University of Applied Sciences and Arts Northwestern Switzerland
School of Engineering



# Novel measurement systems for the estimation of carbonaceous particle fraction of emissions including atmospheric aging

**Alejandro Keller**
**Fachhochschule Nordwestschweiz**
**alejandro.keller@fhnw.ch**

# Part one: The Method

# Our proposed method in a nutshell (particulate matter emissions)

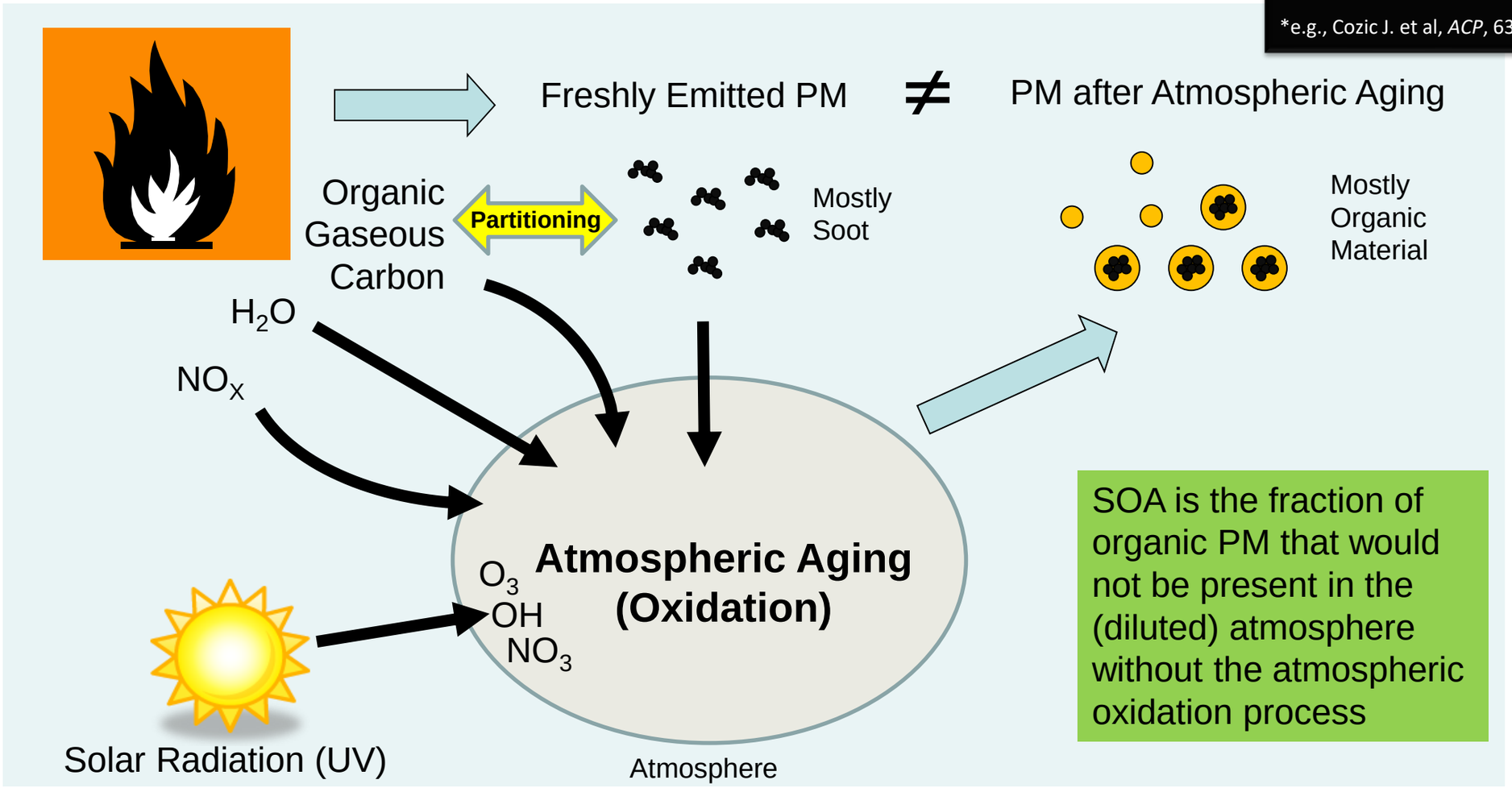
1. Preconditioning through atmospheric-like aging: includes secondary emissions.
2. (Carbon) Fraction based approach: focus on potential health and climate impact.
3. Total Carbon (TC) as quantification metric: a well-established analysis technique (i.e. determination of total particle bound carbon).

