^{14}C-based Source Apportionment of Carbonaceous Aerosols in Switzerland for 2008 – 2012

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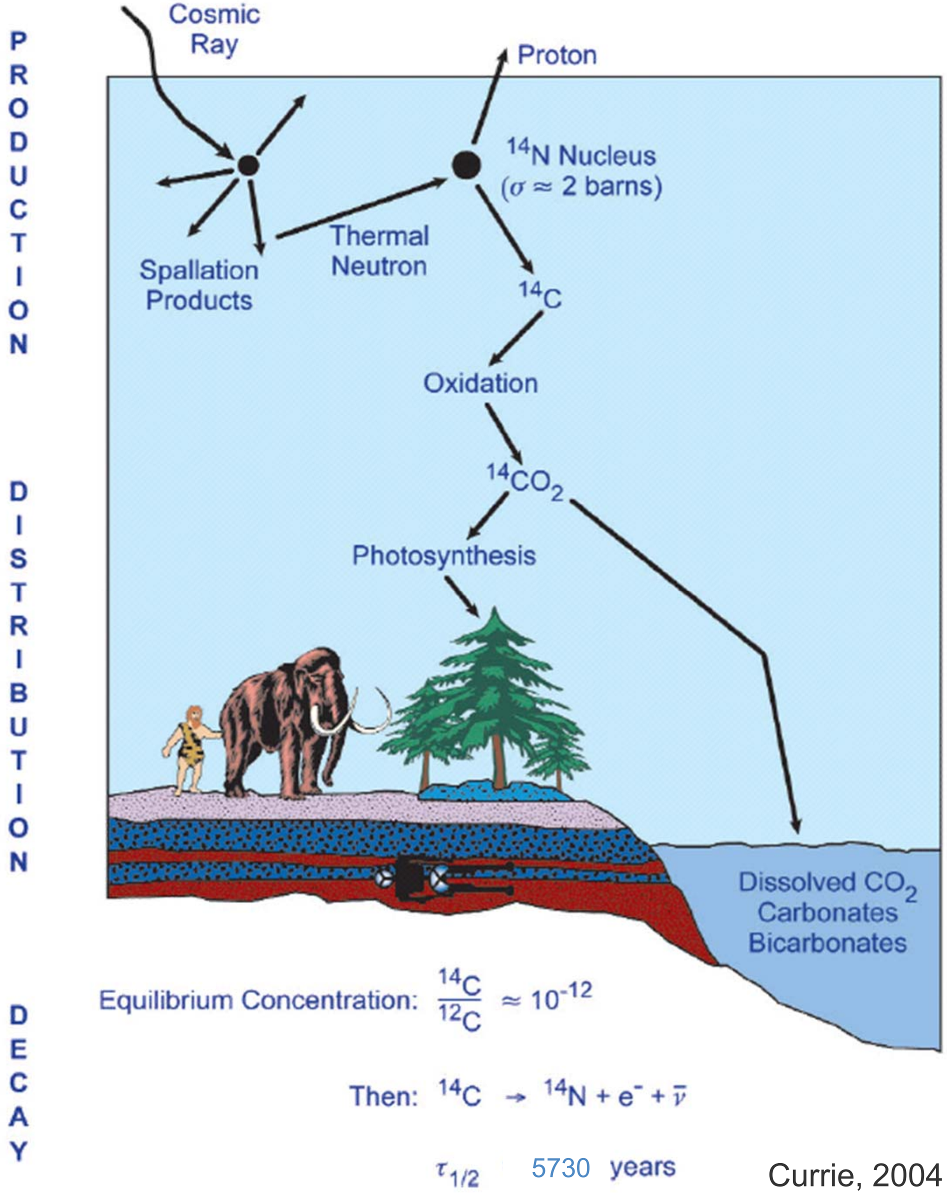
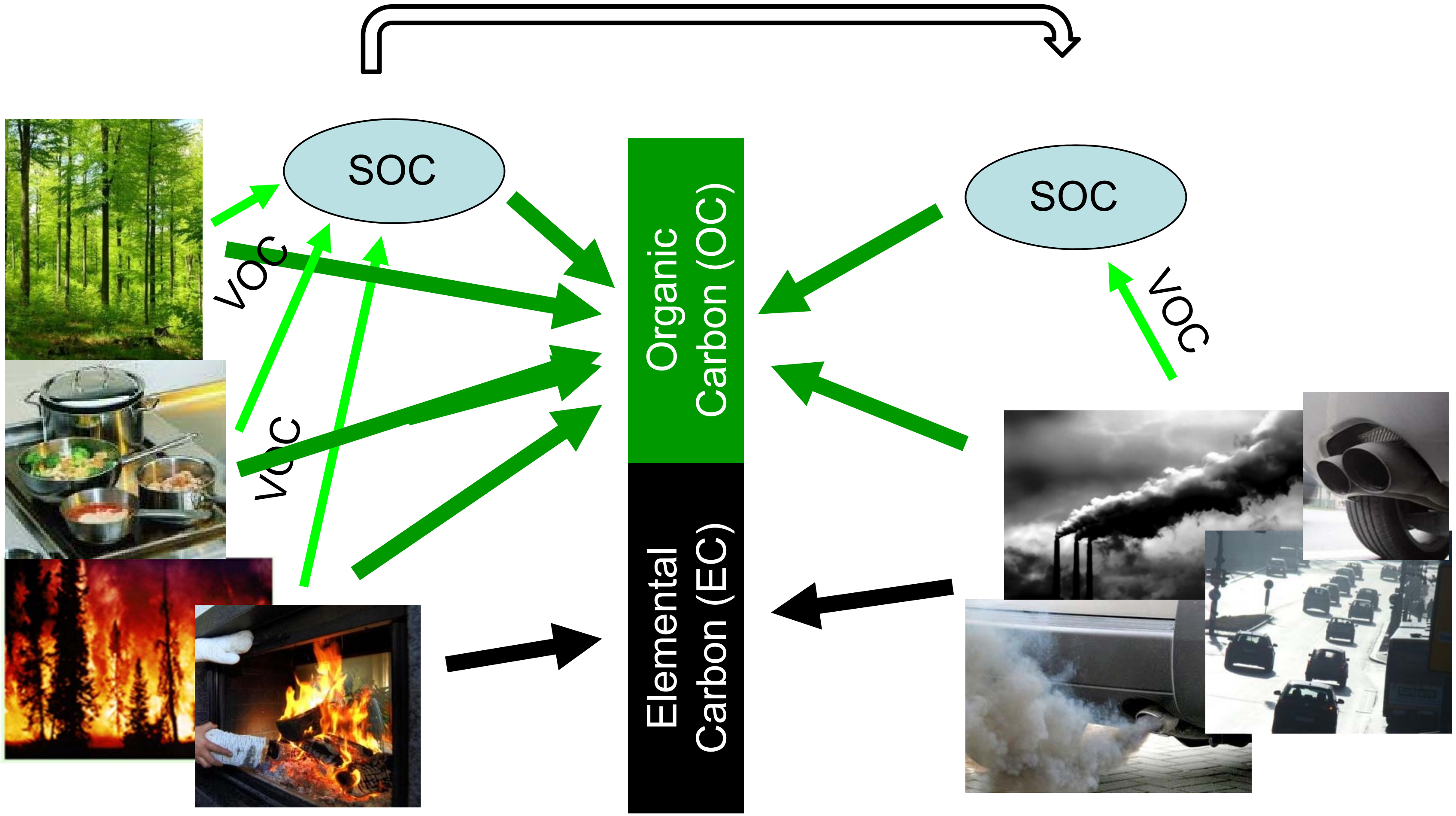
Radiocarbon in the environment



