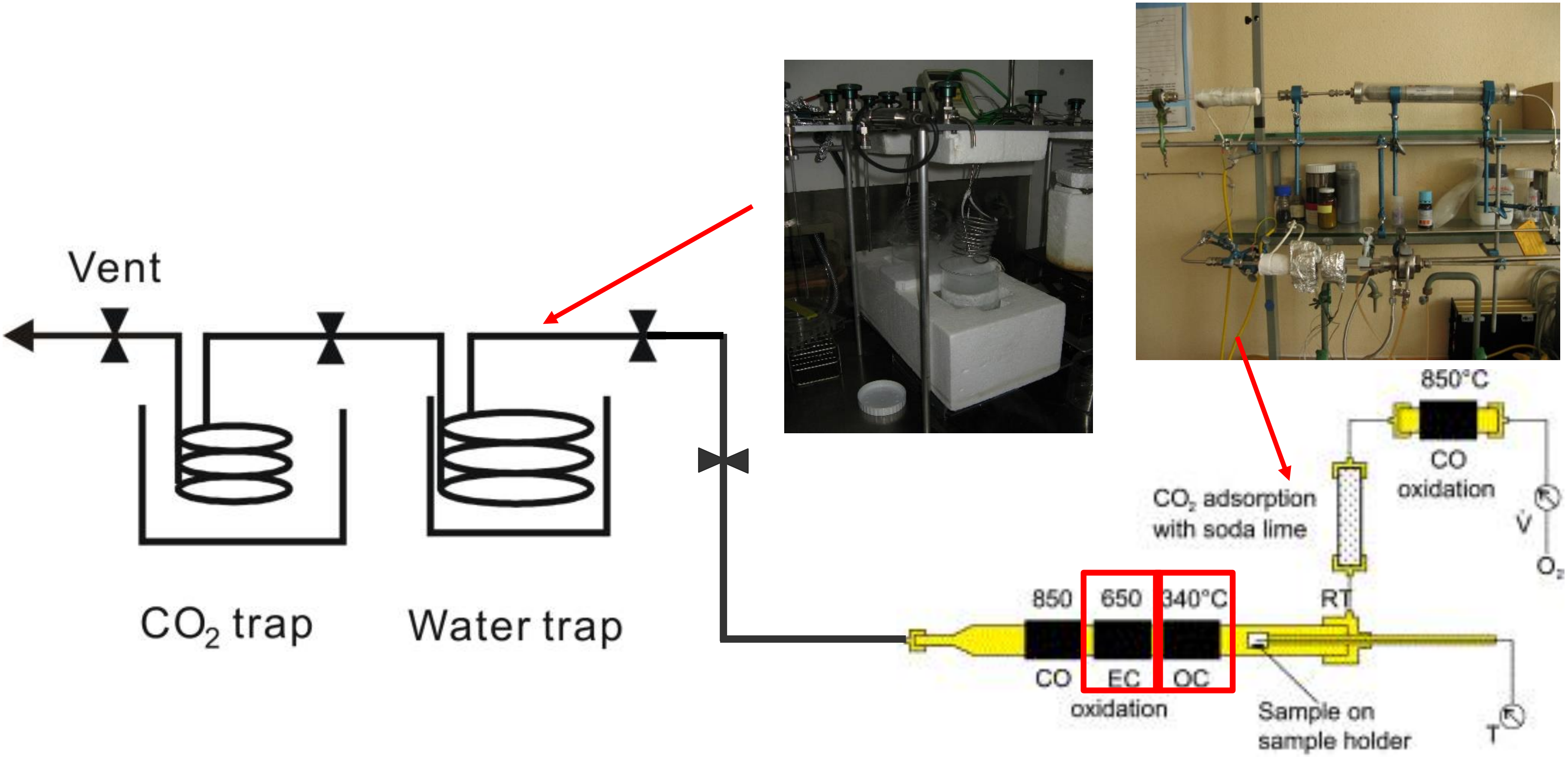
- ✓ NDIR detector to detect CO_2
- ✓ Multiple gas supply He, He/O_2, O_2
- ✓ Programmed oven temperature
- ✓ Continuous optical monitoring

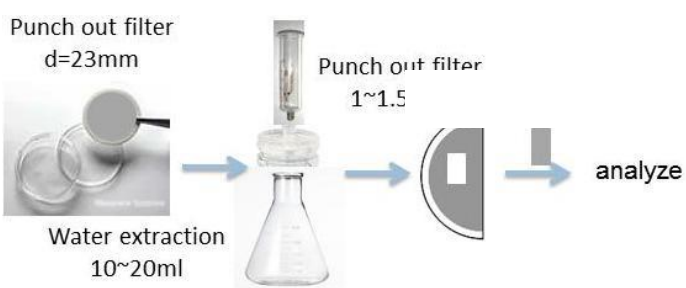
Thermo-optical control of OC charring, OC removal and EC losses possible



Zhang et al., 2012

^{14}C Method – Sample preparation

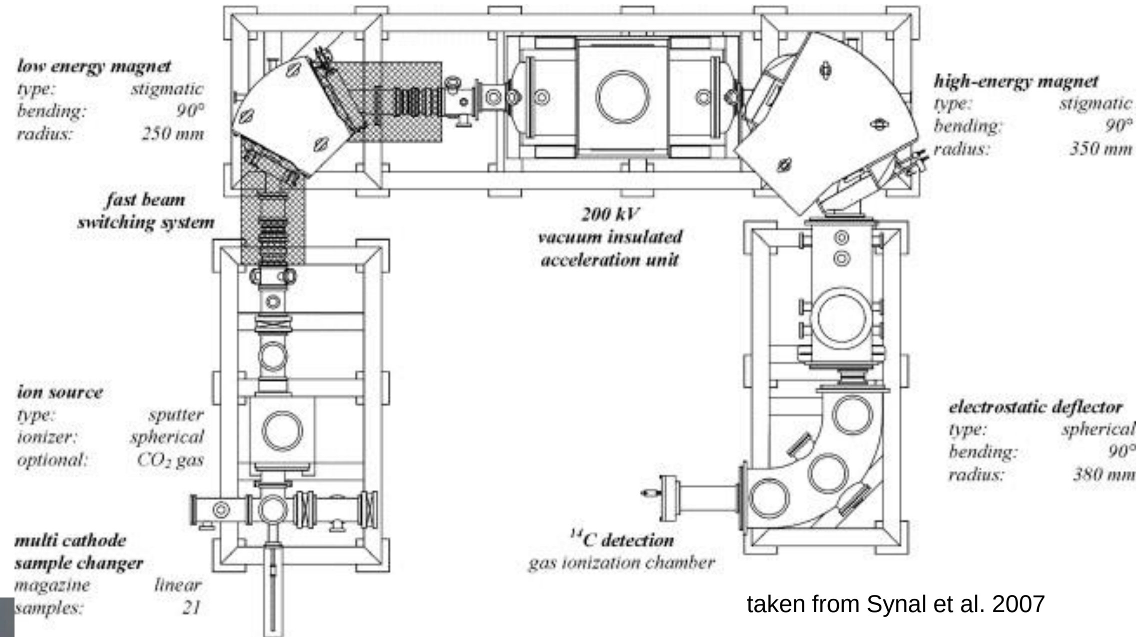




heat water extracted samples for 4h at 375 °C in a Muffle furnace to remove the OC

^{14}C Method – ^{14}C determination

- at the ETH Zürich or University of Bern
- MICADAS
  - MIni radioCArbon DAting System
    - „only“ a size of 2.5 × 3 m²



taken from Synal et al. 2007

taken from: http://www.ams.ethz.ch/research/instrument/micadas/interactive

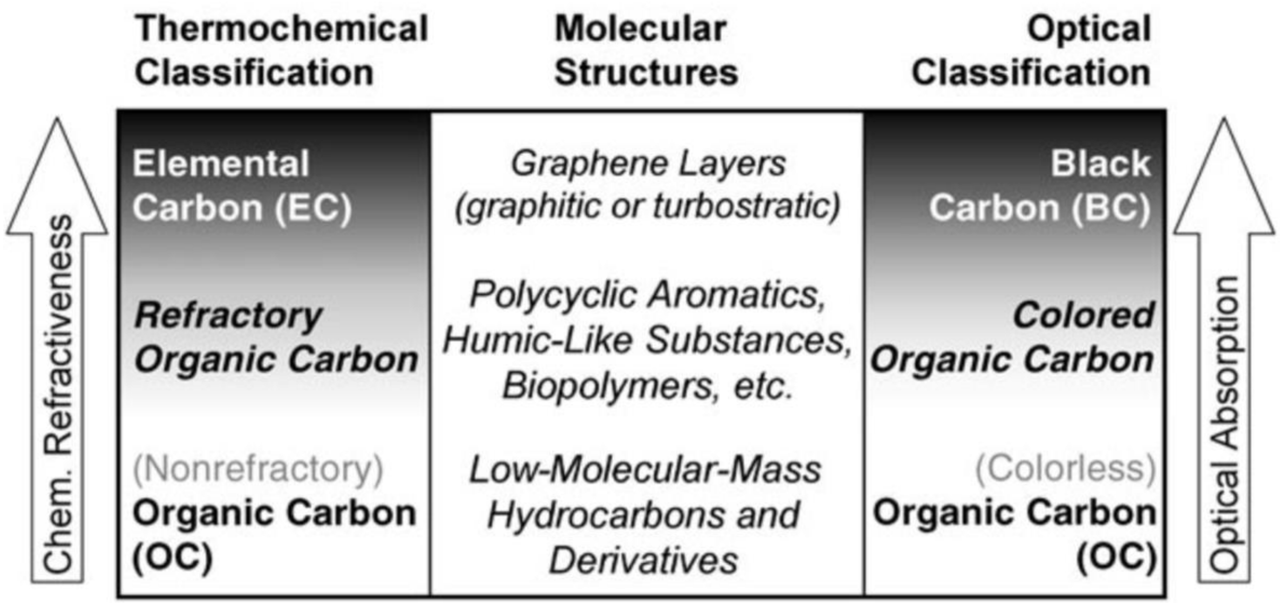
- Gas ion source
  - No graphitization necessary

→ very low detection limit (~5 ug carbon)

^{14}C Method – Advantages/Disadvantages

• Advantages:	• Disadvantages

• No assumptions	• OC and EC have to be physically separated. However:
	  • *there is no clear boundary*
	  • *EC losses during OC removal can occur*
	  • *OC charring can occur*
	• Time consuming and expensive
	• Offline analysis and limited time resolution



Pöschl, 2005

Aethalometer Model - Theory

- The Aethalometer model was first described in:
  - Environ. Sci. Technol. 2008, 42, 3316–3323:

Using Aerosol Light Absorption Measurements for the Quantitative Determination of Wood Burning and Traffic Emission Contributions to Particulate Matter

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Aethalometer Model - Theory

Aethalometer Model - Theory

Traffic emissions:

- Contain mainly pure BC
- Dominate absorption at IR-wavelengths
- Only a weak wavelength dependence

Wood burning emissions:

- Contain light absorbing organic substances
- Ehanced absorption in N-UV range
- Strong wavelength dependence

- spectral dependence of absorption is described by a power law

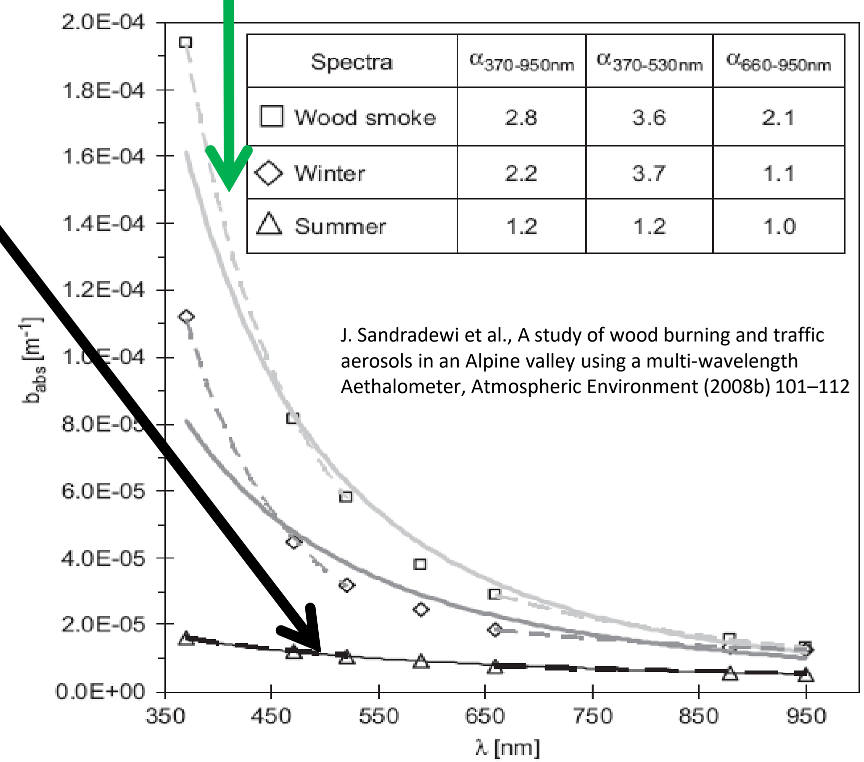
$$b_{abs}(\lambda) \sim \lambda^{-\alpha}$$

b_{abs} ...absorption coefficeint

λ ...wavelenght

α ...Ångstrom exponent

- α for traffic emissions ~1
- α for wood burning > 1



Aethalometer Model - Theory

- Spectral dependence of absorption is described by a power law

$$b_{abs}(\lambda) \sim \lambda^{-\alpha}$$

b_{abs} ...absorption coefficeint
λ ...wavelenght
α ...Ångstrom exponent

- For a wavelength pair:

$$\frac{b_{abs}(\lambda_1)}{b_{abs}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha}$$

- Absorption is split into wood burning (WB) and traffic (TR) contribution

$$b_{abs,total}(\lambda) = b_{abs,TR}(\lambda) + b_{abs,WB}(\lambda)$$

- Consequently:

- $$\frac{b_{abs,WB}(\lambda_1)}{b_{abs,WB}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{WB}}$$ and $$\frac{b_{abs,TR}(\lambda_1)}{b_{abs,TR}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{TR}}$$

- $$b_{abs,WB}(\lambda_2) = \frac{b_{abs}(\lambda_1) - b_{abs}(\lambda_2) \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{TR}}}{\left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{WB}} - \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{TR}}}$$ and $$b_{abs,TR}(\lambda_2) = \frac{b_{abs}(\lambda_1) - b_{abs}(\lambda_2) \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{WB}}}{\left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{TR}} - \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{WB}}}$$