Details: Keller & Burtscher, 2017 DOI: 10.1016/j.jaerosci.2017.08.014

**Fresh:** more soot than organic material.
**Aged:** up to >10x more organic material than soot*.

*e.g., Cozic J. et al, *ACP*, 637-651 (2008)

# Primary PM and Secondary Organic Aerosols (SOA)



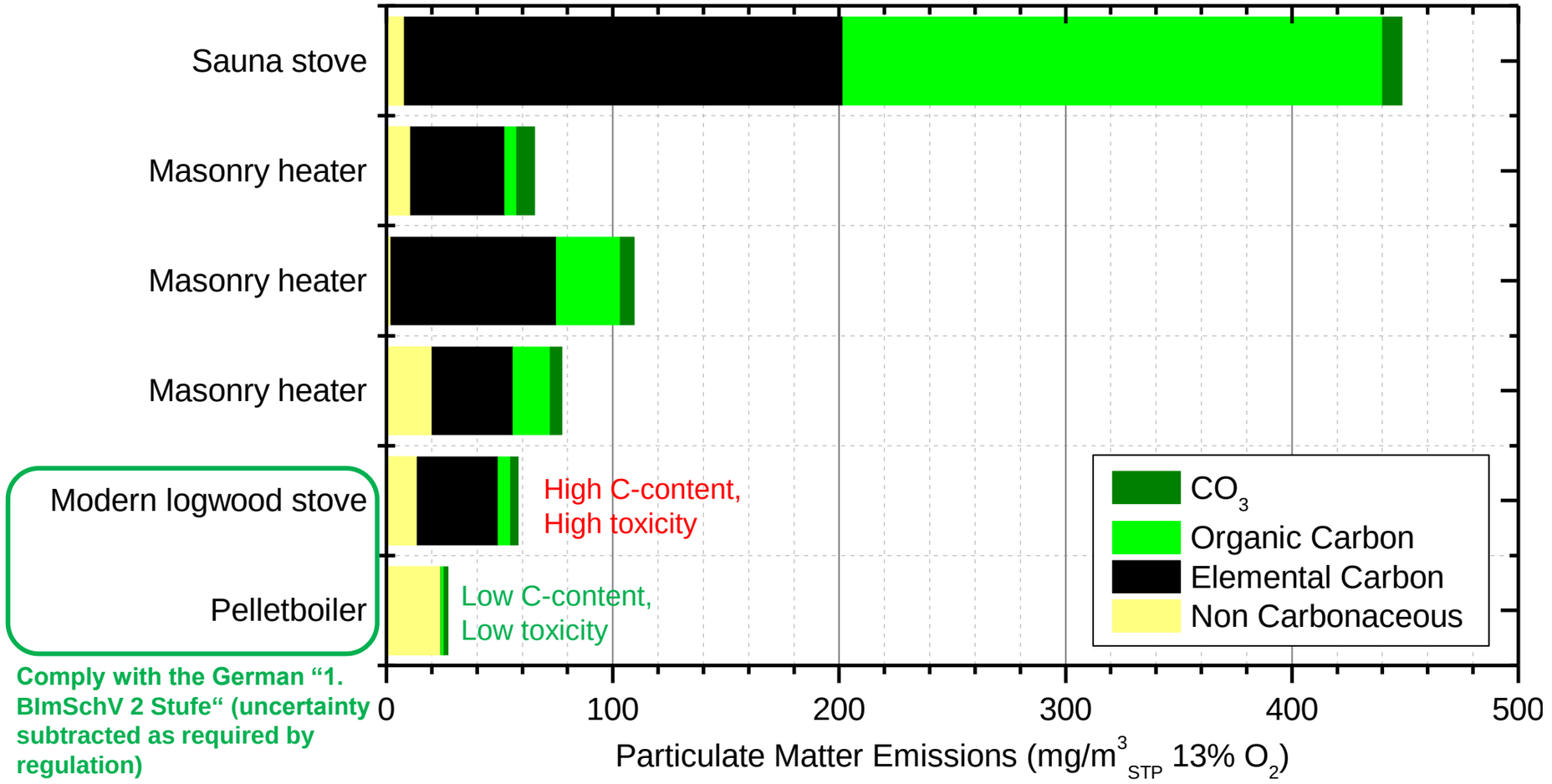

SOA is the fraction of organic PM that would not be present in the (diluted) atmosphere without the atmospheric oxidation process

# What have we learned from oxidation flow reactor (OFR*) experiments

- It is possible within few seconds to produce secondary organic aerosol (SOA) with chemical signature of atmospheric observations.
- FID measurements are not a replacement for OFR. Not are VOC are equally relevant. Few specific organic species are responsible for most of the SOA production (e.g., 22 out of hundreds of species cause over 80% of SOA; Bruns, 2016, DOI: 10.1038/srep27881)
- OFR helpful to optimize appliances or development of emission reduction devices should be aided by measurement of the SOA potential.
- Type approval testing is not representative of the real-world emissions of small combustion appliances. During the start phase, and in the case of pyrolysis or high lambda operation, SOA can multiply the total emissions several-fold.