Curie, 2004

Carbonaceous aerosols & radiocarbon

^{14}C half-live = 5730 years



Modern ^{14}C level

Depleted in ^{14}C

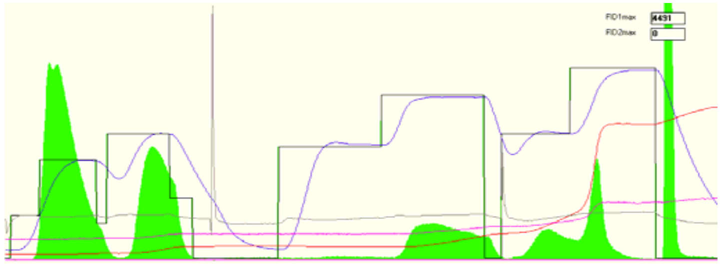
Thermo-optical control of OC/EC separation

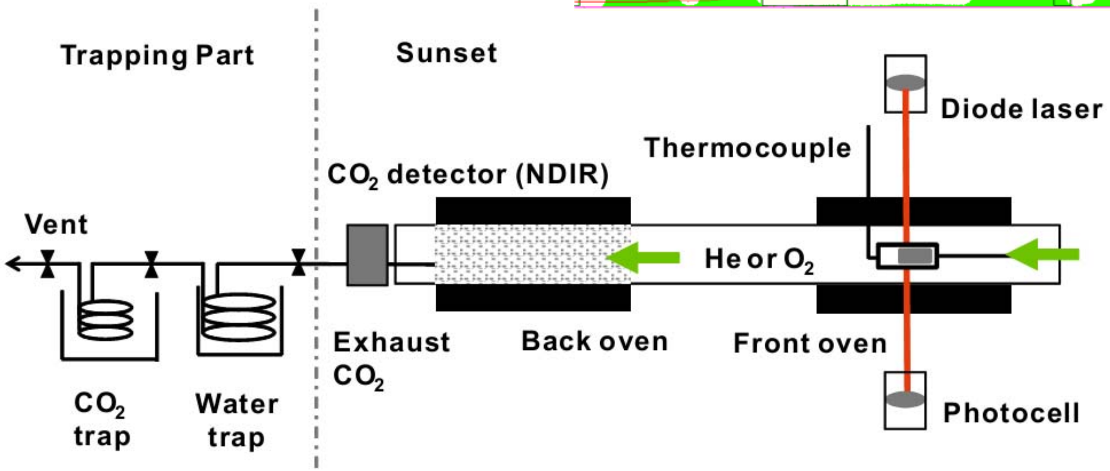
Separation goals for $^{14}C(EC)$:

1. Complete OC removal
2. Negligible charring
3. High EC recovery

New protocol Swiss_4S

- Oxygen-based
- Related to EUSAAR-2
- Water-extracted filters

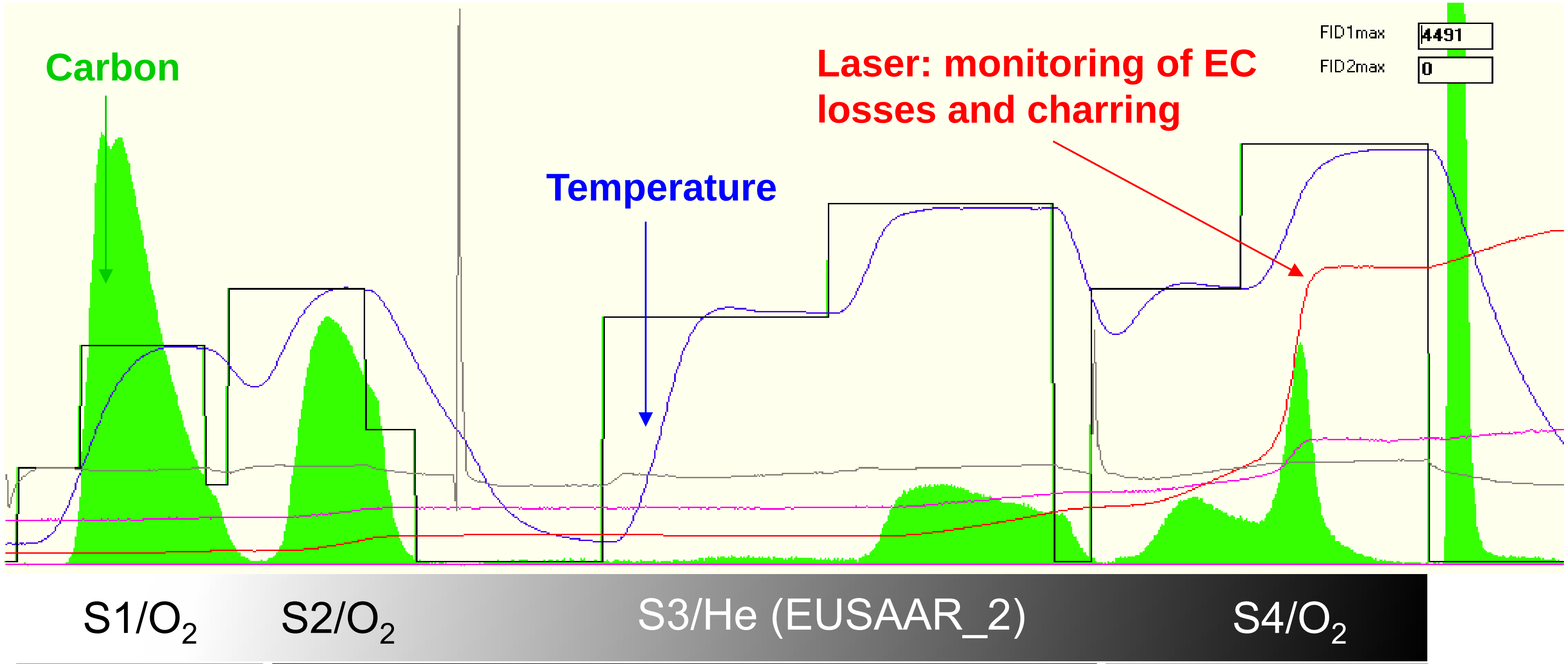




Zhang et al., ACP, 2012

Swiss_4S protocol

EC isolation: Four steps using water-extracted filters

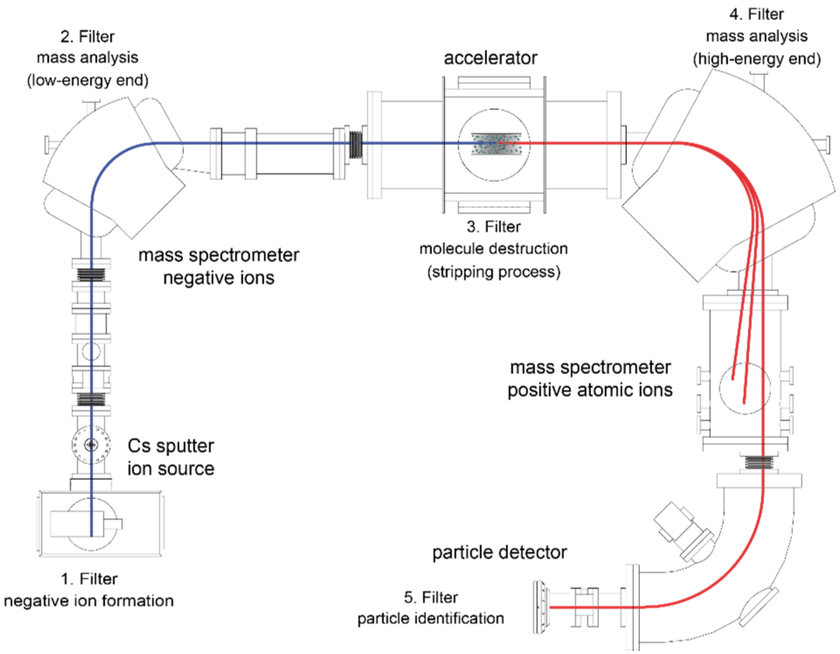


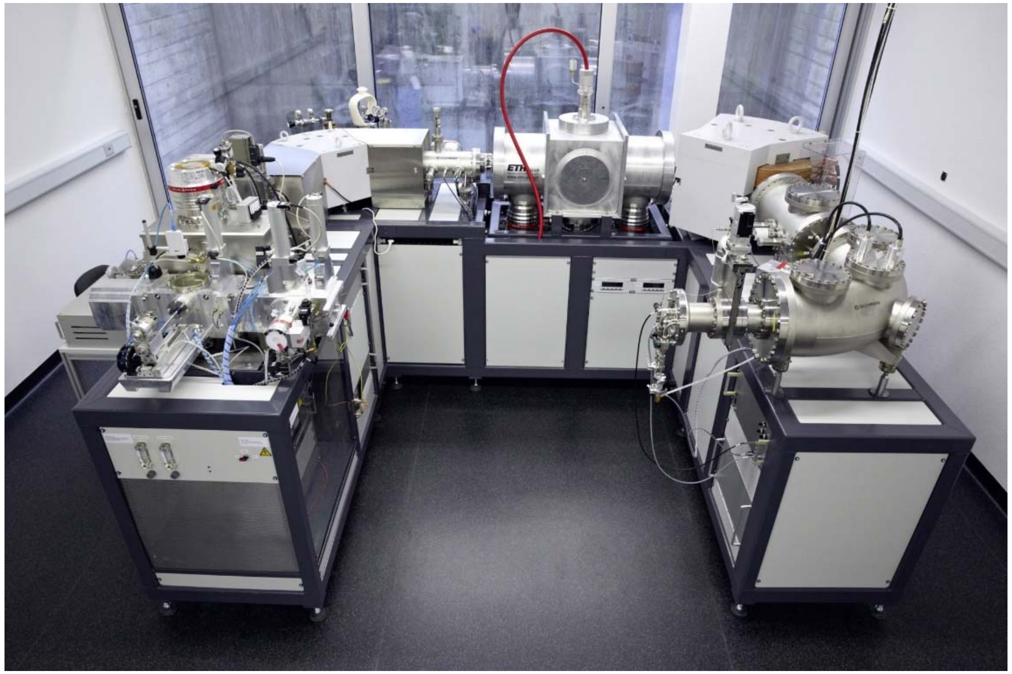
Pure OC | Mixture of OC and EC | Pure EC

Pure OC → Isolation of WINSOC for ^{14}C measurement

Pure EC → Isoltation of EC for ^{14}C measurement

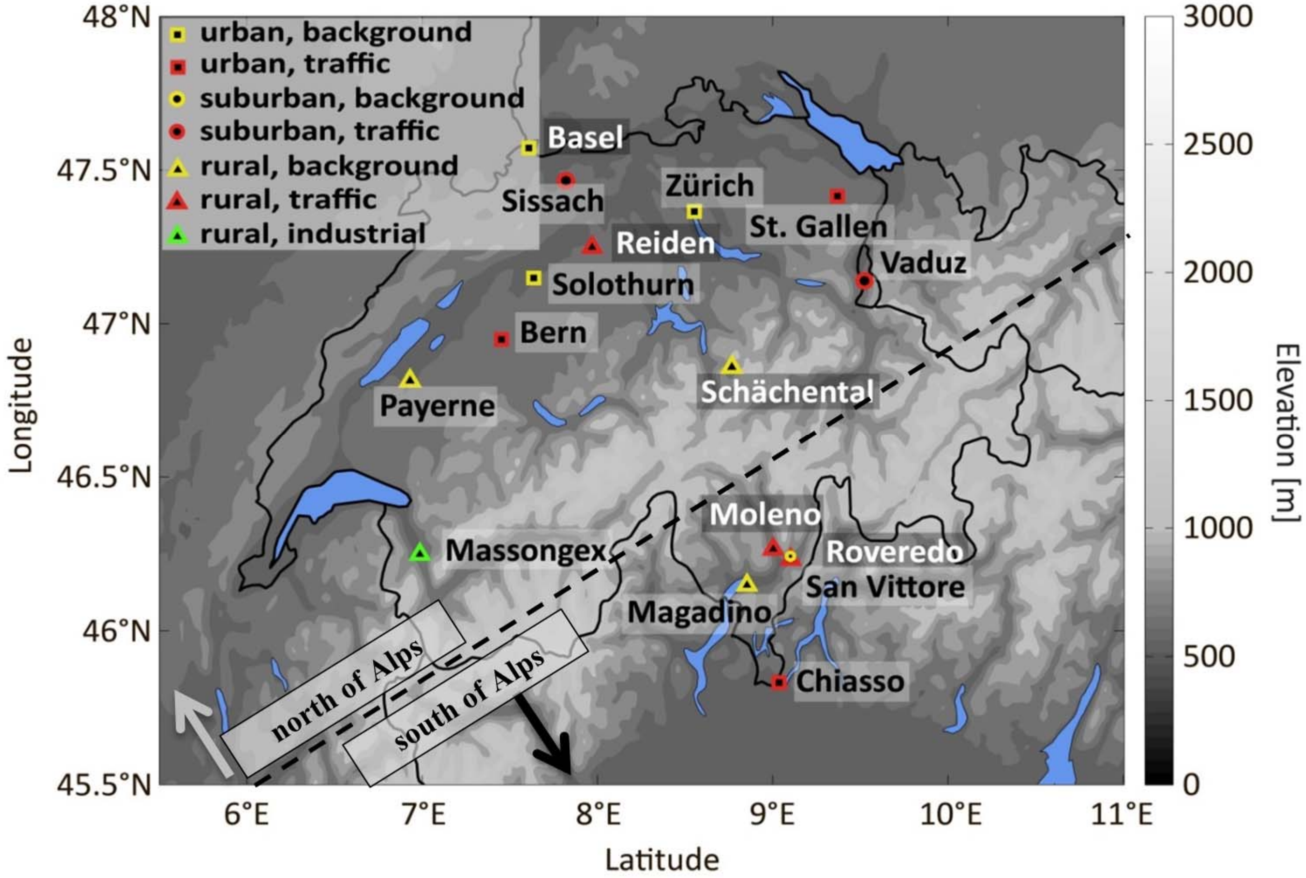
^{14}C analysis: accelerator mass spectrometry