- $$BC = \frac{b_{abs}(\lambda)}{MAC(\lambda)}$$

Aethalometer Model - Theory

- It is also possible to apportion a TR and WB contribution to the total carbonaceous matter (CM)

- *CM = EC + OM*
  - OM … organic matter

- CM has to be determined with an additional method (e.g. EC/OC analysis with Sunset EC/OC analyzer)

- $$CM = \underbrace{C_1 * b_{abs,\,TR}}_{CM_{TR}} + \underbrace{C_2 * b_{abs,\,WB}}_{CM_{WB}} + \underbrace{C_3}_{CM_{other}}$$
  - CM_{other}…non absorbing material, mostly secondary organic aerosol (SOA)

Aethalometer Model - Advantages

- Except a priory assumptions no additional analysis necessary
- Cheap and automatic
- High time resolution
- Easy deployable at different locations
- Also apportionment of CM possible

Aethalometer Model - Assumptions

- Wood burning (WB) and traffic (TR) are the only BC sources
- α_{TR} and α_{WB} have to be assumed a priori
  - α_{TR}: no big issue since it was found to vary only in a narrow range (0.8–1.1)
  - α_{WB}: a wide range of 0.9 to 3.5 was found depending on:
    - combustion conditions and efficiency
    - fuel type
    - aerosol aging

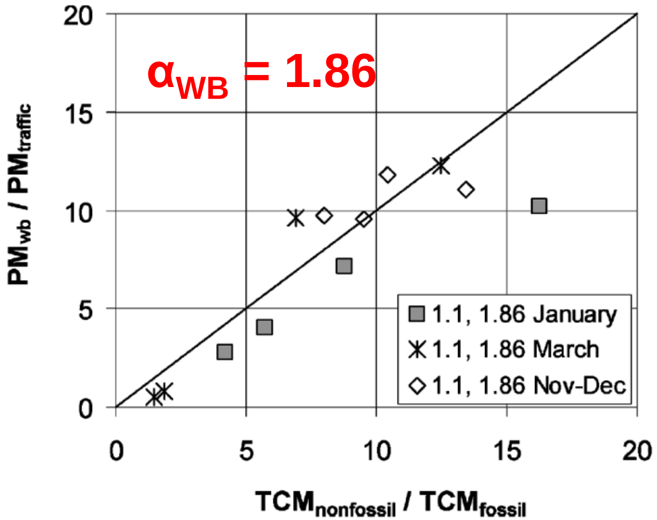
Bond et al., 2013; Kirchstetter et al., 2004; Schnaiter et al., 2003; Schnaiter et al., 2005

Schnaiter et al., 2003; Kirchstetter et al., 2004; Schnaiter et al., 2005; Lewis et al., 2008; Saleh et al., 2013

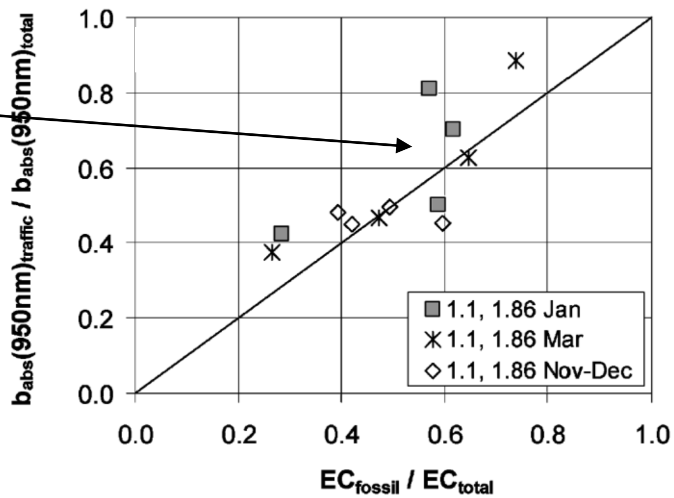
- α_{TR} and α_{WB} are constant
  - Combustion conditions may change over time
  - Aging conditions are not constant over time
    - Usually α increases initially due to aging and can decrease again after long aging
- Same MAC for BC_{TR} and BC_{WB}
- CM apportionment:
  - c_1, c_2 and c_3 are constant
    - However, c_2 and especially c_3 might be highly variable
  - c_1 has to be assumed a priory

Aethalometer Model – α values

- Aethalometer model was first applied by in Roveredo, CH
- α_{TR} was fixed to 1.1
- α_{WB} determined by comparing CM Aethalometer model outputs with ^{14}C results of EC and OC (converted to OM_{NF} and EM_{NF} using literature OM/OC and EM/EC ratios)



- **Limitation:**
  - Only a few (n = 12) ^{14}C measurements on filters with 16h and 24h sampling time
  - Only winter samples → large wood burning contribution
  - α_{WB} was chosen based on CM and not BC apportionment
    - With α_{TR} = 1.1 and α_{WB} = 1.86 R^2 = 0.5 and slope is 1.1

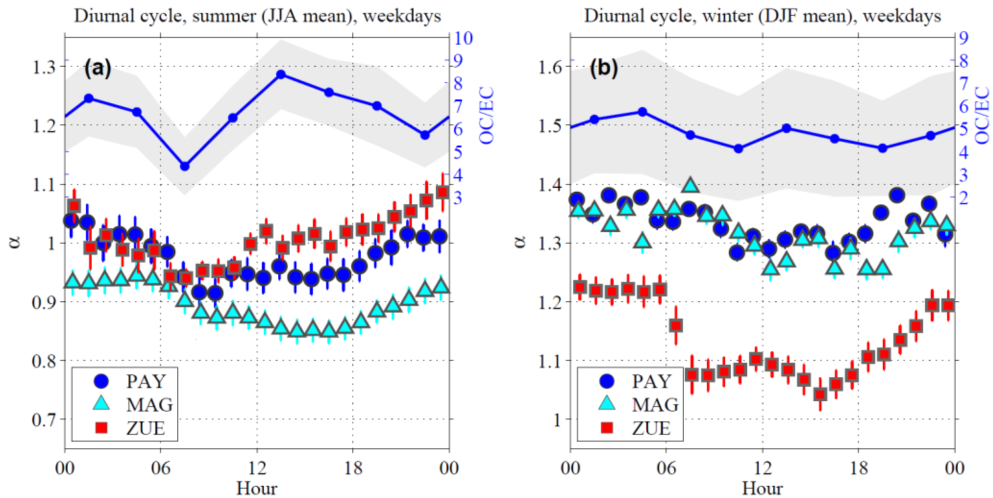


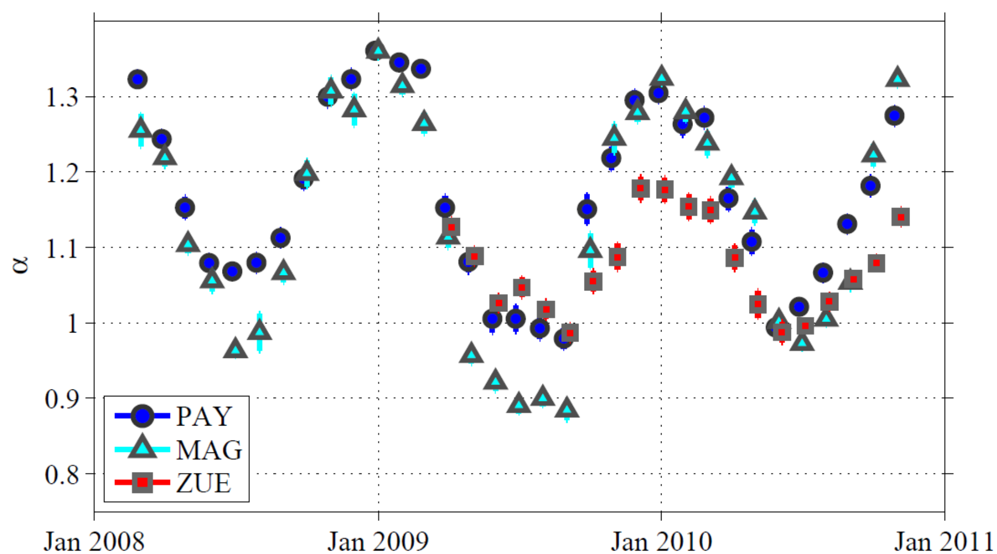
- Based on the Sandradewi et al. 2008 work following studies mostly used α_{WB} = 1.8–2.2
  - Sandradewi et al., 2008b; Favez et al., 2010; Perron et al., 2010; Herich et al., 2011; Harrison et al., 2012; Crippa et al., 2013; Harrison et al., 2013; Mohr et al., 2013
  - Without any further reference measurements
    - E.g. ^{14}C analysis in EC from different seasons, countries…

Aethalometer Model – α values

- From traffic or diesel soot emission studies
  α_{TR} = 0.8 - 1.1
  - E.g., Bond et al., 2013; Kirchstetter et al., 2004; Schnaiter et al., 2003; Schnaiter et al., 2005

- α_{TR} can also be determined looking at periods were only traffic aerosols are present
  - E.g., Herich et al. 2011 found an α_{TR} of 0.9

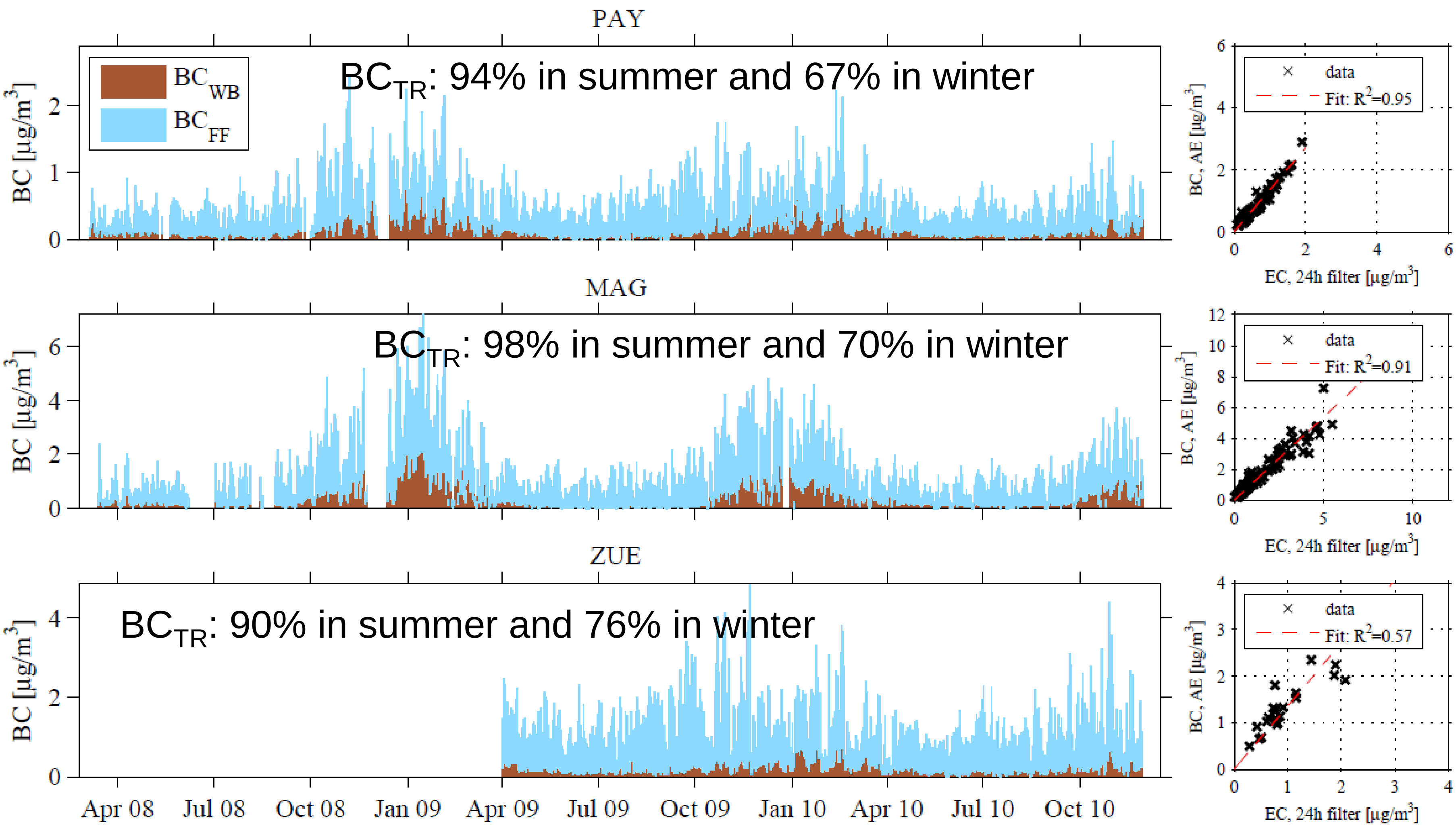




Herich et al. 2011. "A 2.5 year's source apportionment study of black carbon from wood burning and fossil fuel combustion at urban and rural sites in Switzerland." Atmos. Meas. Tech. 4(7): 1409-1420.