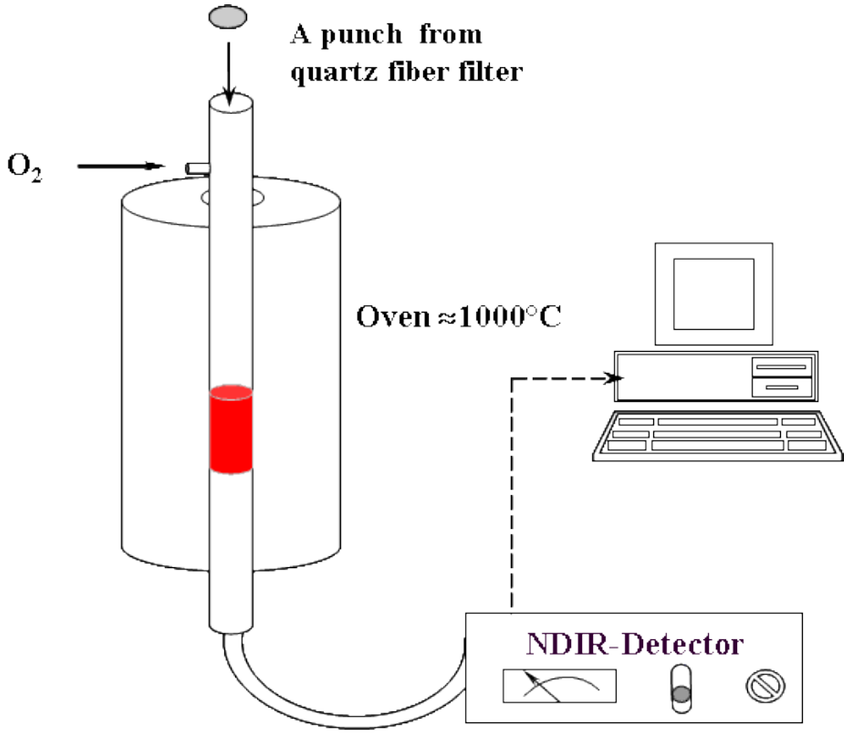
*An OFR is a device the mimics atmospheric chemistry within minutes or seconds

# Emissions Composition (Small Combustion Installations)




**Comply with the German "1. BImSchV 2 Stufe" (uncertainty subtracted as required by regulation)**

Source: Lamberg et al. / Atm. Env. 45 (2011) 7635-7643




Total Carbon (TC) is the mass of all carbon atoms in a sample. This includes the mass of soot (elemental carbon, EC) as well as the mass of carbon atoms in organic molecules (organic carbon, OC). Usually measured by means of $CO_2$ determination. Carbonates are also detected by this technique.
(graphic: TU-Wien)

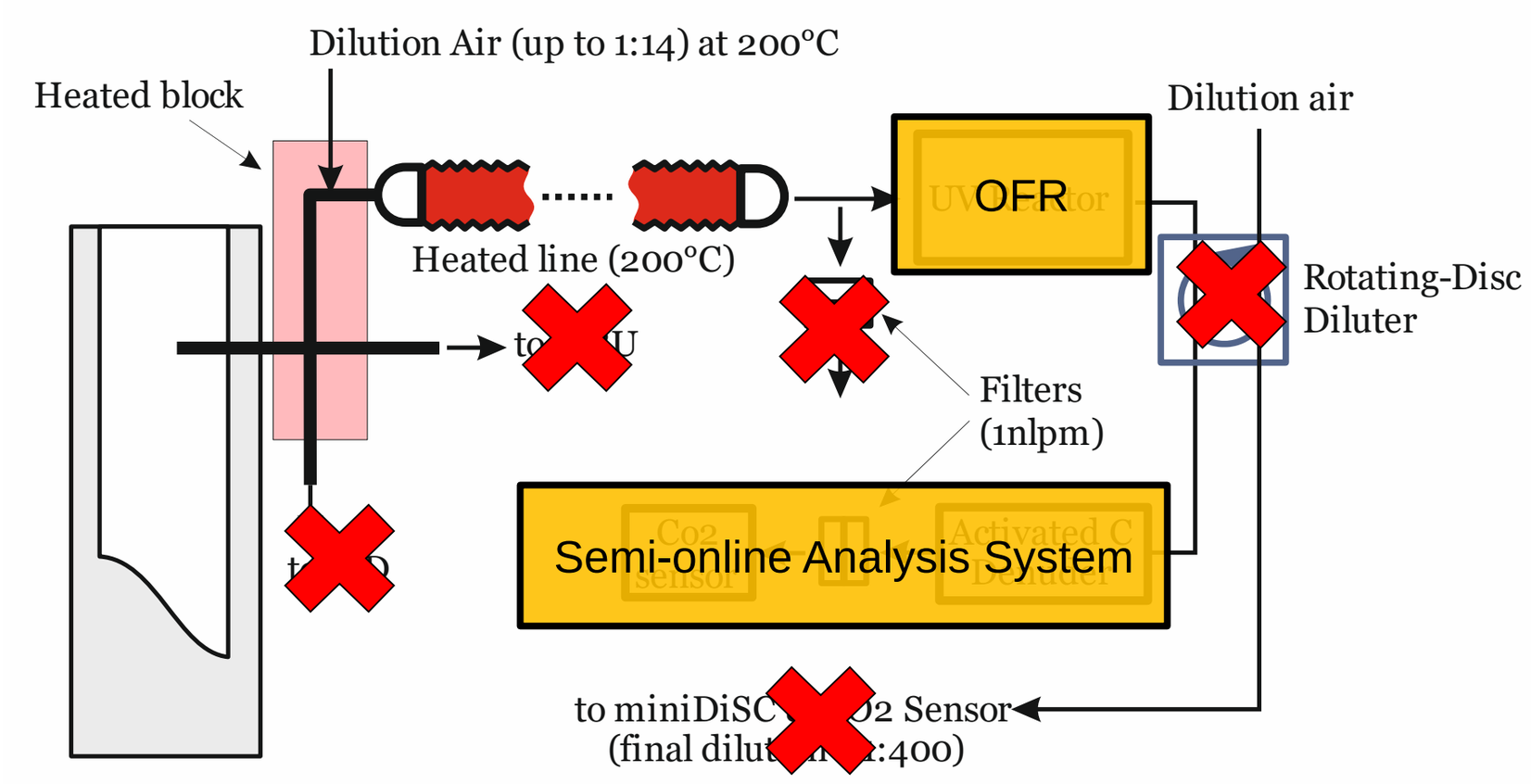
# The Metric: Why total carbon (TC)?