Synal, 2013
Szidat et al., 2014

^{14}C Project Switzerland

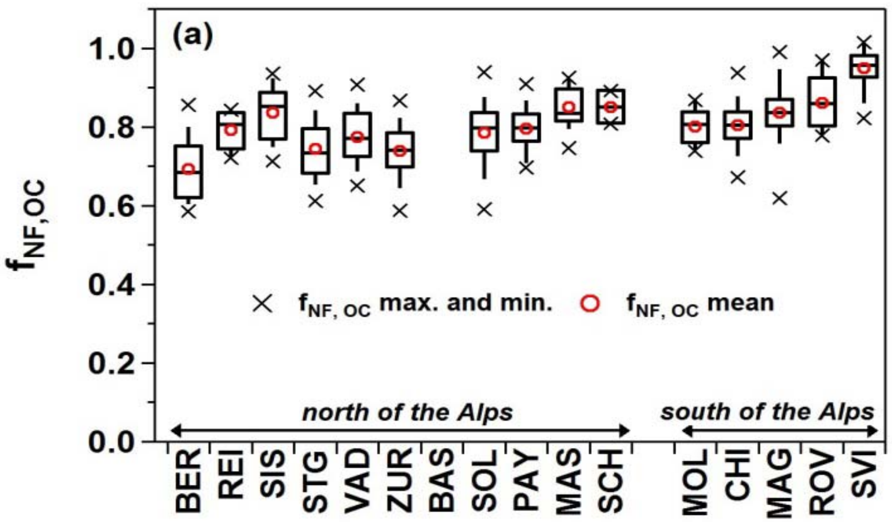


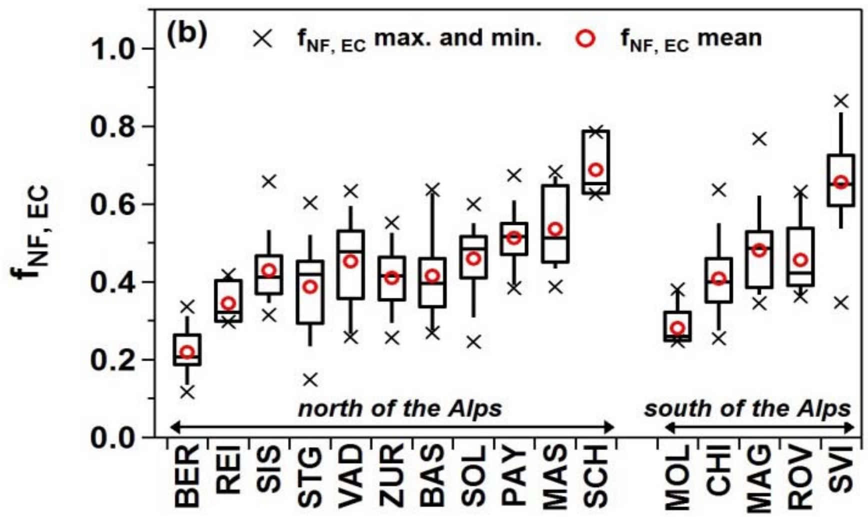
- Focus: winter-smog-episode days (PM10 > 50 µg/m³)
- 5 days per station and year for 2008 – 2013

→ *640 ^{14}C measurements*

→ *One of the world's largest ^{14}C dataset in aerosol research*

^{14}C data – all results

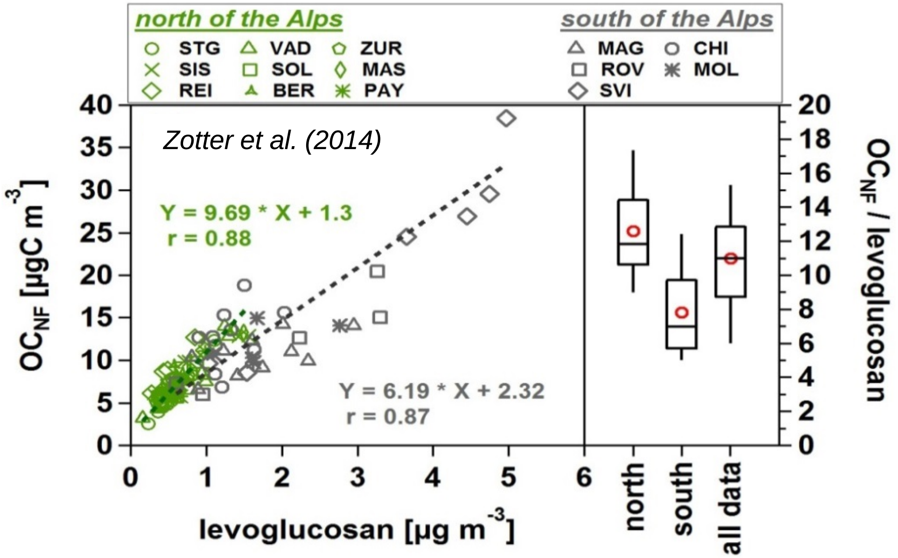




- OC is mostly non-fossil (~70% to ~95%)
- Traffic contribution to OC max. 30%

- EC_{NF}/EC: 40% - 50% for most stations
- Wood burning almost as important as traffic
- EC_{NF} „extreme“ values in Schächental (80%) and San Vittore (87%)

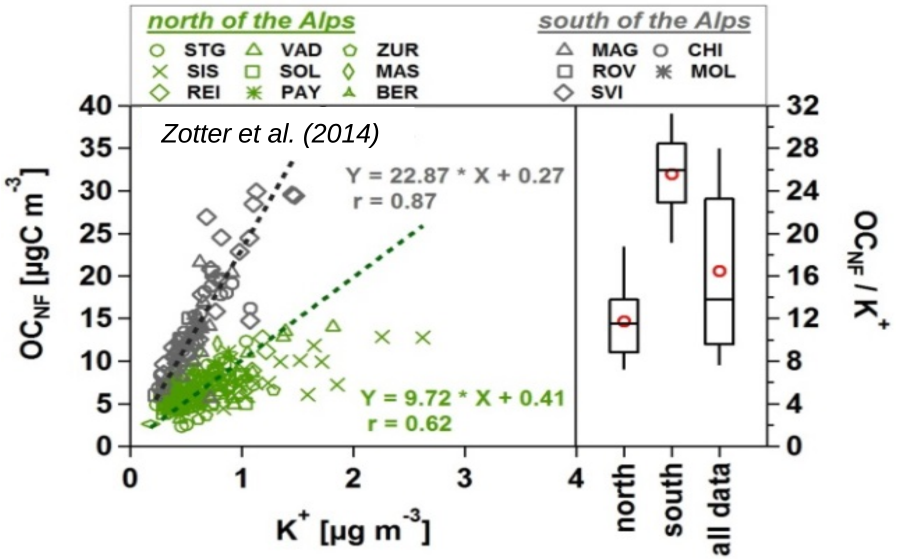
^{14}C data & other wood-burning markers



OC_{NF} vs. levoglucosan

- High correlation
- Small intercept

→ Major fraction of OC_{NF} from wood burning



OC_{NF} vs. potassium (K^+)

- Clearly different ratios for stations north and south of the Alps

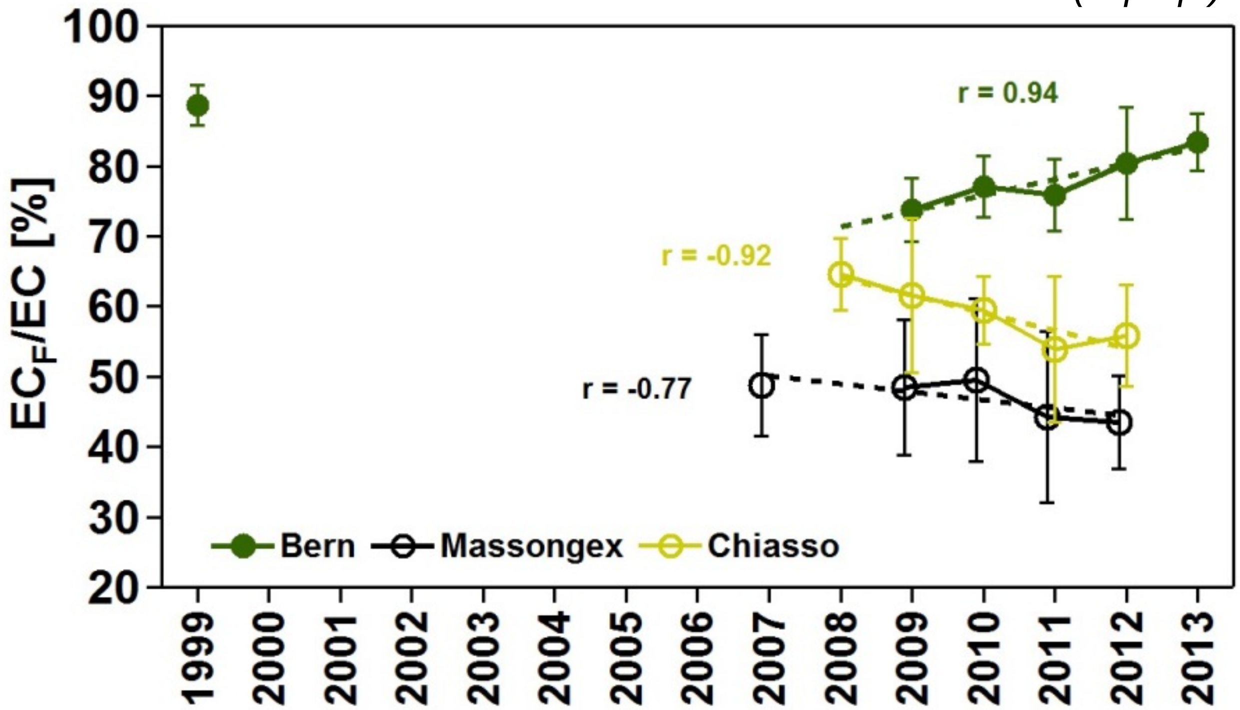
→ More OC emitted in the south

→ Larger fraction of highly efficient wood burners (e.g. Pellet burners) in the north

^{14}C results: Trends

Fossil fraction of EC

Zotter et al. (in prep.)