Aethalometer Model – Examples

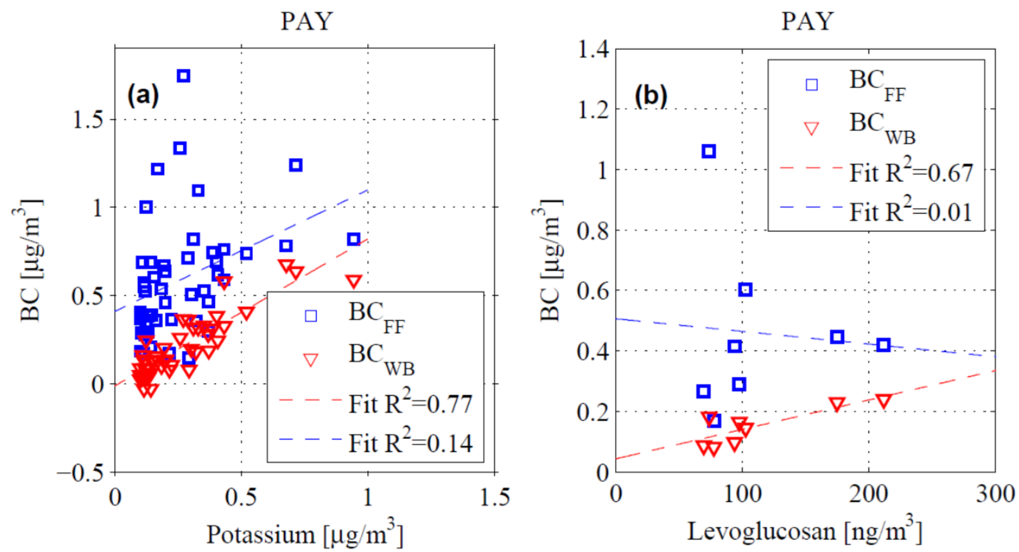
<u>*Switzerland (Herich et al. 2011)*</u>

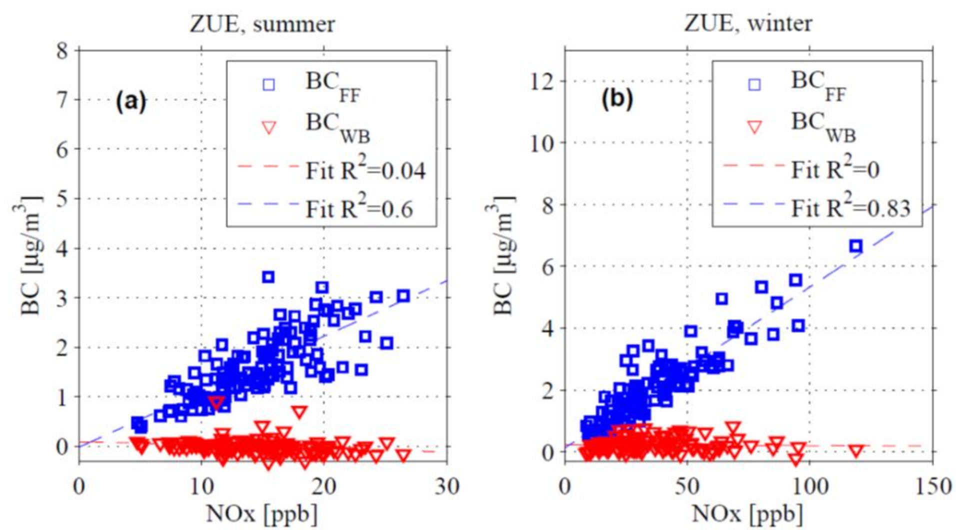


Aethalometer Model – Examples

<u>*Switzerland*</u> (Herich et al. 2011)

- Comparison with auxiliary data
  - Good correlation between BC_{wb} and Potassium and Levoglucosan in winter
  - Good correlation between BC_{TR} and NO_x



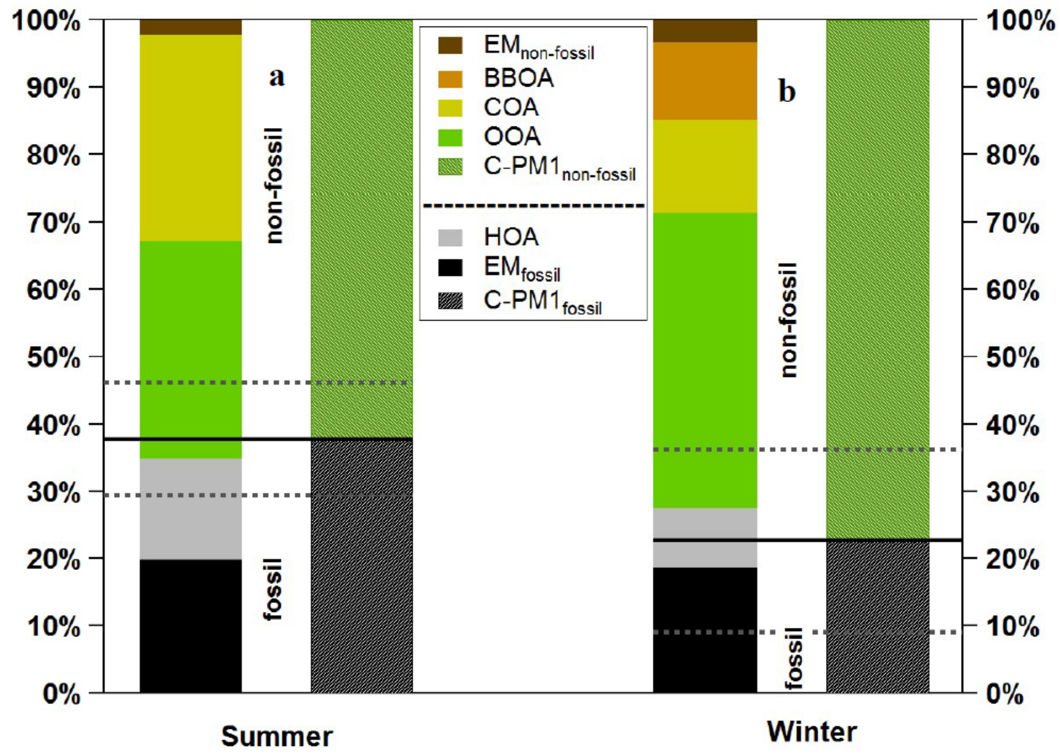


Aethalometer Model – Examples

<u>*Paris*</u> (Beekmann et al. 2015)

- MEGAPOLI campaign
  - 1 to 31 July 2009
    and January to February 2010
  - Several sites in and around Paris
  - Good example of combining multiple measurement and source apportionment methods
    - AMS with PMF
    - ^{14}C analysis of TC
    - BC and Aethalometer model

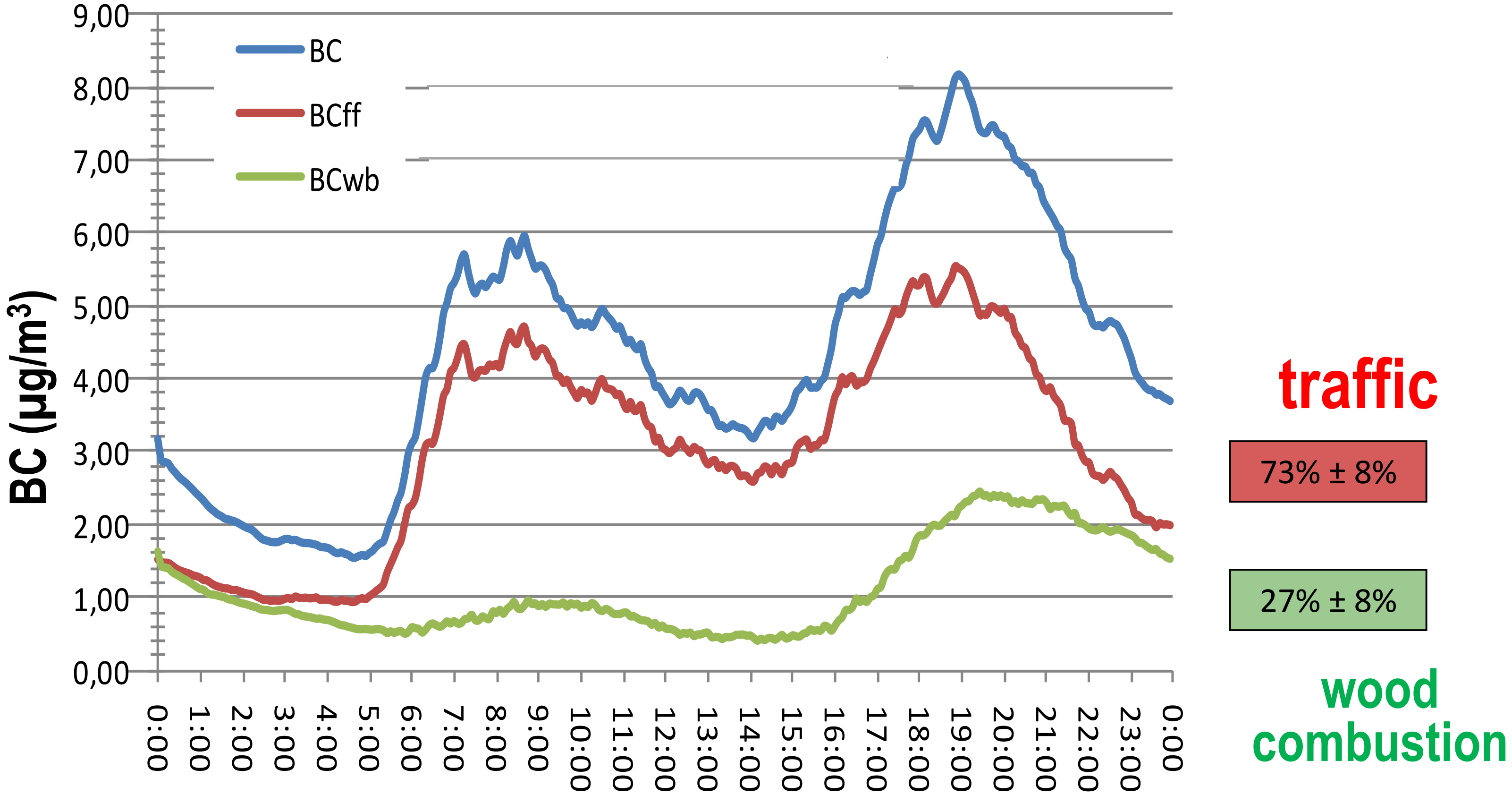
LHVP: Urban background site in Paris



Beekmann et al, 2015: In situ, satellite measurement and model evidence on the dominant regional contribution to fine particulate matter levels in the Paris megacity, <u>Atmos. Chem. Phys., 15, 9577-9591</u>

Aethalometer Model – Examples

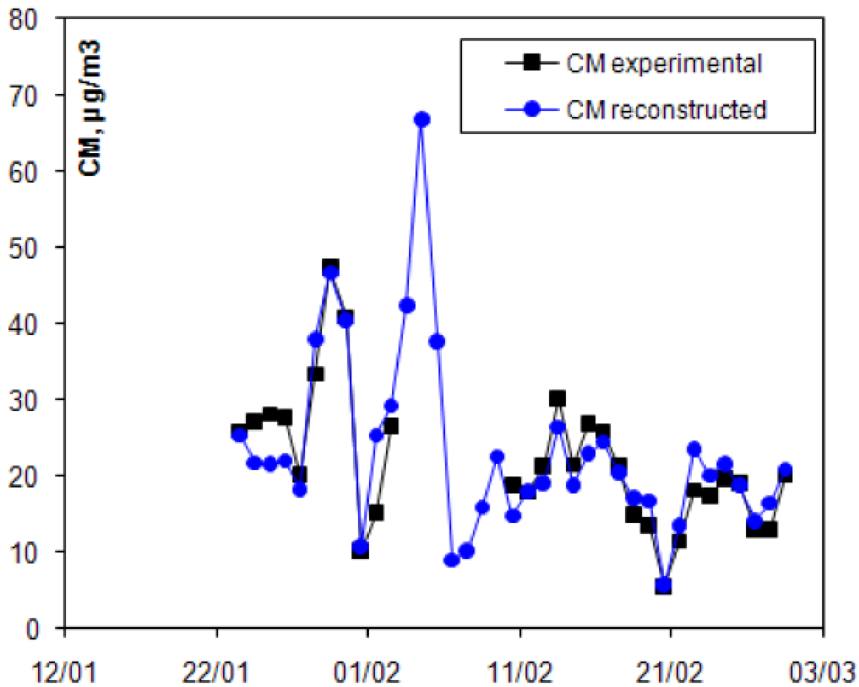
Zagorje (SI) weekdays (Source G. Mocnik)

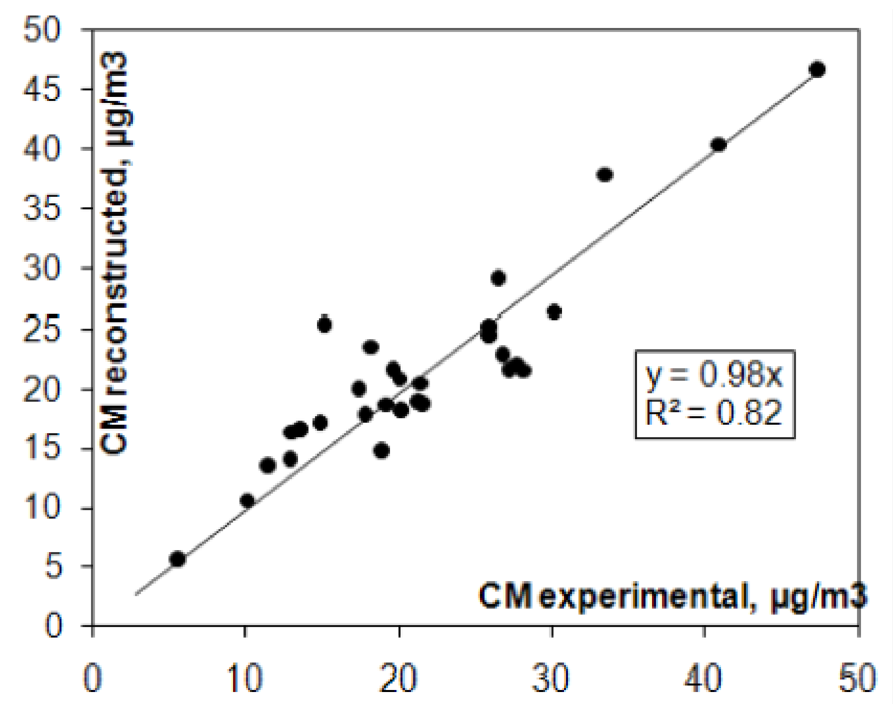


Aethalometer Model – Examples

Nova Gorica in Slovenia (Source G. Mocnik)