1. TC is directly related to the combustion quality. This is not the case for, e.g., PME (TC fraction of PME is between 5% and 90% for “certifiable” appliances*)
2. Total carbon is a better metric for health and climate impact than PME
3. Single value and less complicated than, e.g., OC/EC
4. Method already available as commercial devices and is also offered by independent laboratories
5. **Potential for automatic semi-online analysis system (e.g. TCA device from Aerosol d.o.o.)**

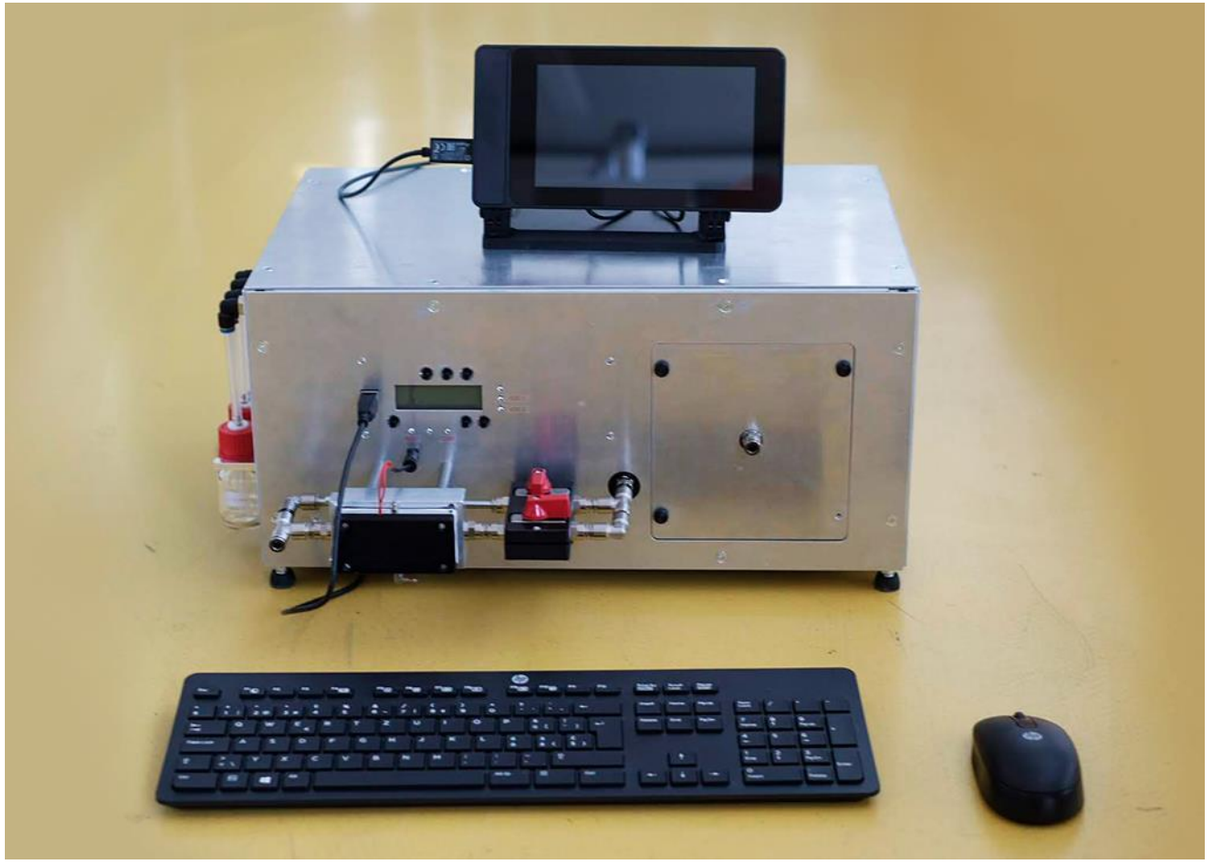
*see, e.g., Lamberg, Atm. Env. **45**, 2011

