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


$^1$Department of Chemistry and Biochemistry, University of Bern, Switzerland
$^2$Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland
$^3$Laboratory of Ion Beam Physics, Swiss Federal Institute of Technology, Zürich, Switzerland
$^4$University of Milano, Department of Environmental Science, Italy

peter.zotter@psi.ch
Radiocarbon in the environment

Equilibrium Concentration: $\frac{^{14}\text{C}}{^{12}\text{C}} \approx 10^{-12}$

Then: $^{14}\text{C} \rightarrow ^{14}\text{N} + e^- + \bar{\nu}$

$\tau_{1/2} = 5730$ years

Currie, 2004
Elemental Carbon (EC)  
Organic Carbon (OC)  
SOC  

Modern $^{14}$C level  
Depleted in $^{14}$C  

$^{14}$C half-life = 5730 years
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
Swiss_4S protocol

EC isolation: Four steps using water-extracted filters

S1/O2
Pure OC

S2/O2
Mixture of OC and EC

S3/He (EUSAAR_2)

S4/O2
Pure EC

Isolation of WINSOC for \(^{14}\text{C}\) measurement

Isolation of EC for \(^{14}\text{C}\) measurement

Laser: monitoring of EC losses and charring

Temperature

Carbon
14C analysis: accelerator mass spectrometry

- Synal et al. 2007,
- Ruff et al. 2007

Synal, 2013
Szidat et al., 2014
- **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**
• 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%)
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

Zotter et al. (2014)
Fossil fraction of EC

- 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

\[14C \text{ results: Trends}\]

Zotter et al. (in prep.)

- Bern:
  - 2009-2013: from ~74% up to ~83%
  - But 2013 ~6% less fossil than 1999

\[14C \text{ results: Trends}\]

Zotter et al. (in prep.)
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
- Decrease in Zürich: ~66% to 59%
• Clear relationship between temperature and EC$_{NF}$
• Higher non-fossil contributions with lower temperatures
  → More wood-burning due to more residential heating
• Yearly cycle at the urban background station in Zürich
• August 2008 – July 2009; 2 – 3 filters per month
• 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}
Thank you for your attention

This work was funded by:
the Swiss Federal Office for the Environment, inNet Monitoring AG, Liechtenstein and the Swiss cantons Basel-Stadt, Basel-Landschaft, Graubünden, Solothurn, Valais and Ticino
• Low spectral dependence of the $b_{abs}$ from traffic ($\alpha_{TR} \sim 1$)
• Enhanced $b_{abs}$ for wood burning in the near ultraviolet
• $\alpha_{TR}$ and $\alpha_{WB}$ have to be assumed a priori
Previous campaigns
- ZUR Jan.06
- MOL Jan.06
- REI Feb.06
- MAS Dec.06
- ROV Jan.05
- ROV Dec.05
- ROV Mar.05

- SIS
- ZUR
- MAG
- PAY

Spring and summer 2007 - 2008
- ZUR

\[ Y = 1.003 \times X - 0.002 \]
\[ r = 0.79 \]
• $^{14}$C results of EC used as reference to find “best” $\alpha$-values

• Both methods correlate well ($r = 0.79$)

• $\alpha_{WB} = 1.4–1.7$ (lowest 1st and highest 3rd quartile) for $\alpha_{TR} = 0.9–1.1$
• Collect sample **continuously**.

• **Optical absorption** ~ change in ATN.

• Measure optical absorption **continuously** : $\lambda = 370$ to $950$ nm.

• Convert **optical absorption** to **concentration of BC**:
  
  • $BC(t) = \frac{b_{abs}(t)}{\sigma}$

\[ ATN = \ln \left( \frac{I_0}{I} \right) \]

\[ b_{abs} \sim \Delta ATN / \Delta t \]
Aethalometer

- measures light absorption ($\lambda = 370, 470, 520, 590, 660, 880$ and $950$ nm) from 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

\[ b_{abs}(\lambda) \sim \lambda^{-\alpha} \quad \text{Ångstrom Exponent} \]

\[ b_{abs}(\lambda) = b_{absTR}(\lambda) + b_{absWB}(\lambda) \]