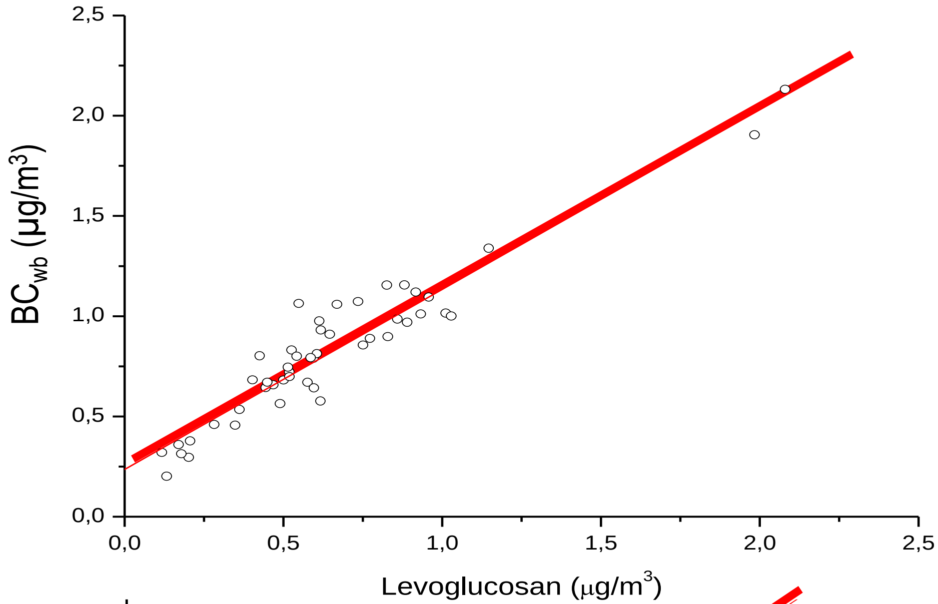
- $CM_{experimental}$ = EC + OM
    - OM = OC * 1.8 (OM:OC ratio from literature)
- Good agreement of modeled and measured CM



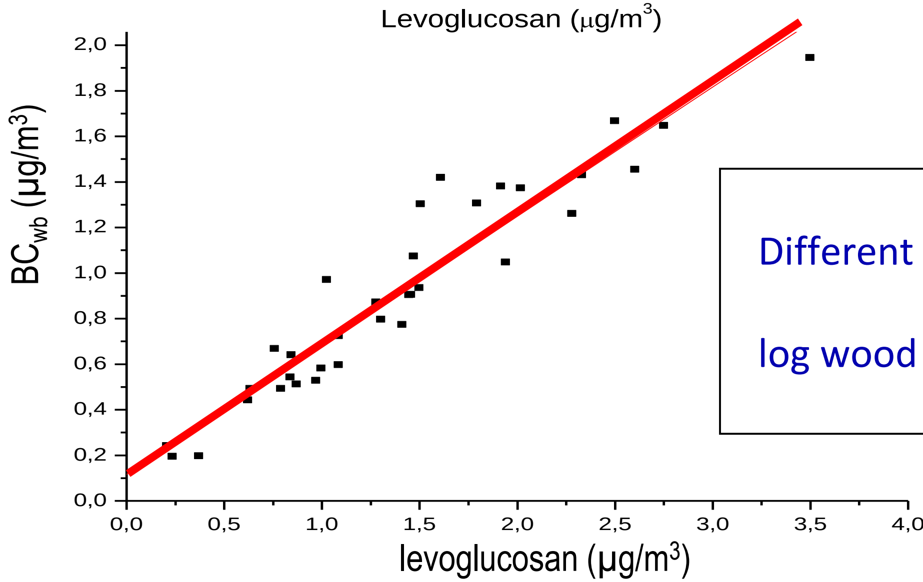


Aethalometer Model – Examples

Nova Gorica



Zagorje



Different slopes -> **different fuels**:

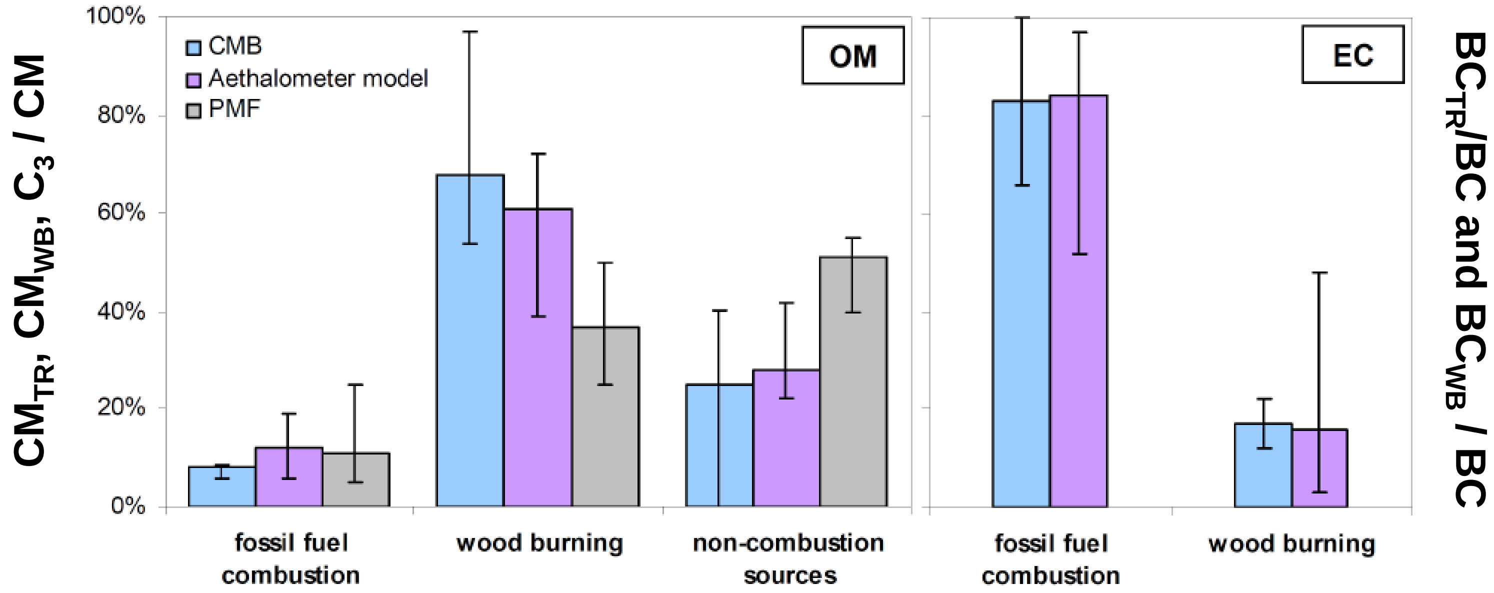
log wood vs. wood chips, pellets

Aethalometer Model – Examples

Grenoble (2 weeks in winter, Favez et al. 2010)

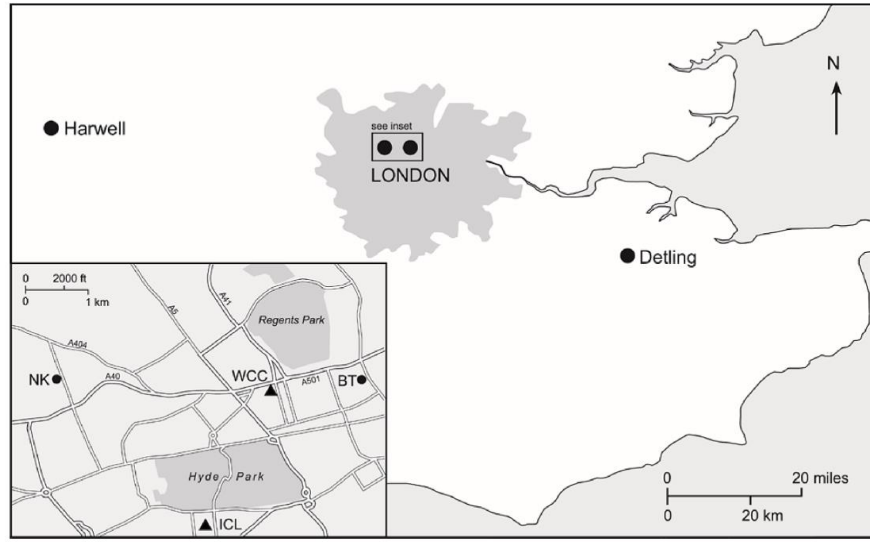
- Comparison of different measrement methods and source apportionement models
- Good agreement for BC from Aethalometer model and CMB (using source profiles and tracers)
- Slight differences between models for CM apportionment, especially for WB and other sources

→ CM_{TR} and CM_{WB} apportionment has higher uncertainties than BC_{TR} + BC_{WB}



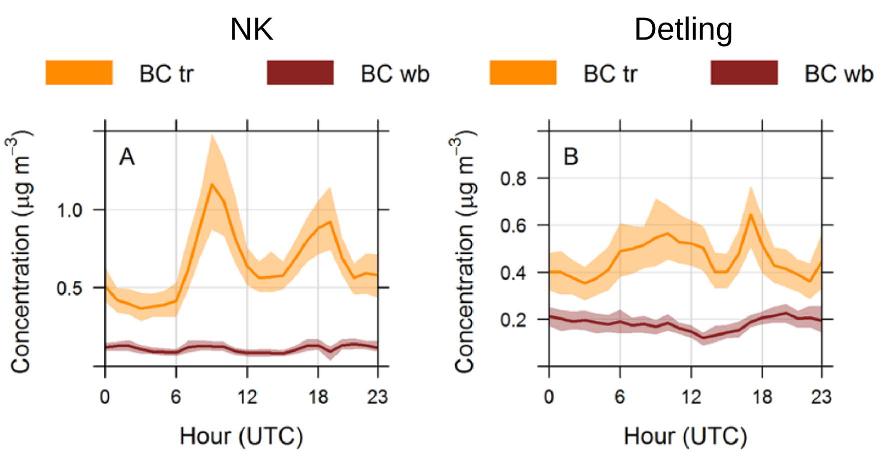
Favez, O. et al. 2010. "Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France)." Atmos. Chem. Phys. **10**(12): 5295-5314.

Aethalometer Model – Examples



<u>ClearfLo</u> (Jan. and Feb. 2013, Crilley et al. 2014)

- 2 rural sites and 1 urban background site
- Low BC and especially BC_{WB} concentrations
- Comparison of tracer approach and Aethalometer model
  - Ok for BC_{TR} and EC_{ff}
  - Differences for BC_{WB} and EC_{bb} but fractions are low and uncertainties are large
  - Depending on which emission ratios from literature are applied EC_{bb}/EC varies from 3 to 32 and from 6 to 50% at NK and Detling respectively



	EC_{bb}	BC_{wb}	EC_{ff}	BC_{tr}
Harwell	24 ± 16 %	NA	76 ± 16 %	NA
NK	7 ± 2 %	15 ± 12 %	93 ± 2 %	85 ± 12 %
Detling	14 ± 16 %	30 ± 13 %	82 ± 20 %	70 ± 13 %

Crilley et al. 2015.: Sources and contributions of wood smoke during winter in London: assessing local and regional influences, <u>Atmos. Chem. Phys</u>., 15, 3149-3171

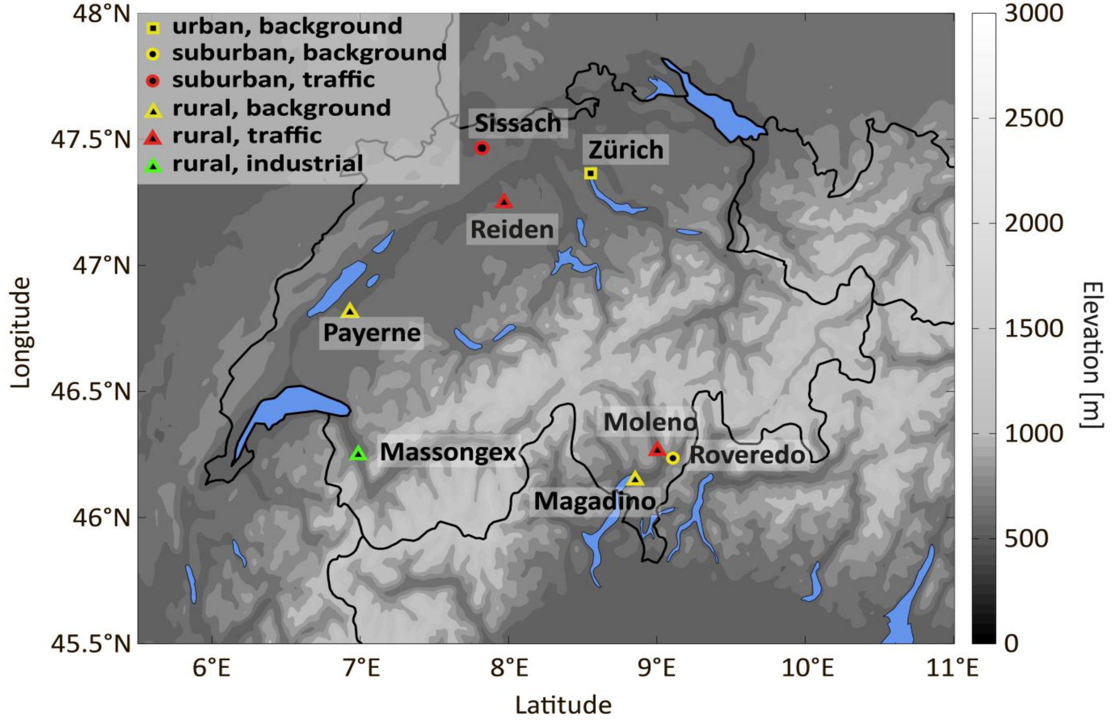
Evaluation of Aethalometer Model - Introduction

- Only very few data points used for α value determination in first Aethalometer model application (Sandradewi et al. 2008)
- Since then most studies use these α values without further evaluation using reference methods
- Some studies have questioned the applicability of the Aethalometer model
  - Herich et al. 2011 questioned the CM apportionment. They found
    - a standard error of ±30% for c_1, c_2 and c_3
    - a high sensitivity of c_1 and c_2 on the chosen α values
  - Harrison et al. 2013 doubts results of Aethalometer model in London and found
    - a high sensitivity of results on small changes in α values
    - possible other UV absorbing contributors than WB to the Aethalometer signal
  - Garg et al. 2016 found in India
    - α values down to 1 for flaming biomass-combustion
    - α >1 for older vehicles operating with poorly optimized engines

    → α was mostly determined by the combustion efficiency
- The following questions were raised by these studies:
  - Can appropriate α values be selected to give realistic results?
  - Does the Aehtalometer model work in situations other than the polluted Swiss alpine valley?
  - Is the Aethalometer model more suitable for high concentrations and when WB is the dominant light absorbing component?
- A proper evaluation of errors and uncertainties is not available yet
  - Most studies just do a sensitivity test on the α and c values

Evaluation of Aethalometer Model - Introduction

Zotter, P. et al., 2017. "Evaluation of the absorption Ångström exponents for traffic and wood burning in the Aethalometer-based source apportionment using radiocarbon measurements of ambient aerosol." Atmos. Chem. Phys. 17(6): 4229-4249.