# Part two: The Devices

# Original experimental setup
## (Presented as the long term-approach of EN-PME-TEST)



# The novel Oxidation Flow Reactor (and aerosol coating unit)



# OFR Main Components

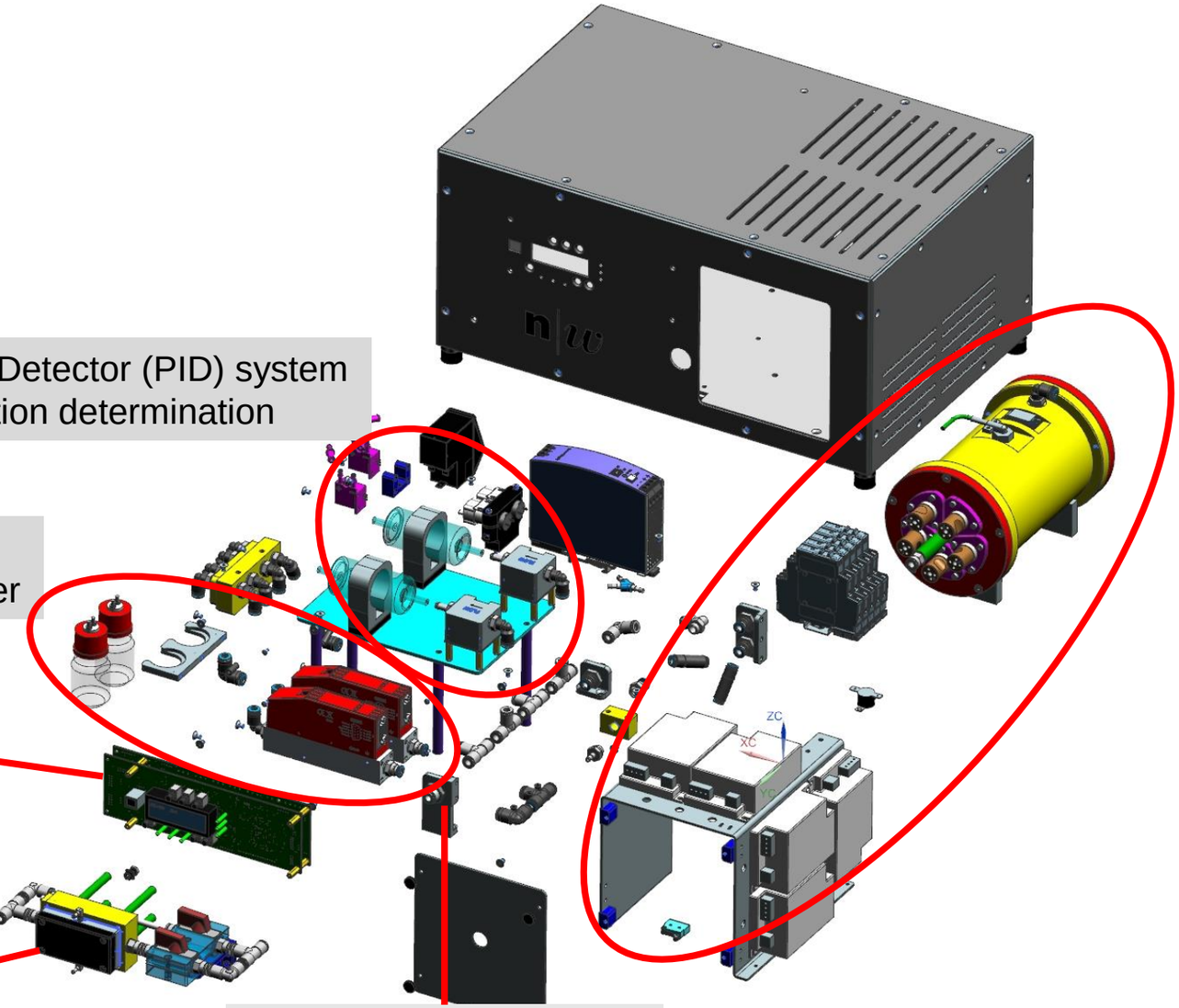
Not required for emission measurements

2x Photoionization Detector (PID) system for VOC concentration determination

2x VOC dosing:
Mass Flow Controllers + VOC container

Control Electronics (including Microprocessor)

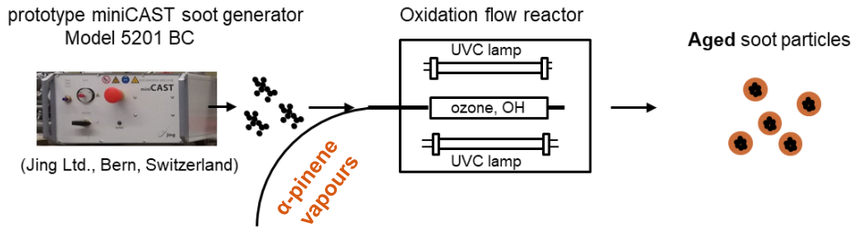
Sample humidifier (optional)