- No trend for most of the stations
- Decreases in Chiasso: ~65% to ~56%
- Decrease in Massongex: ~49% to ~43%
- Bern:
  - 2009-2013: from ~74% up to ~83%
  - But 2013 ~6% less fossil than 1999

^{14}C results: Trends

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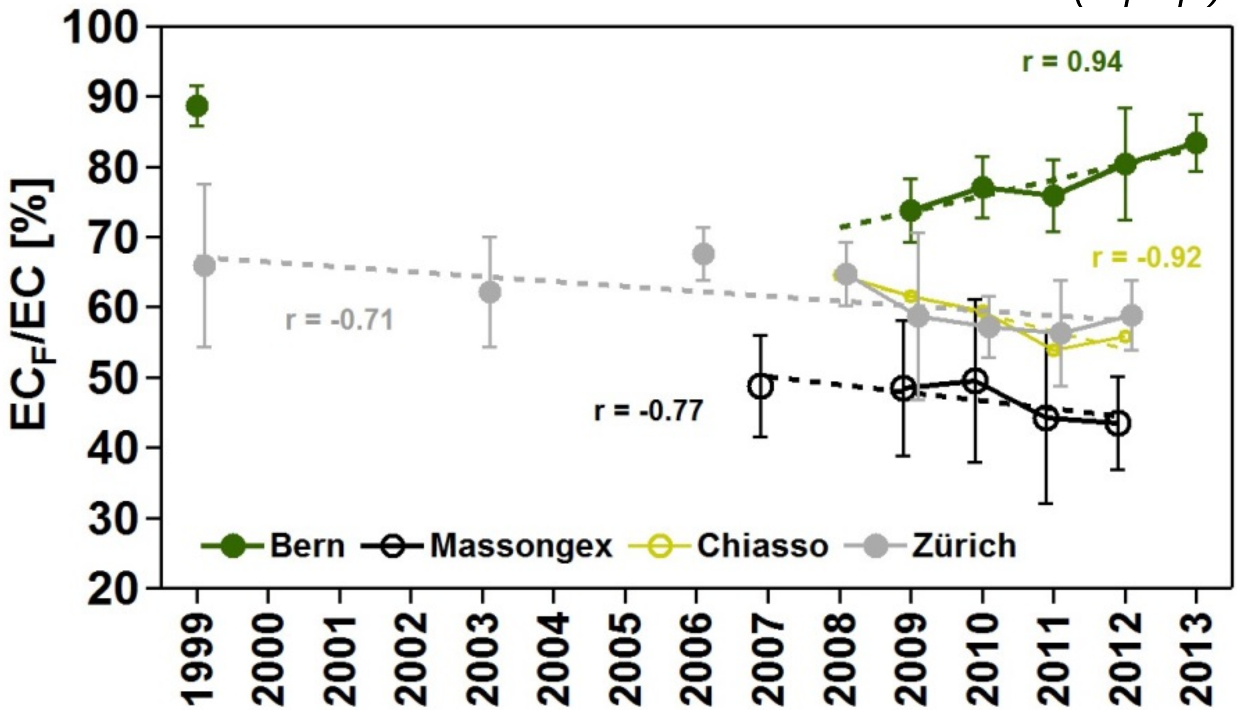

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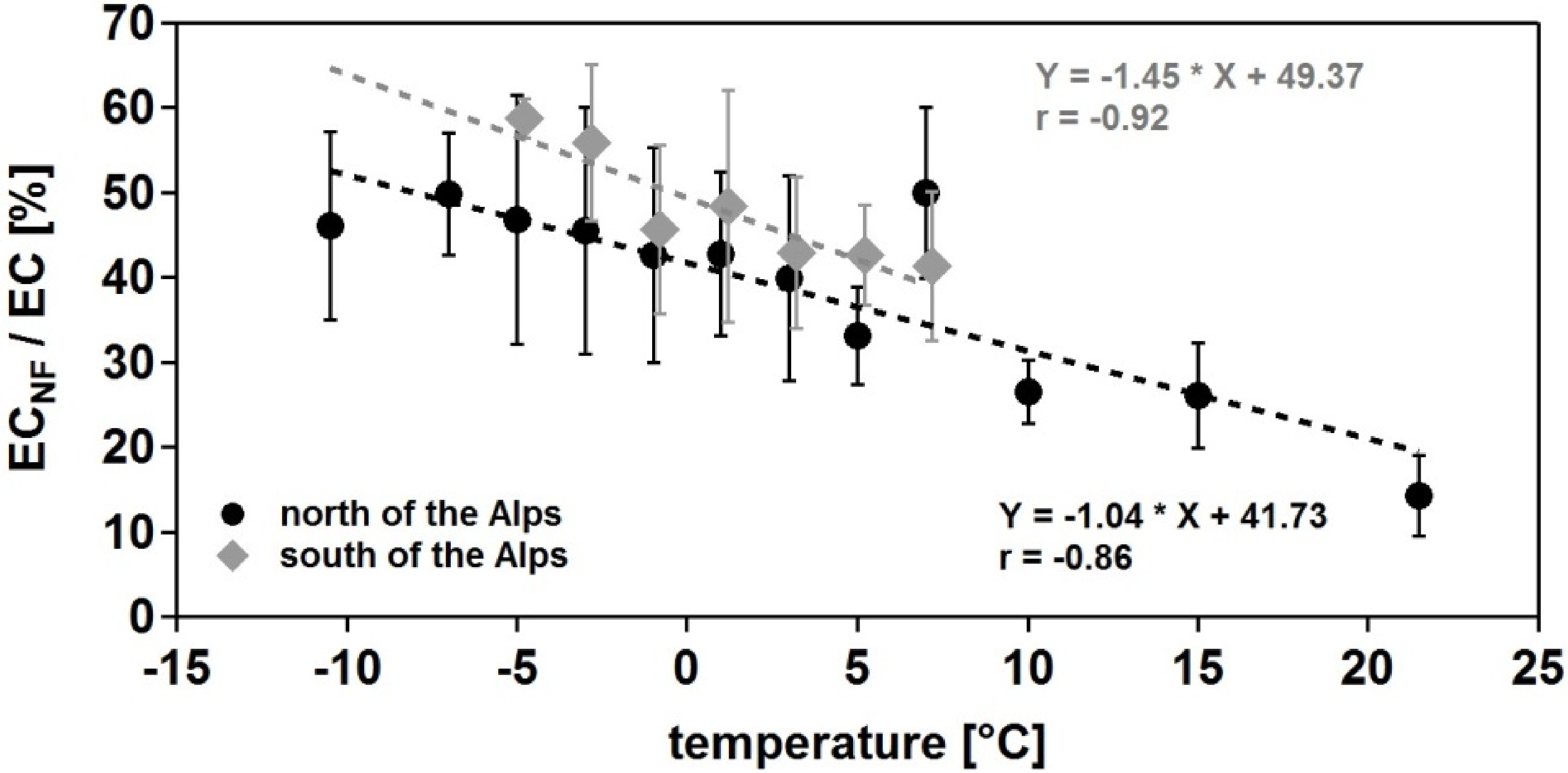
- Bern:
  - 2009-2013: from ~74% up to ~83%
  - but 2013 ~6% less fossil than 1999
- Decrease in Zürich: ~66% to 59%