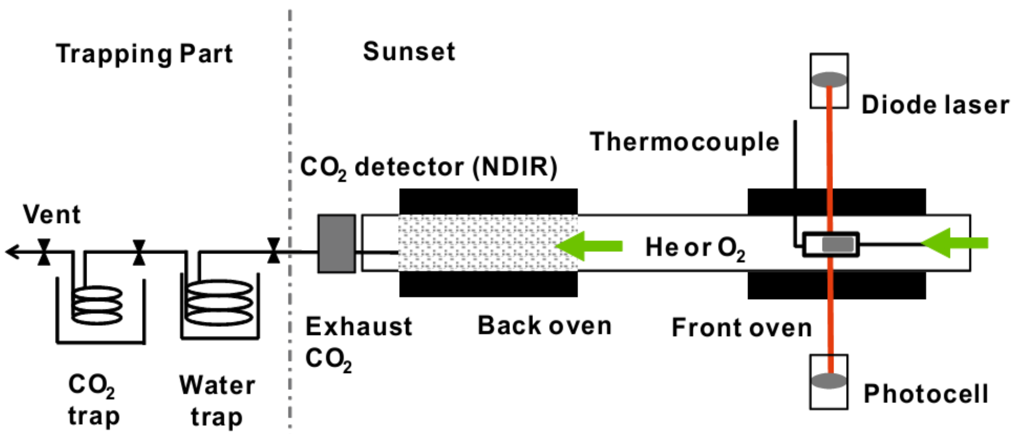
- 8 Stations across Switzerland with different source characteristics
- ^{14}C and Aethalometer data from several campaigns during 2005-2012
  - Szidat et al., 2007, Sandradewi et al., 2008a and 2008b, Perron et al., 2010, Zotter et al., 2014 Herich et al., 2011, Herich et al., 2014
- Mainly winter but also some spring and summer data
  - In total 101 ^{14}C measurements in EC on filters with 16h to 40h sampling time

Evaluation of Aethalometer Model - Introduction

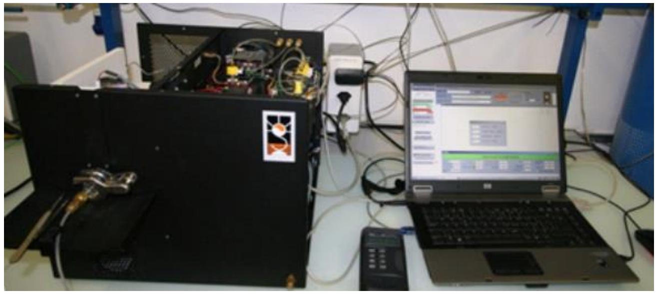
- ^{14}C data of EC fraction is used as a reference
  - New method for ^{14}C measurement of EC applied using Sunset EC/OC analyser for sample preparation (Zhang et al. 2012)
  - Optimization of the thermal treatment with respect to lowest charring (< 5%) and highest EC yield (>60%).
  - ^{14}C in EC measured for different EC yields and ^{14}C results are then extrapolated to 100% EC yield

→ No biases in EC_F/EC due to OC charring during OC removal

→ Slightly higher non-fossil EC fractions than data used for Aethalometer model development



Sunset EC/OC analyzer



Zhang, Y. L. et al. 2012. "On the isolation of OC and EC and the optimal strategy of radiocarbon-based source apportionment of carbonaceous aerosols." Atmospheric Chemistry and Physics 12(22): 10841-10856.

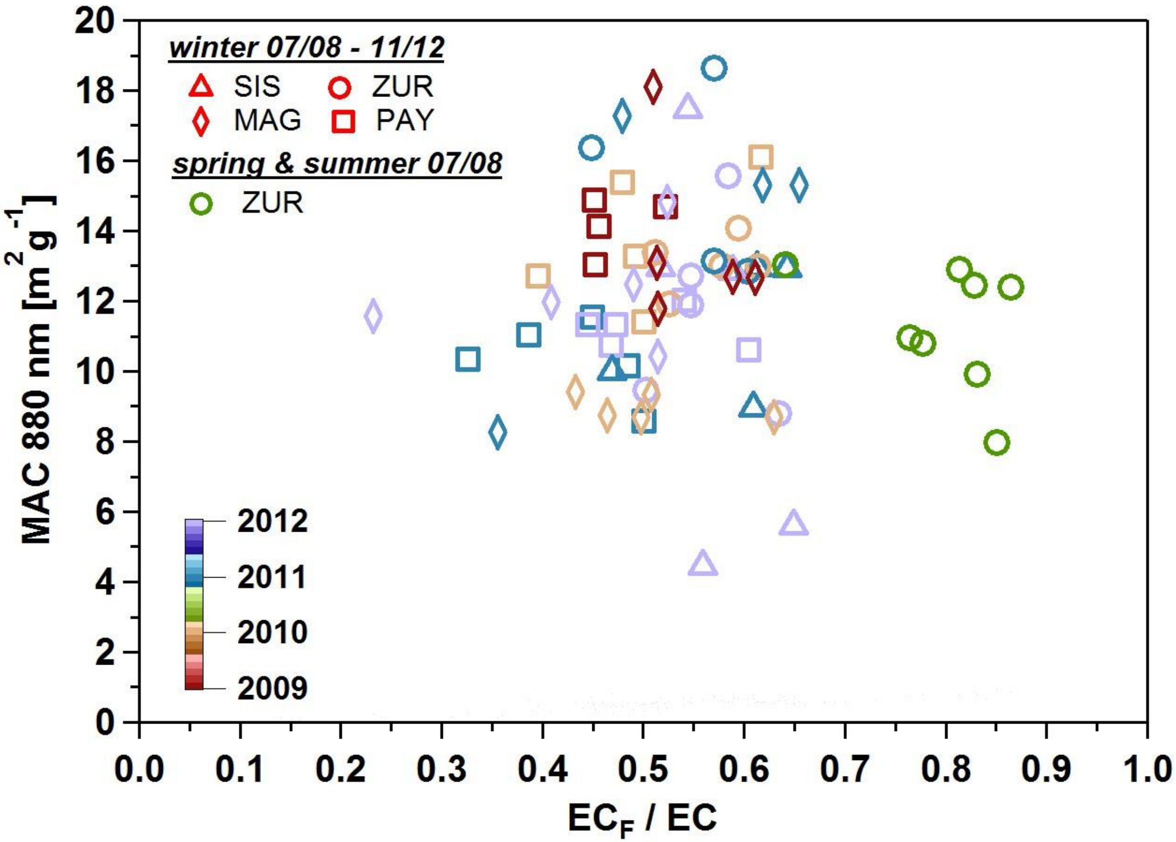
Evaluation of Aethalometer Model - Introduction

- The best combination of α_{TR} and α_{WB} is obtained by fitting the Aethalometer model outputs (BC_{TR}/BC_{TOT}) against the ^{14}C data (EC_F/EC)

$$\frac{BC_{TR}}{BC_{tot}} = \frac{1}{1 - \frac{MAC_{TR}(\lambda_2)}{MAC_{WB}(\lambda_2)} \cdot \frac{1 - \frac{b_{abs}(\lambda_2)}{b_{abs}(\lambda_1)} \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{TR}}}{1 - \frac{b_{abs}(\lambda_2)}{b_{abs}(\lambda_1)} \cdot \left(\frac{\lambda_1}{\lambda_2}\right)^{-\alpha_{WB}}}} = EC_F/EC$$

  - A least square fitting weighted by the inverse number of data points in EC_F/EC bins of 0.1 as most of the data presented in this study fall within a range of ECF/EC = 0.4–0.6
  - Ratio of MAC values for traffic and wood burning can also be included as independent fit parameter

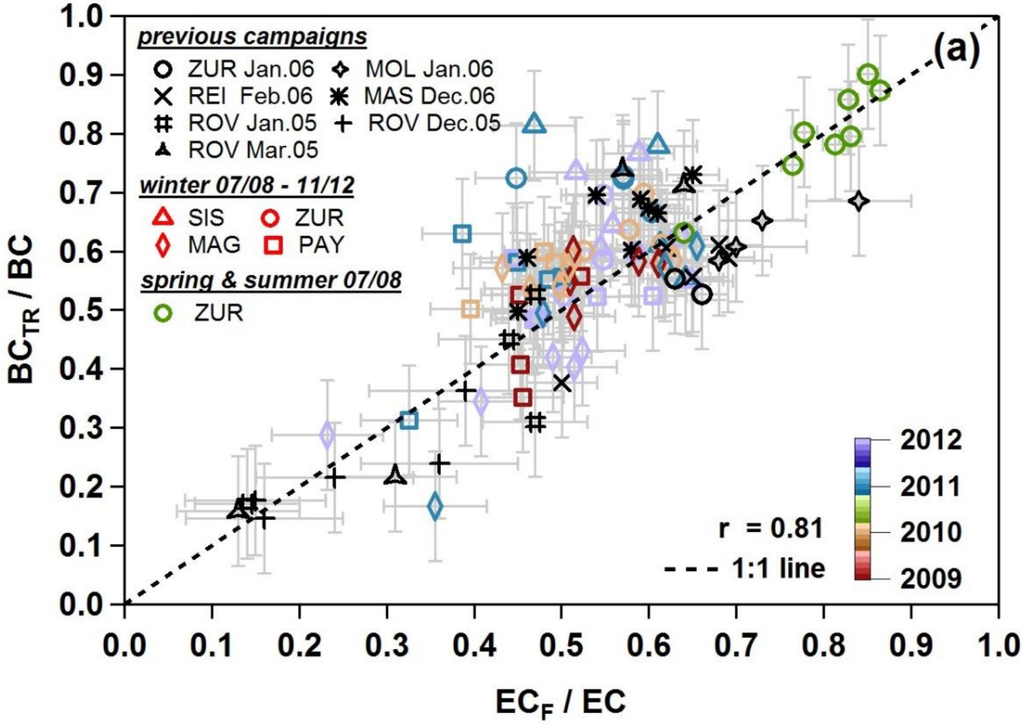
Evaluation of Aethalometer Model – MAC values

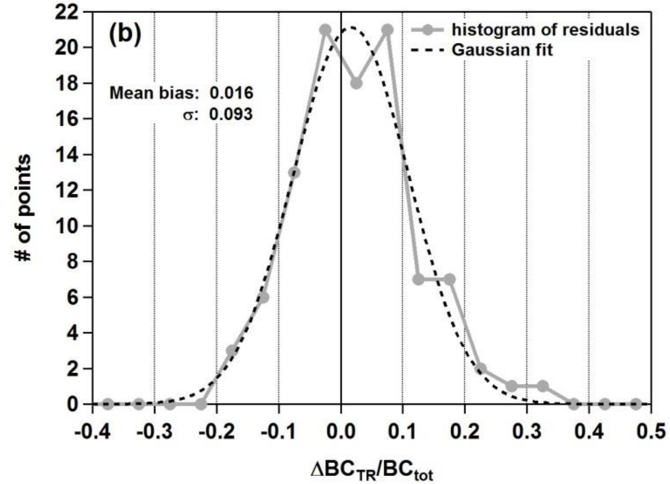


- No change in MAC for different EC_F/EC fractions
- MAC_{WB} / MAC_{TR} of 1 is obtained when included as independet fit variable

→ MAC values for traffic and wood burning BC seem to be the same

Evaluation of Aethalometer Model – Best α values

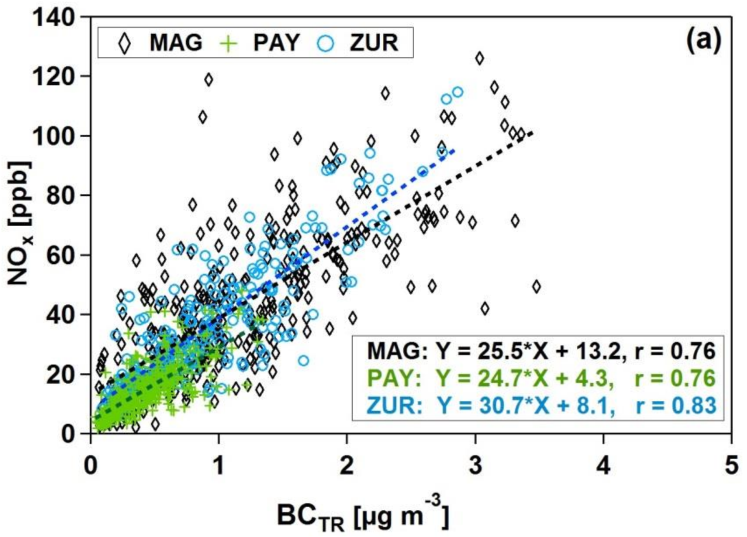


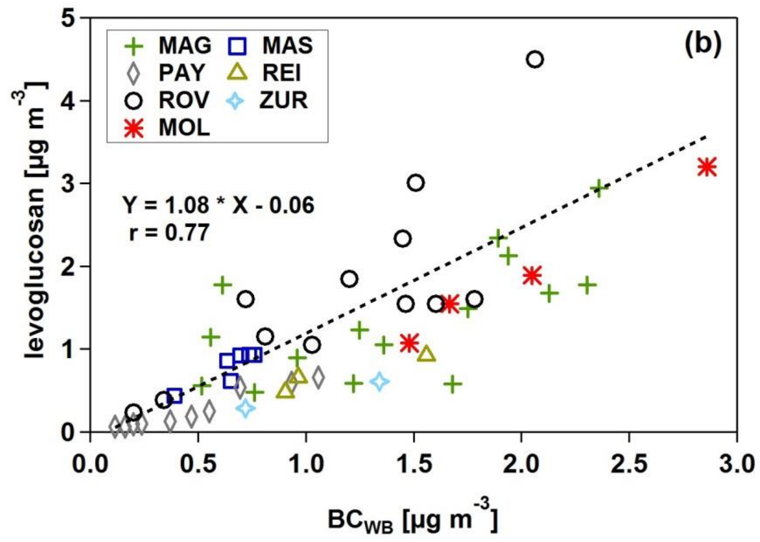


- Good correlation between Aethalometer and ^{14}C results
- Best fit result: α_{TR} = 0.9 and α_{WB} = 1.68
- Only 9.3% fitting residuals ($\Delta BC_{TR}/BC = BC_{TR}/BC – EC_F/EC$) and 1.6% positive bias

→ **single α_{WB} and α_{TR} pair reproduces reasonably well the ^{14}C results**