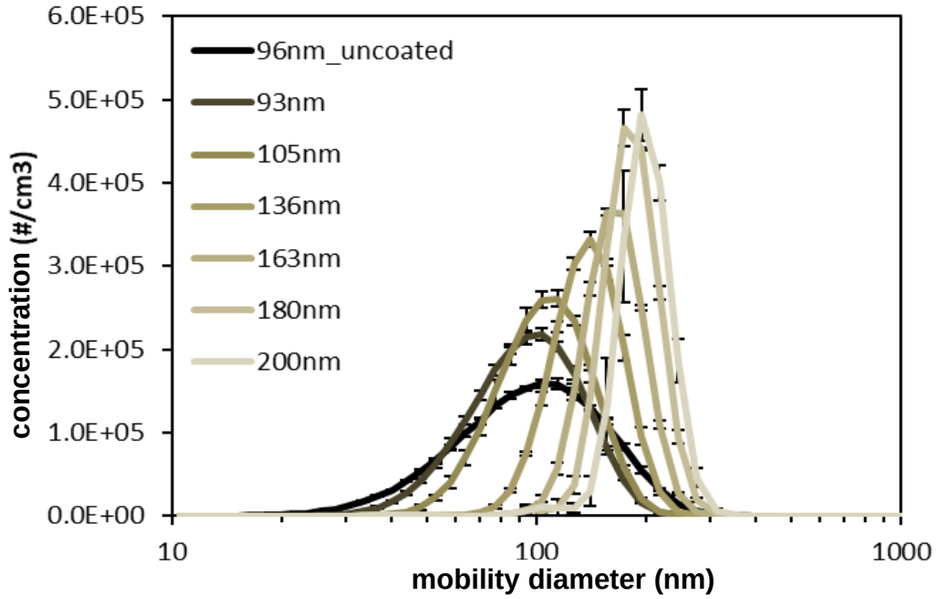
Relative Humidity Sensor

Oxidation Flow Reactor (OFR)

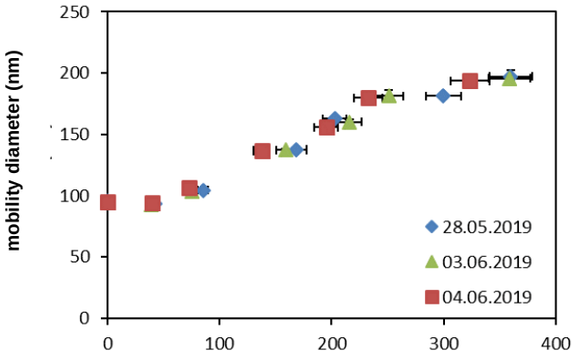
# Oxidation flow reactor, day to day variation experiment (soot + α-pinene)