^{14}C data vs. temperature

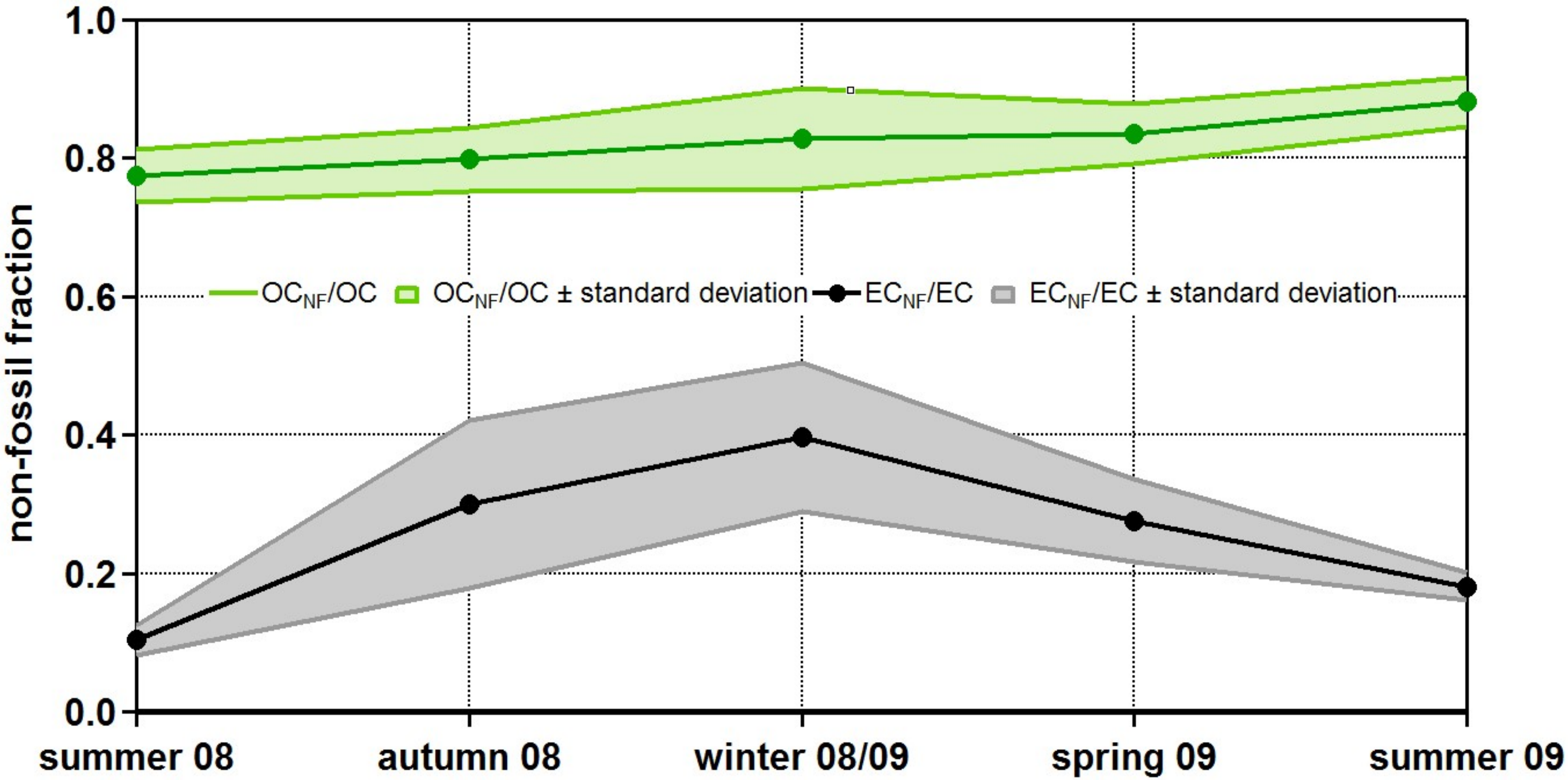


- Clear relationship between temperature and EC_{NF}
- Higher non-fossil contributions with lower temperatures

→ More wood-burning due to more residential heating

^{14}C data – yearly cycle

- Yearly cycle at the urban background station in Zürich
- August 2008 – July 2009; 2 – 3 filters per month



Summary

- OC_{NF} on average 70% - 95% with slightly higher values south of the Alps
- EC_{NF} on average 19% - 66% with extreme values in Alpine valleys up to 87%
- Wood burning is the major source of carbonaceous aerosols in Switzerland during winter smog episodes
- Larger fraction of highly efficient wood burners north of the Alps
- Clear yearly cycle for EC_{NF} in Zürich, but no seasonal variability for OC_{NF}