Evaluation of Aethalometer Model – Comparison with other data





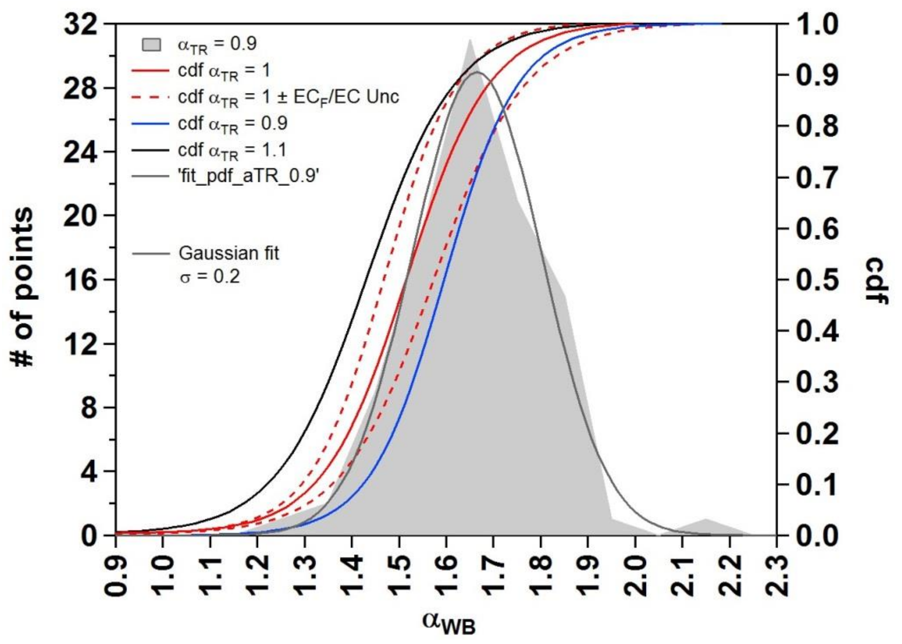
- Good correlation of BC_{TR} with NO_x
- Good correlation of BC_{WB} with levoglucosan

Evaluation of Aethalometer Model – α value distribution

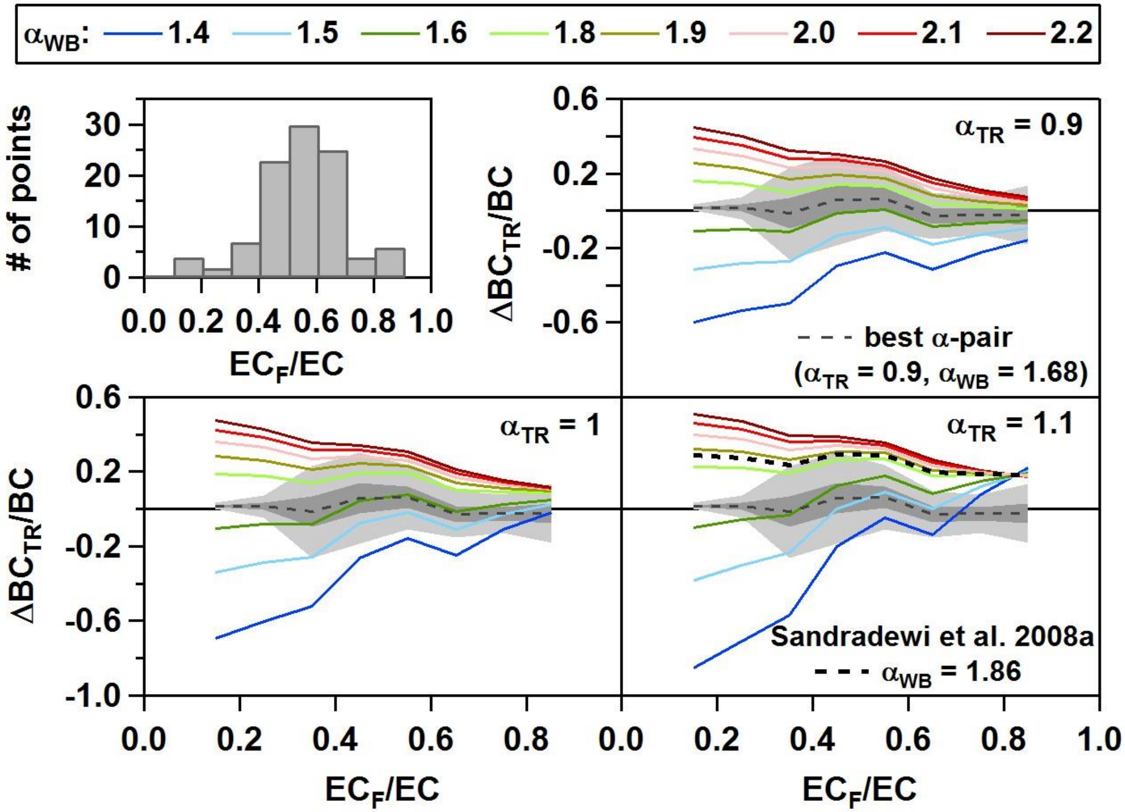
- With a priori selected α_{TR}, αWB was also calculated for each individual data point
- No clear station-to-station or season-to-season differences in α_{WB} (α_{TR} = 0.9)
- However, α_{TR} and α_{WB} are interdependent
  - Increase in α_{TR} by 0.1 results in a decrease in α_{WB} by 0.1

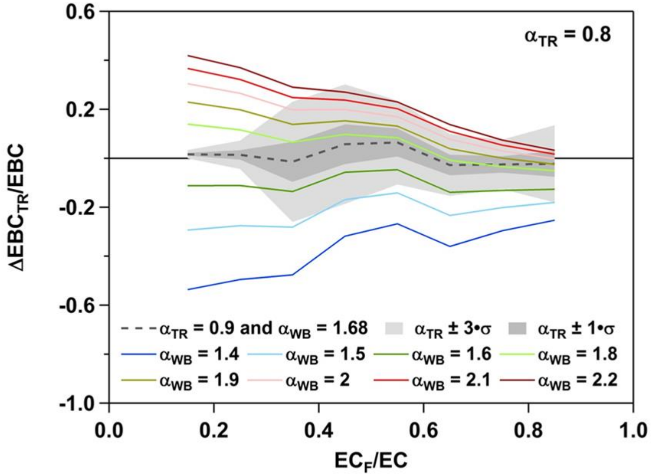
  → randomly altered α_{TR} and α_{WB} (e.g. ± 0.1) could result in high $\Delta BC_{TR}/BC$

station	α_{WB} range	α_{WB} mean ± standard deviation
SIS	1.23–1.84	1.55 ± 0.21 (n = 9)
ZUR (winter)	1.47–1.80	1.67 ± 0.11 (n = 14)
ZUR (summer)	1.34–1.90	1.60 ± 0.14 (n = 8)
MAG	1.53–1.85	1.69 ± 0.09 (n = 19)
PAY	1.42–1.80	1.63 ± 0.10 (n = 19)
MOL	1.85–2.17	1.93 ± 0.16 (n = 4)
ROV	1.43–1.85	1.68 ± 0.11 (n = 13)
REI	1.70–1.86	1.81 ± 0.06 (n = 5)
MAS	1.46–1.65	1.56 ± 0.06 (n = 8)



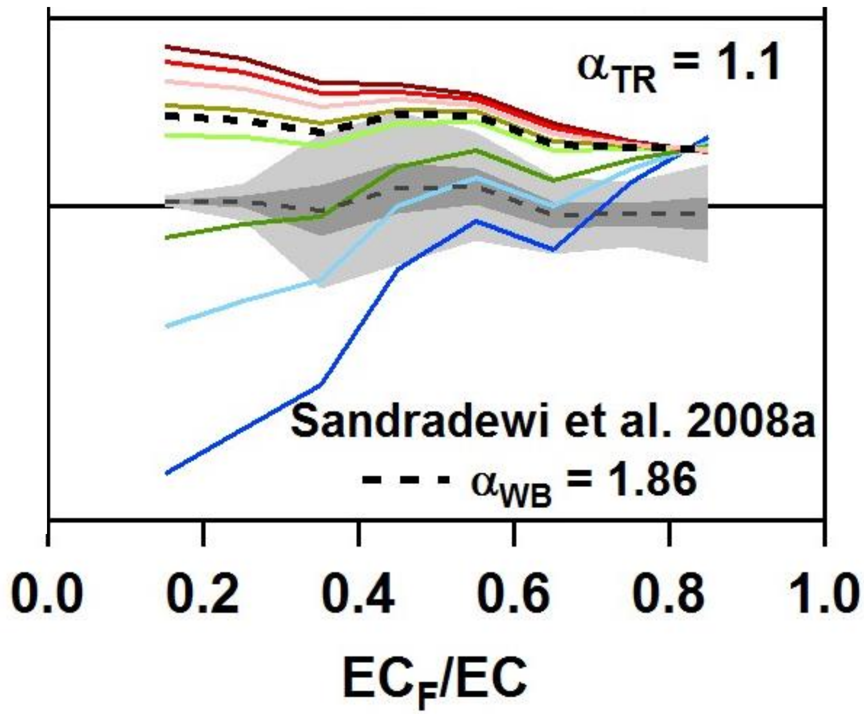
Evaluation of Aethalometer Model – Other α combinations





- $\Delta BC_{TR}/BC$ depend on EC_F/EC → good agreement cannot be obtained over the entire EC_F/EC range using other α-pairs
- Combinations of α_{TR} = 0.8, 1.0 and α_{WB} = 1.8, 1.6 are possible but only for EC_F/EC ~40 – 85%

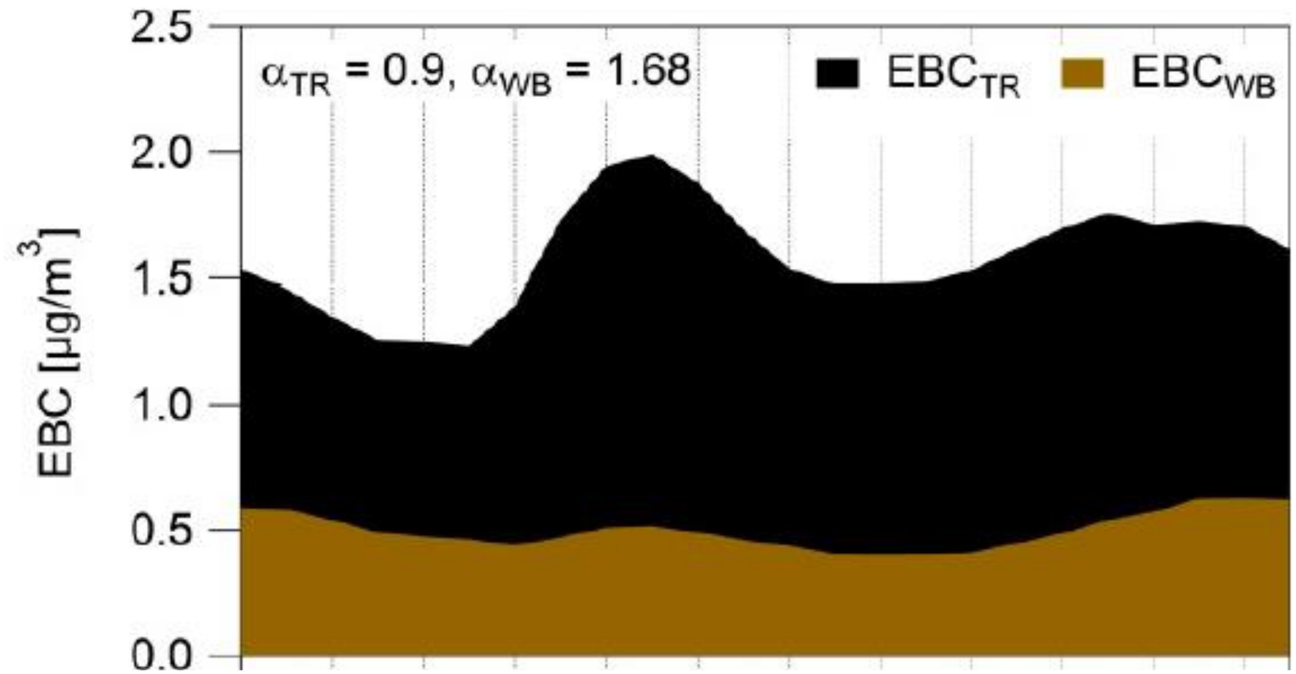
Evaluation of Aethalometer Model – Other α combinations



- Applying α values from Sandradewi et al. 2008 to our data set results in large residuals
- If Sandradewi et al. (2008a) would have optimized their α_{WB} to the EC_F/EC instead of CM_F/CM results would have been (with α_{TR} = 1.1)
- **α_{WB} = 1.72 and**
- **α_{WB} = 1.64** (with extrapolation of EC_F/EC to 100% EC yield)

Evaluation of Aethalometer Model – High time resolution

Average diurnal cycle for week days in Zurich



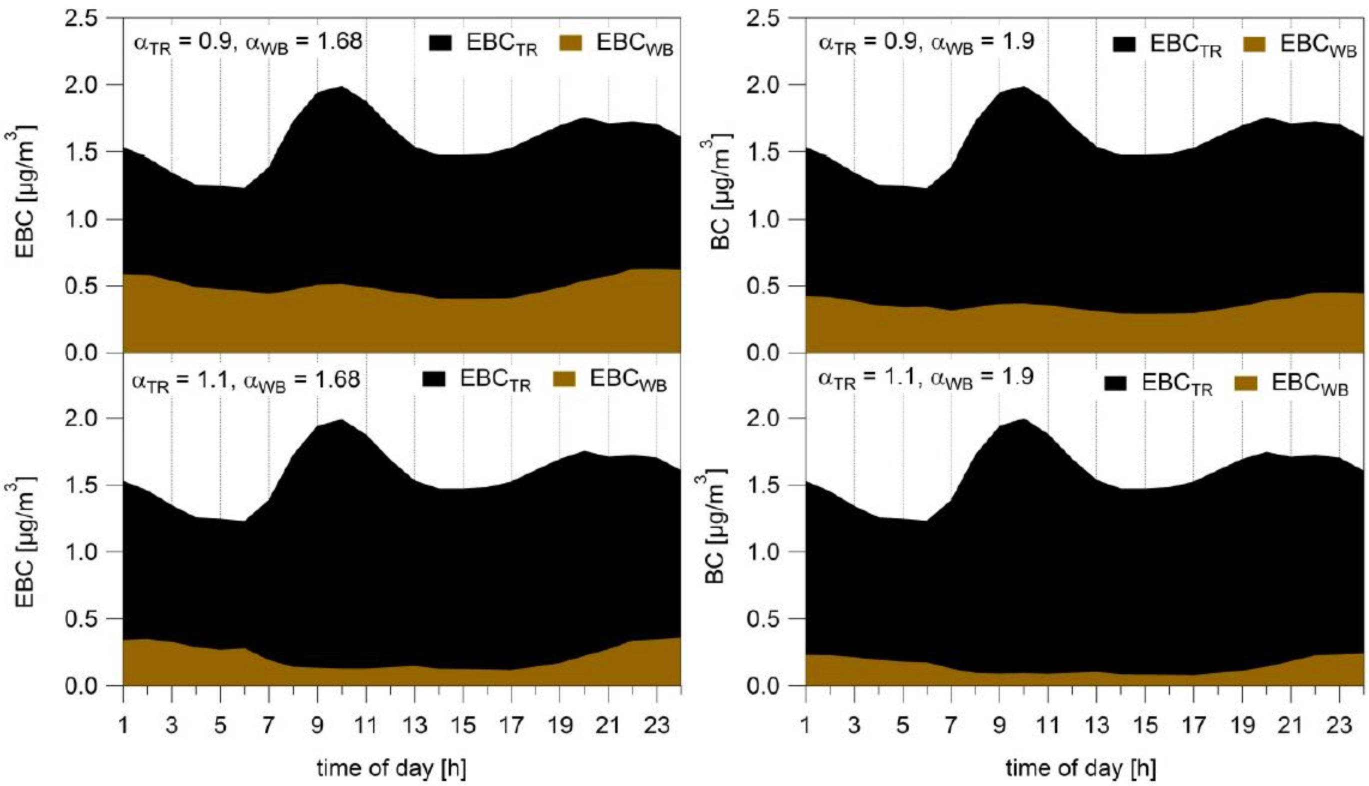
- EBC_{WB} follows EBC_{TR} with an evident increase during morning hours.
- This increase is statistically larger than the uncertainties