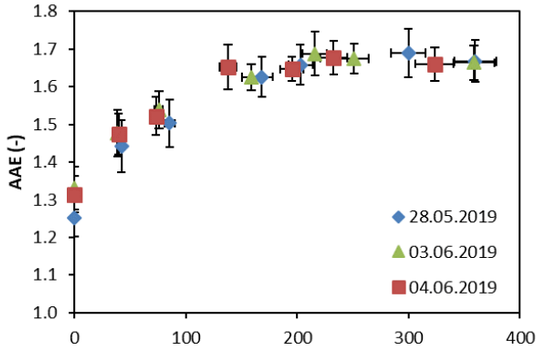

Particle growth up to a factor of 2



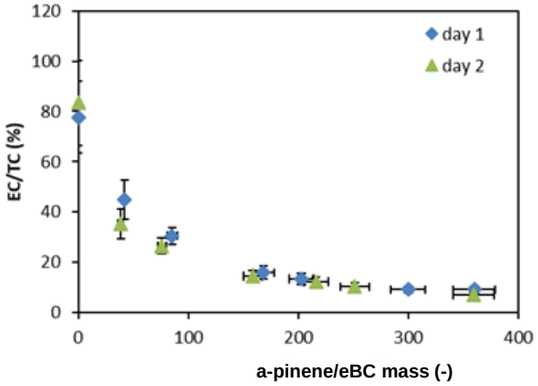

Particle size tuning

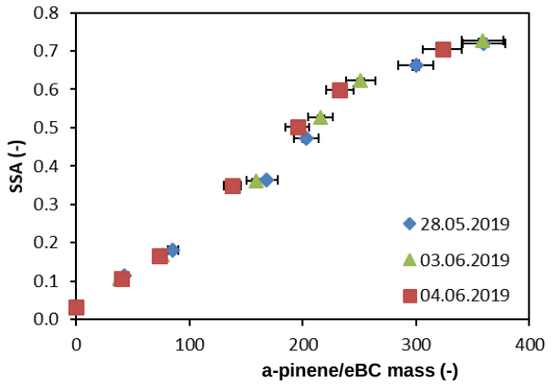



Tuning of optical properties




Tuning of chemical composition



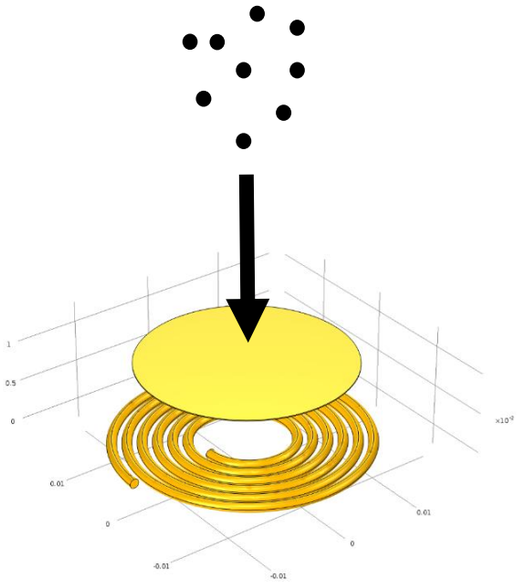

M. Ess, A. Keller et al., to be submitted

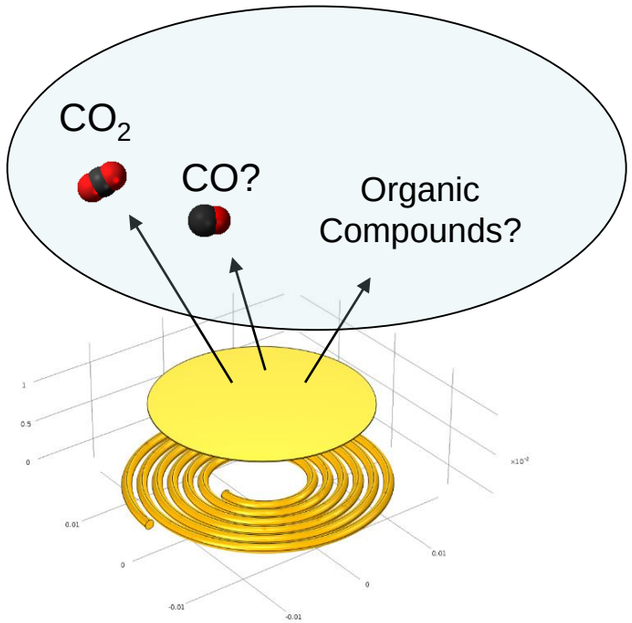
# Interesting Applications

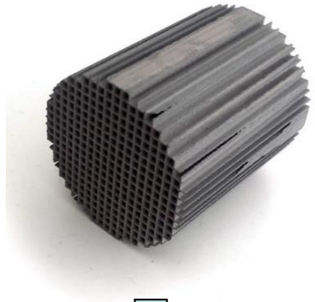
- Potential formation for secondary organic aerosols formation **(Emission Monitoring)**
- Lab-based study of health effects **(Health)**
- Lab-based calibration of, e.g., absorption photometers **(Air quality)**
- Production of new standard aerosols for, e.g., filter testing **(Industry)**

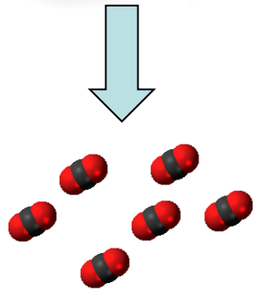
# FAst Thermal CArbon Totalizer (FATCAT)

3. Catalytic converter

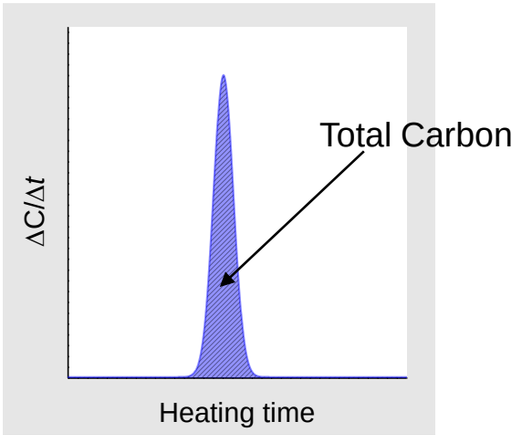






Limit of Detection
LoD = 0.19 µg-C
(Using 3σ criterium)