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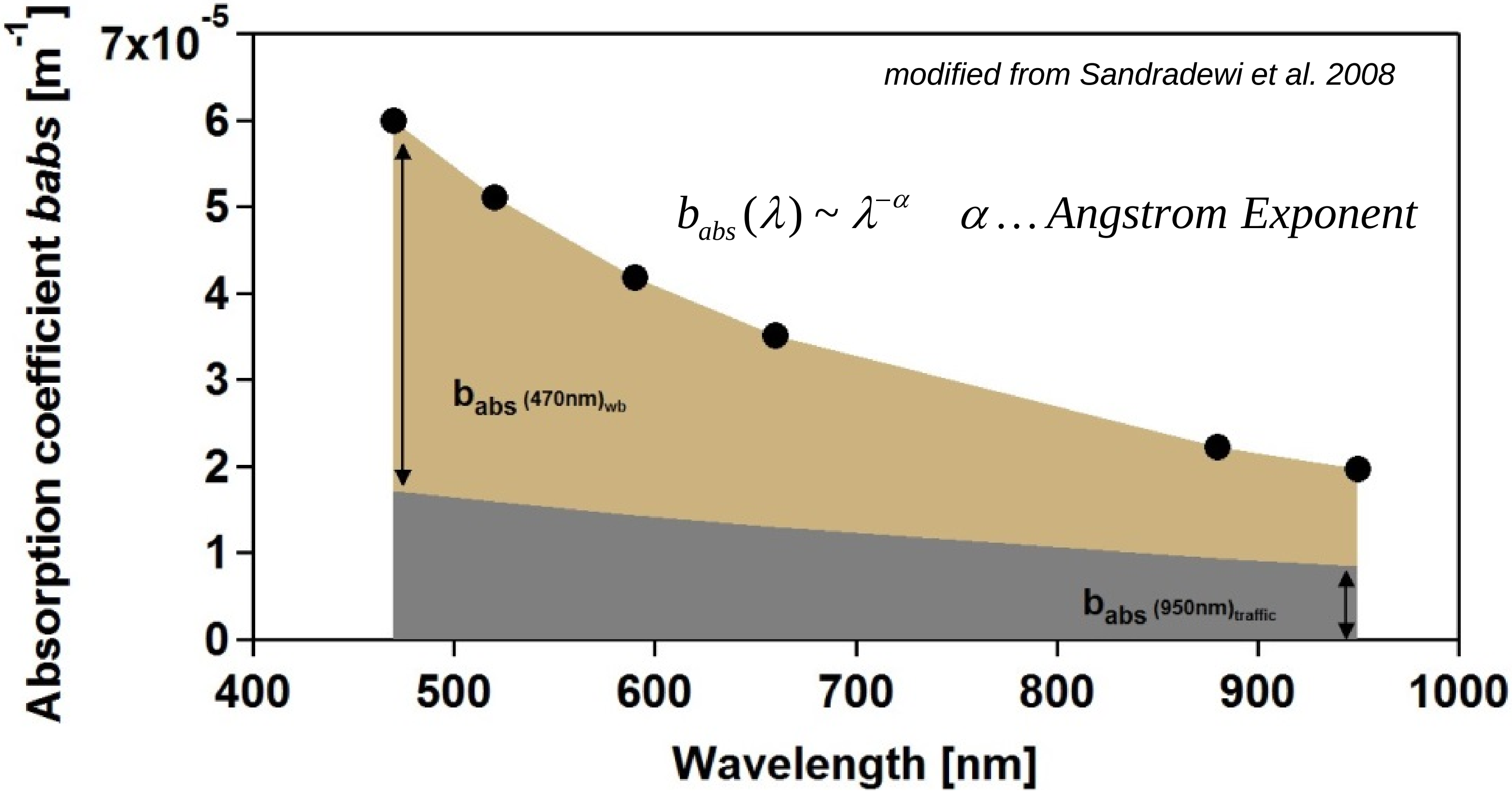
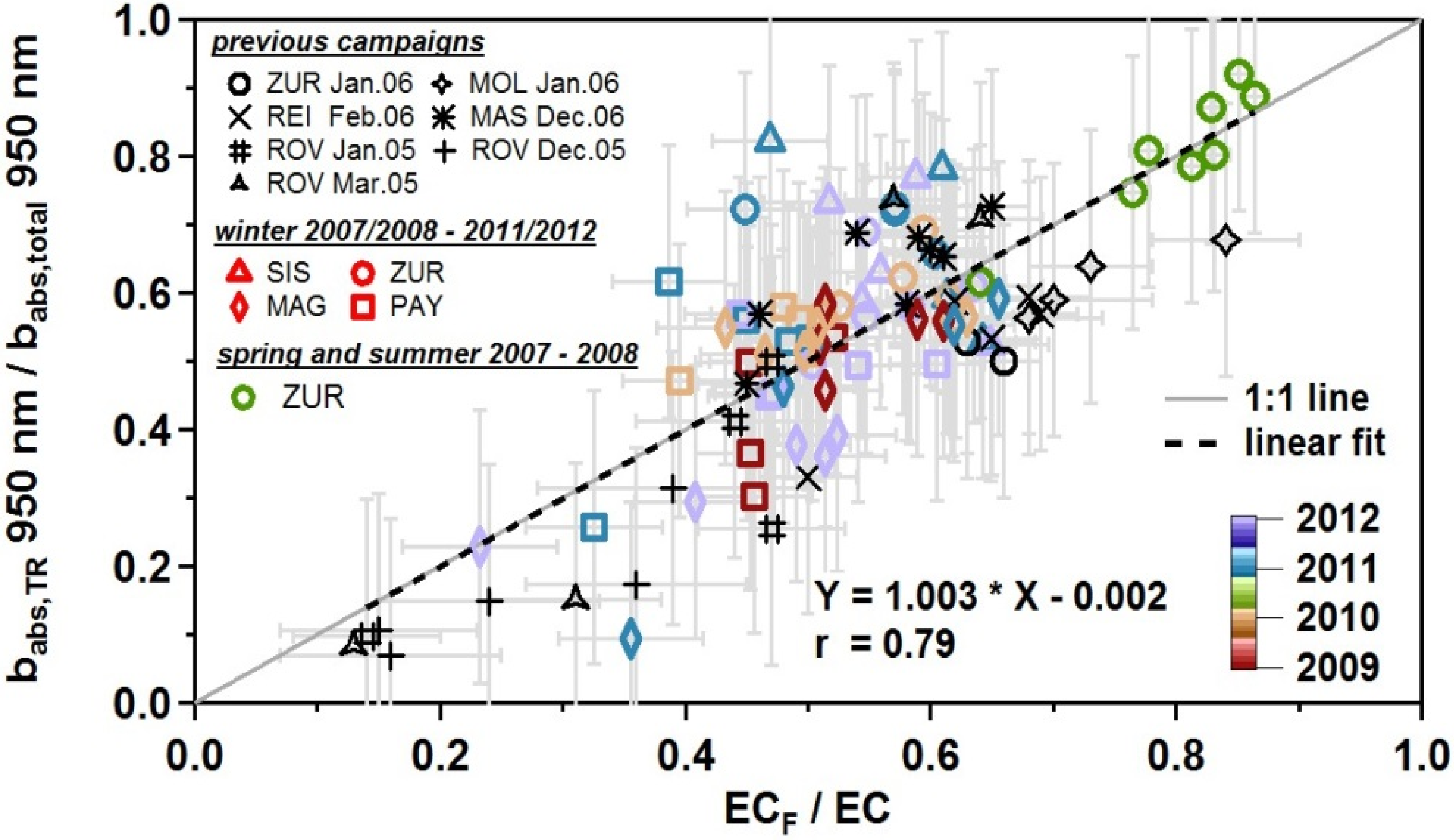
^{14}C vs. Aethalometer



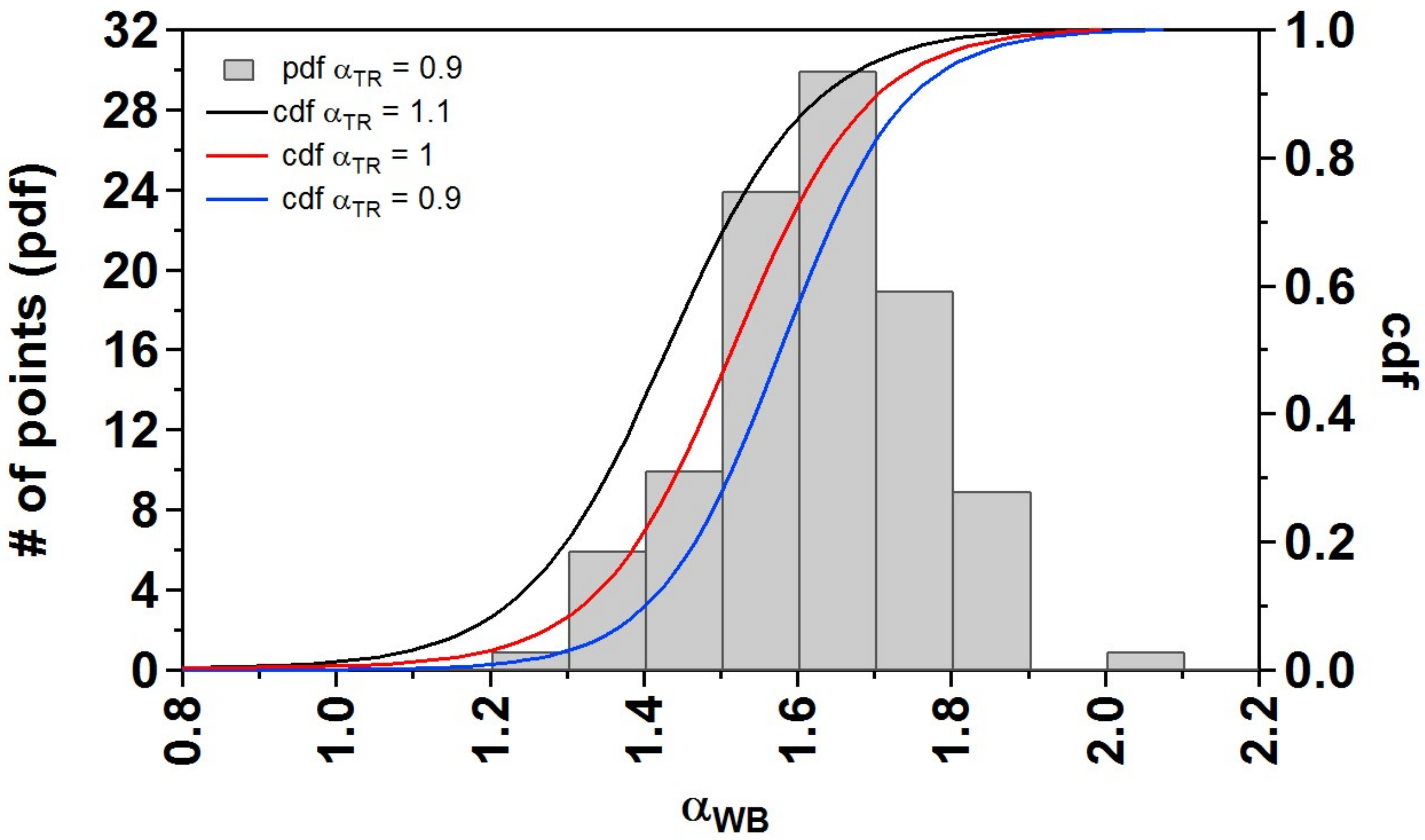
- Low spectral dependence of the b_{abs} from traffic (α_{TR} ~1)
- Enhanced *babs* for wood burning in the near ultraviolet
- α_{TR} and α_{WB} have to be assumed a priori