→ Some false attribution of EBC_{TR} and EBC_{WB}

→ Most probably due to the constant a priory assumed pair of α_{WB} and α_{TR}

Evaluation of Aethalometer Model – High time resolution

Average diurnal cycle for week days in Zurich

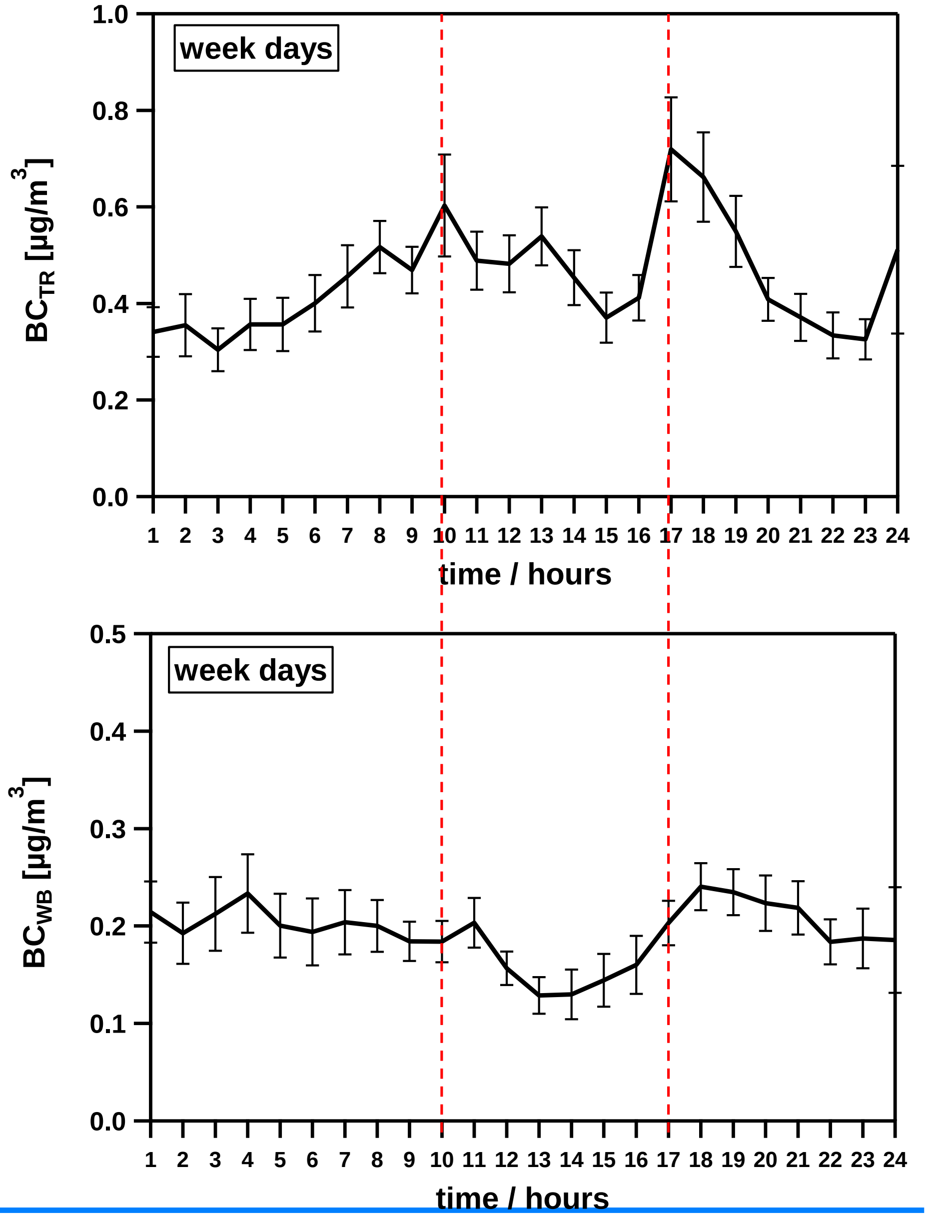


- By applying α_{TR} of 1.1 the morning peak disappears indicating that a higher α_{TR} would be more representative of fresh traffic emissions in the case of ZUR

→ Be careful when applying the Aethalometer model to high time resolution data, especially for low EBC concentrations and rush hours

Evaluation of Aethalometer Model – High time resolution

- Measurements during the ClearfLo project in Jan. and Feb. 2013 at Detling (~60km south east of London)
- α_{TR} = 1 and α_{WB} = 2
- No cross correlation between BC_{TR} and BC_{WB} during traffic peaks



Evaluation of Aethalometer Model – Wavelength sensitivity

a) Calculation of best α values

wavelength pair	α_{WB}	α_{TR}	μ of $\Delta BC_{TR}/BC$	σ of $\Delta BC_{TR}/BC$
470 & 950 nm	1.68	0.90	2%	9%
470 & 880 nm	1.75	0.90*	7%	11%
370 & 950 nm	2.09	0.90*	17%	12%
370 & 880 nm	2.09	0.90*	18%	13%

*no physically meaningful value for αTR could be obtained by the fitting Equation 13 against ECF/EC and therefore, αTR was set to 0.9

b) EC_F/EC vs. BC_{TR}/BC with α_{TR} = 0.90 and α_{WB} = 1.68

wavelength pair	mean $\Delta BC_{TR}/BC$	negative BC_{TR}/BC points	r (with EC_F/EC)
470 & 950 nm	2%	0%	0.80
470 & 880 nm	3%	3%	0.65
370 & 950 nm	-12%	16%	0.63
370 & 880 nm	-15%	19%	0.58

- Any combination with 370 nm as N-UV wavelength resulted in
  - larger residuals
  - a significant number of negative points
  - weaker correlations with EC_F/EC

  → 470 nm should be used as N-UV wavelength in the Aethalometer model
- 880 nm as N-IR wavelength shows also acceptable results

Conclusion – BC source apportionment methods

- Only direct method is the ^{14}C method, however it is:
  - Complex, costly, time consuming, limited time resolution
- Receptor modelling using source specific chemical tracers and emission ratios
  - Relies on literature data for emission ratios
  - Mostly assumes constant emissions ratios
  - Emission rations, especially for wood burning show substantial variation depending on fuel type and combustion conditions
- Aethalometer model
  - 2 component model using the fact that the absorption of wood smoke is enhanced at N-UV wavelengths compared to N-IR wavelengths
  - Only a priory assumption of α values necessary
  - Relatively cheap since no additional analyses necessary
  - High time resolution

Conclusion – Evaluation of Aethalometer model

- No significant dependence of MAC for different EC_F/EC fractions
  - → MAC values for traffic and wood burning BC seem to be the same
- Good agreement between Aethalometer model and ^{14}C results using a single α_{WB} and α_{TR} pair for different locations and seasons
  - Best fit result: $\alpha_{TR} = 0.9$ and $\alpha_{WB} = 1.68$
- Also combinations of $\alpha_{TR} = 0.8, 1.0$ and $\alpha_{WB} = 1.8, 1.6$, respectively, are possible but only for EC_F/EC ~40 – 85% because ΔBC_{TR}/BC depends on EC_F/EC
- Using 370 nm as N-UV wavelength resulted in larger residuals, a significant number of negative points and weaker correlations with EC_F/EC
- In Zurich there seems that EBC_{WB} follows EBC_{TR} during morning rush hours
  - Some false attribution of EBC_{TR} and EBC_{WB} due to the constant a priory assumed α pair
  - False attribution during the morning peak disappears by applying α_{TR} of 1.1
  - → A higher α_{TR} would be more representative of fresh traffic emissions in Zurich

Conclusion – Evaluation of Aethalometer model

Still more research on α values in the Aethalometer model needs to be done

- More data needed
  - from spring, summer and autumn
  - from different countries
- Data from measurement sites with
  - a less modern car fleet than European standard
  - residential biomass combustion with less well-constrained combustion efficiencies

Recommendations for applying Athalometer model

- Apply the Aethalometer model only when other BC sources than traffic and wood burning can be excluded

- Evaluation of the choice of α_{WB} and α_{TR} using a reference method is highly valuable and should be performed when applying the Aethalometer model, if possible

- In the absence of such reference measurements, however, assuming a single set of α_{TR} and α_{WB} yields acceptable results

- If no data evaluation is carried out use **α_{TR} = 0.9 and α_{WB} = 1.68**

- Depending on the EC_F/EC range also other α combinations are possible
  - EC_F/EC 40 – 85%: α_{TR} = 0.8, 1.0 and α_{WB} = 1.8, 1.6, respectively

Recommendations for applying Athalometer model

- Evaluate Aethalometer model outputs with auxiliary data and compare relationships with literature
  - BC_{TR} vs. NO_x and BC_{WB} vs. levoglucosan or potassium
- Evaluate high time resolution Aethalometer model outputs if cross correlations between BC_{WB} and BC_{TR} during rush hour peaks occur
- Be careful when applying the CM apportionment
  - The assumption that c_2 and especially c_3 are constant might not reflect the reality
  - Especially c_3 (mostly for apportioning SOA) is expected to substantially vary during the day and from day to day
- Evaluate total α values at times when measurements are only influenced by 1 source
  - Traffic site in summer for the α_{TR} determination
  - Rural site in winter during night time for α_{WB} evaluation
- ***In general: Be aware about limitations and uncertainties***

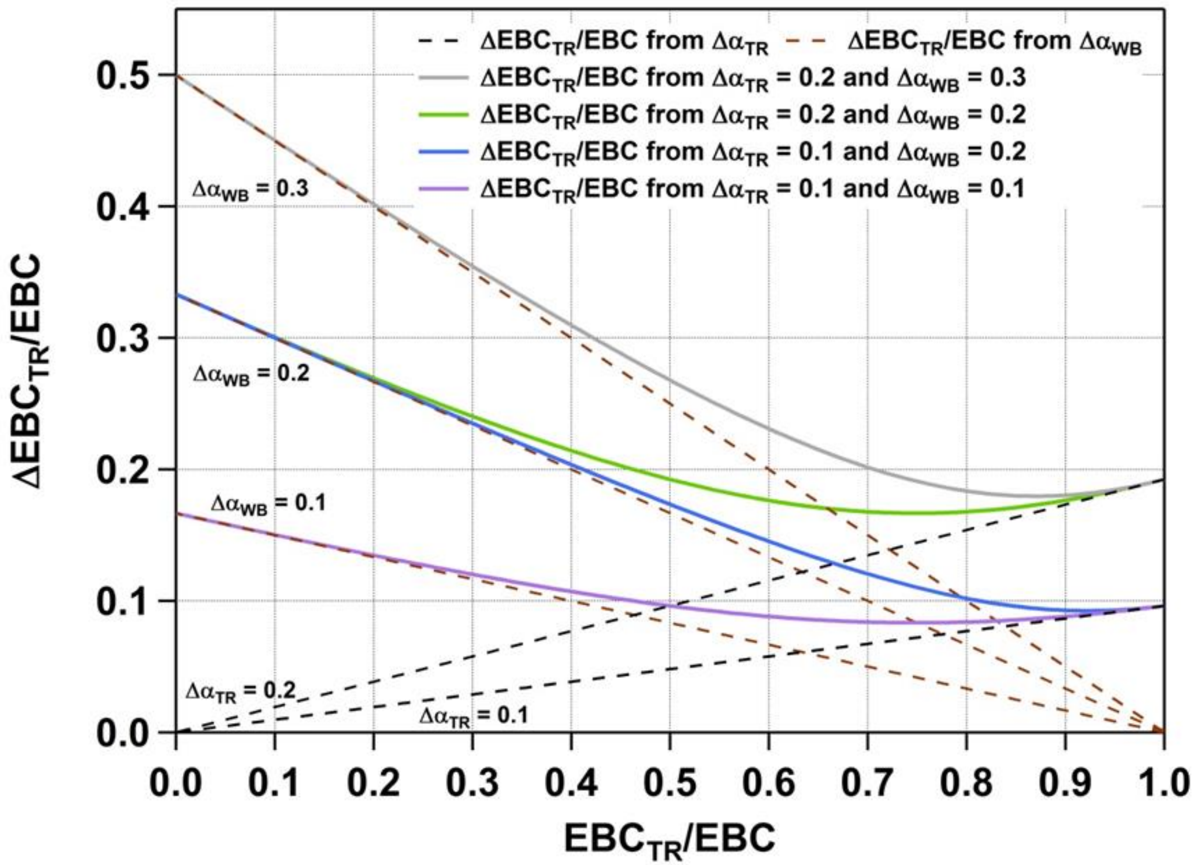
COLOSSAL
Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL

cost
EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

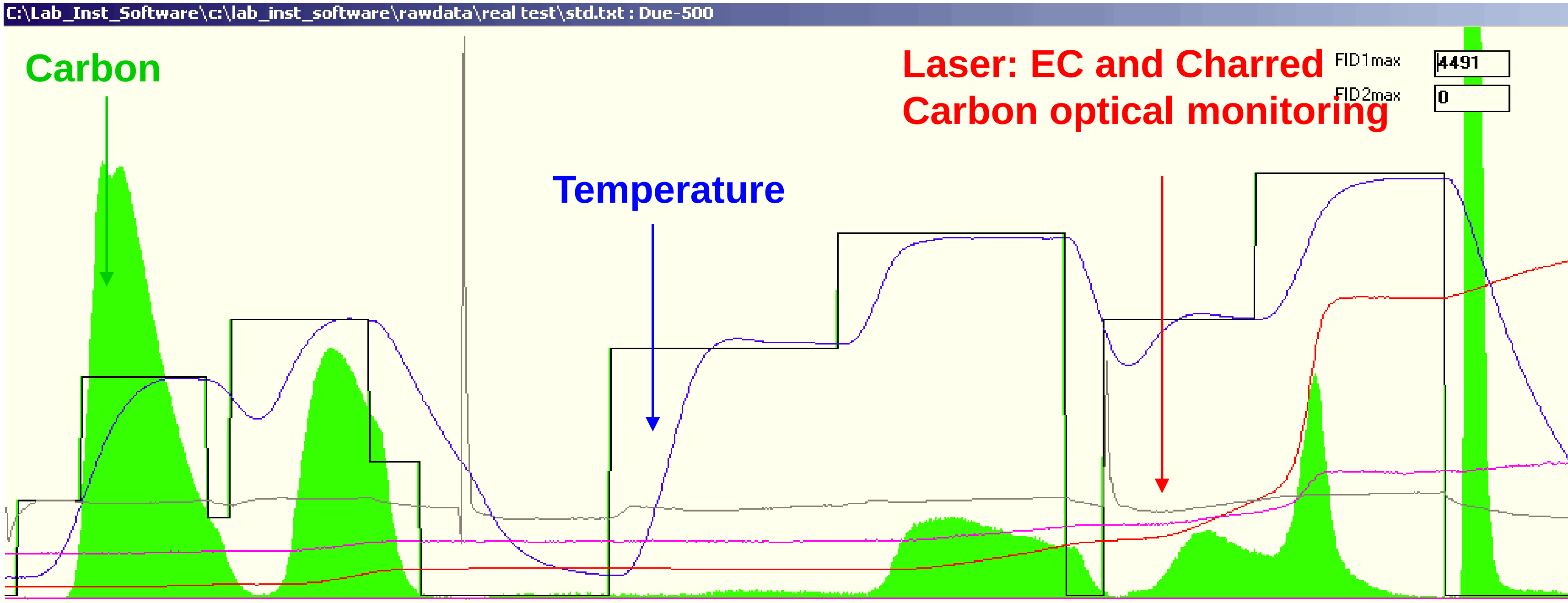
COST is supported by the EU Framework Programme Horizon 2020

Thank you for your attention

Appendix


ΔEBC_TR/EBC from Δα_TR
ΔEBC_TR/EBC from Δα_WB
ΔEBC_TR/EBC from Δα_TR = 0.2 and Δα_WB = 0.3
ΔEBC_TR/EBC from Δα_TR = 0.2 and Δα_WB = 0.2
ΔEBC_TR/EBC from Δα_TR = 0.1 and Δα_WB = 0.2
ΔEBC_TR/EBC from Δα_TR = 0.1 and Δα_WB = 0.1
Δα_WB = 0.3
Δα_WB = 0.2
Δα_WB = 0.1
Δα_TR = 0.2
Δα_TR = 0.1
ΔEBC_TR/EBC
EBC_TR/EBC
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

^{14}C Method - Introduction



$S1/O_2$ $S2/O_2$ S3/He $S4/O_2$

Pure OC | **Mixture of OC and EC** | **Pure EC**

Aims at recovering OC for ^{14}C measurement

Aims at recovering EC for ^{14}C measurement

Summary (method)

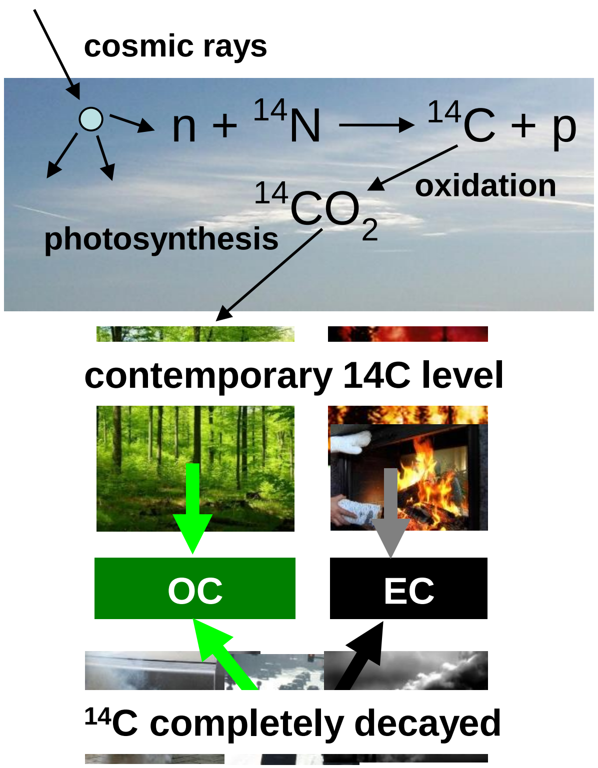
The optimized protocol

Swiss_4S	
Step	**Gas, T/°C,t/s**
S1	**O_2, 180, 50**
	O_2, 375, 150
S2	**O_2, 475, 120**
S3	**He, 450, 180**
	He, 650, 180
S4	**O_2, 500, 120**
	O_2, 760, 150

1. Charring can be quantified, which is minimized (<5%)
2. OC is completely removed before EC step.
3. EC recovery is increased to 70 - 90%.
4. ^{14}C of total EC can be estimated by extrapolation of EC yield to 100%.

Introduction

Source apportionment with the radiocarbon analysis

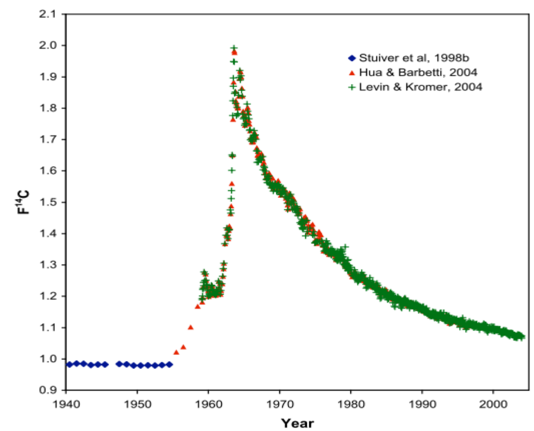


^{14}C half life = 5730 years

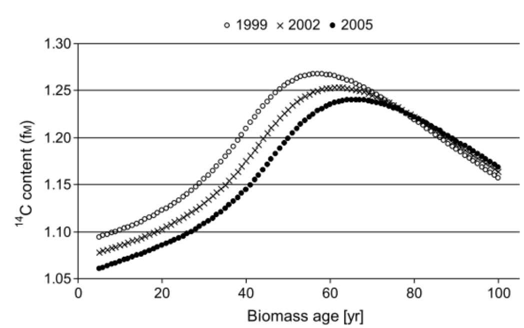
$$fm = \frac{\left(\,^{14}C / \,^{12}C\right)_{Sample}}{\left(\,^{14}C / \,^{12}C\right)_{AD1950}}$$

fm…fraction of modern carbon

$fm_{fossil} = 0$, $fm_{biogenic} = 1$



- $fm_{CO2} \sim 1.05$
  - Levin et al. 2008
- $fm_{tree} \sim 1.05\text{-}1.15$
  - Mohn et al. 2008



- correction for bomb ^{14}C
  - $fm_{ref\ bio} = fm_{CO_2}$
  - $fm_{ref\ EC} = fm_{tree}$
  - $fm_{ref\ OC} = x{*}fm_{ref\ bio} + y{*}fm_{ref\ EC}$

What is Black Carbon?

Defined by five essential characteristics

- Composition
- Morphology
- Volatility
- Solubility
- Light absorption

"BC" Measurement Methods

Light Absorption Coefficient (σ_{ap})

- Derived from optical methods, e.g.,
  - Filter-based (aethalometer, PSAP, MAAP, COSMOS)
  - Suspended particles (e.g., photo-acoustic, extinction minus scattering)
- Equivalent Black Carbon (EBC)
  - derived from σ_{ap} using a mass absorption efficiency (MAE)
  - the MAE used to calculate EBC must be specified
- BC Properties: absorption

Elemental Carbon (EC)

- Derived from measurement of CO_2 evolved from thermal or thermo-optical methods
  - e.g., IMPROVE or EUSAAR protocols
- BC Properties: composition, refractory, (absorption)

Refractory Black Carbon (rBC)

- Derived from laser incandescence methods
- BC Properties: composition, refractory, absorption

Source specific tracers and emission ratios

- Measurement of OC, EC and source specific tracers
  - E.g. levoglucosan, potassium, …
- Applying emissions ratios from literature for source apportionment
  - OC_{bb}/EC_{bb}, levoglucosan/$OC_{bb,}$ OC_{tr}/EC_{tr}
  - Calculations:
    - OC_{bb} = levoglucosan$_{measured}$ x levoglucosan/OC_{bb}
    - $EC_{bb} = OC_{bb}$ x OC_{bb}/EC_{bb}
    - $EC_{tr} = EC_{measured} - EC_{bb}$
    - $OC_{tr} = EC_{tr}$ x OC_{tr}/EC_{tr}

  } E.g.:
    - Gelencsér A. et al. 2007: *JGR* 112(D23): D23S04
    - Crilley L. R. et al. 2015: *ACP* 15(6): 3149-3171.

  - ***Limitation:***
    - Assumption of constant emission ratios
    - Emission ratios are dependent on the combustion conditions and fuel type
    - Wide range of emission ratios have been previously reported
      - OM_{bb}/EC_{bb}:
        - 3 – 63 (Schauer et al., 2001; Fine et al., 2001, 2002, 2004a, 2004b; Schmidl et al., 2008)
      - OM_{tr}/EC_{tr}:
        - 0.25 – 0.45 for Europe (El Haddad et al. 2013)
        - 0.9 – 1.4 for the US (Zhang et al., 2005; Sun et al., 2012; Stroud et al., 2012)

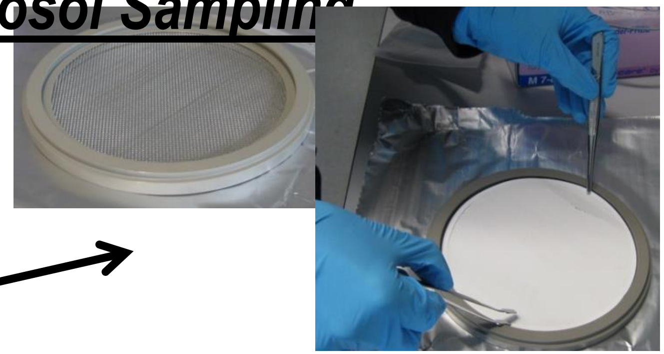
Methods

Aerosol Sampling

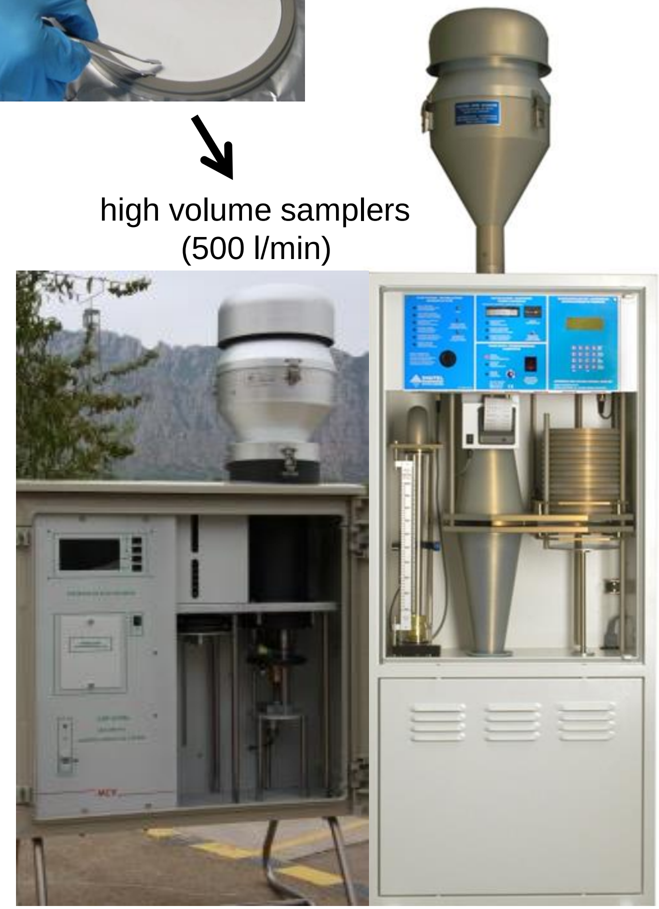
empty filter (Ø 15cm)

pre-baking to remove OC

filterholders



high volume samplers (500 l/min)



water extraction

offline analysis

Quellenzuordnung mit Aethalometer - Beispiele

- Aufspaltung der totalen kohlenstoffhältigen Masse (CM) in einen Verkehrs- und einen Holzfeuerungsanteil

- *CM = EC + OM*
  - OM … organische Masse

- CM mit anderer Messmethode bestimmt (z.B.: EC OC Messung mit Sunset)

- $CM = C_1 * b_{abs,\ TR} + C_2 * b_{abs,\ WB} + C_3$

CM_{TR} ← **Verkehr**

CM_{WB} ← **Holzfeuerung**

C_3 ← **nicht aus Verbrennung**

- C_1 muss angenommen werden
  - ~260 000 µg/m² (aus Literatur z.B. Sandradewi et al. 2008, Favez et. al 2009)
  - Es empfiehlt sich eine Sensitivitätsanalyse für C_1 durchzuführen

Quellenzuordnung mittels Aethalometer - Beispiele

- Daten aus Nova Gorica in Slowenien (Quelle Grisa Mocnic)
- $CM_{experimental}$ = EC + OM
    - OM = OC * 1.8 (OM:OC ratio aus Literatur)
- Gute Übereinstimmung von CM gerechnet und gemessen