^{14}C vs. Aethalometer



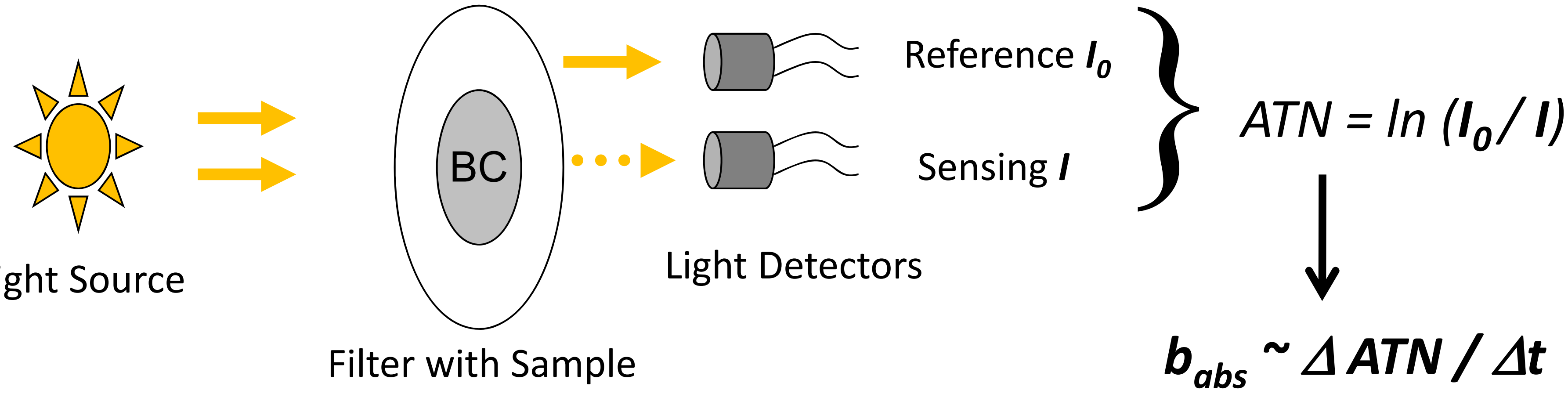
^{14}C vs. Aethalometer

- ^{14}C results of EC used as reference to find "best" α-values
- Both methods correlate well (r = 0.79)



- α_{WB} = 1.4–1.7 (lowest 1st and highest 3rd quartile) for α_{TR} = 0.9–1.1

Aethalometer



- Collect sample continuously.
- *Optical absorption* ~ change in ATN.
- Measure optical absorption continuously : λ = 370 to 950 nm.
- Convert *optical absorption* to *concentration of BC:*
  - $BC(t) = b_{abs}(t) / \sigma$

slide taken from Aerosol

^{14}C vs. Aethalometer

Aethalometer

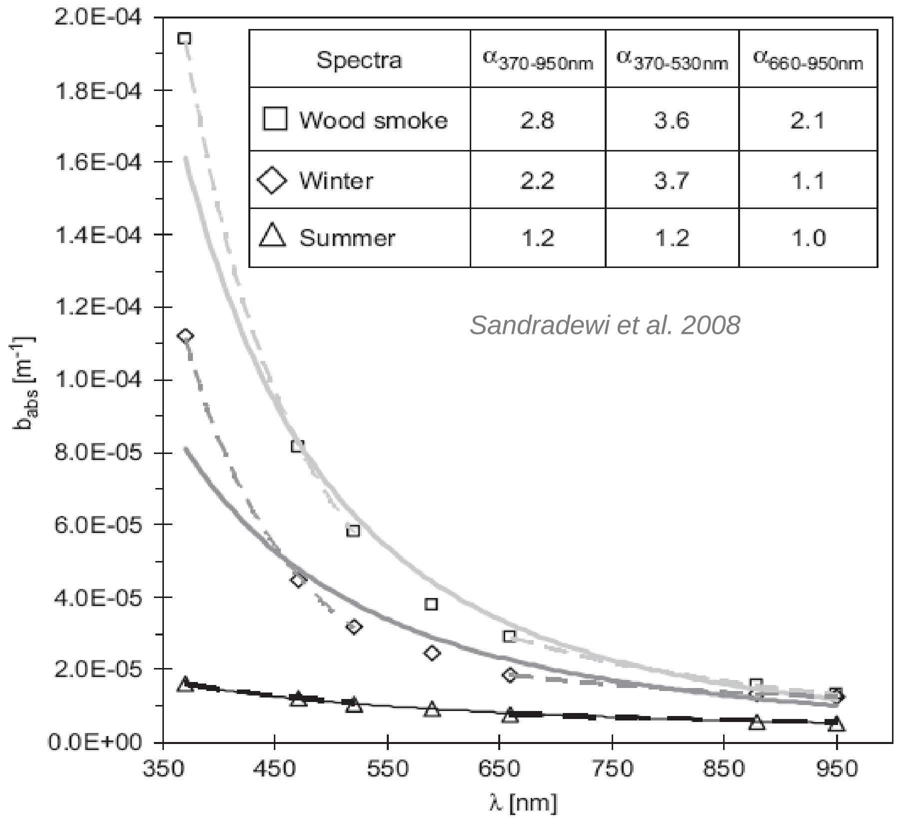
- measures light absorption (λ = 370, 470, 520, 590, 660, 880 and 950 nm) form which the equivalent BC concentration can be deduced

Traffic emissions:

- contain mainly BC
- dominate absorption at IR-wavelengths
- exhibit only a weak wavelength dependence

Wood burning emissions:

- contain a significant number of light absorbing organic substances
- have an enhanced absorption in the UV range
- exhibit a strong wavelength dependence



Spectra	$\alpha_{370\text{-}950nm}$	$\alpha_{370\text{-}530nm}$	$\alpha_{660\text{-}950nm}$
□ Wood smoke	2.8	3.6	2.1
◇ Winter	2.2	3.7	1.1
△ Summer	1.2	1.2	1.0

$$\frac{b_{abs,TR}(470\,nm)}{b_{abs,TR}(880\,nm)} = \left(\frac{450}{880}\right)^{-\alpha_{TR}}$$

$$\frac{b_{abs,WB}(470\,nm)}{b_{abs,WB}(880\,nm)} = \left(\frac{450}{880}\right)^{-\alpha_{WB}}$$

- $b_{abs}(\lambda) \sim \lambda^{-\alpha}$ α ... Ångstrom Exponent
- $b_{abs}(\lambda) = b_{absTR}(\lambda) + b_{absWB}(\lambda)$