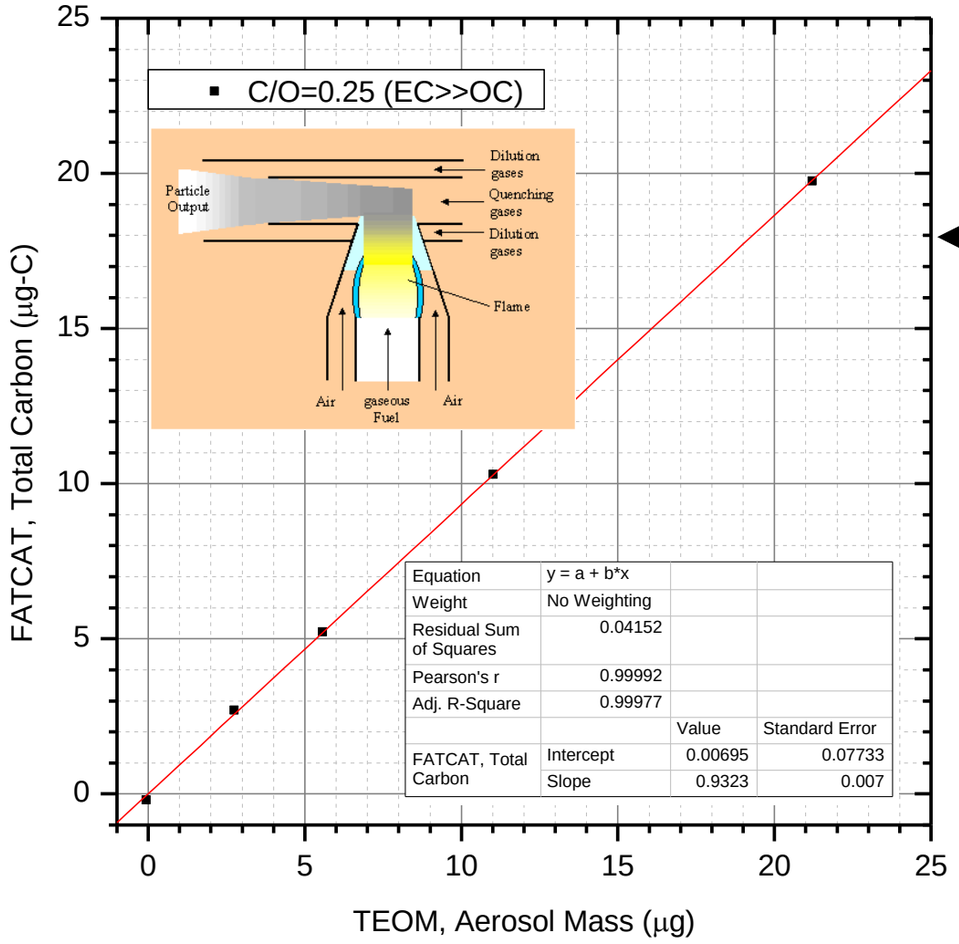



1. Capture particles on a filter

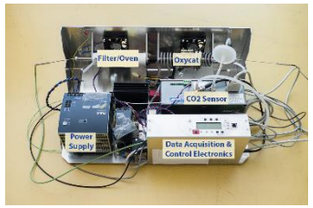
2. Flash-heat up the filter to ~800°C (< 1 minute)

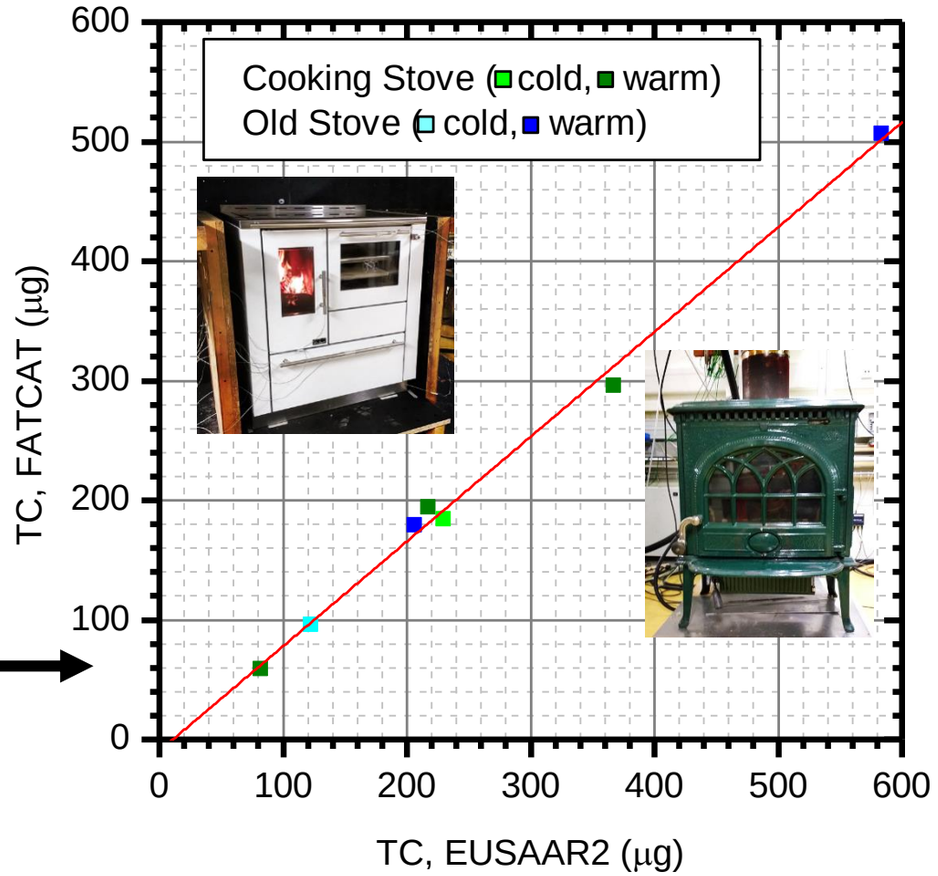
4. CO2 detection (NDIR)

# FAst Thermal CArbon Totalizer (FATCAT)




| | | | |
|---|---|---|---|
| Equation | y = a + b*x | | |
| Weight | No Weighting | | |
| Residual Sum of Squares | 0.04152 | | |
| Pearson's r | 0.99992 | | |
| Adj. R-Square | 0.99977 | | |
| | | Value | Standard Error |
| FATCAT, Total Carbon | Intercept | 0.00695 | 0.07733 |
| | Slope | 0.9323 | 0.007 |



We are looking for collaboration with teams from this community. Please contact us if you are interested.
Commercial partners are welcome!

# Part three: The Results…

# Thanks to:

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

FATCAT funding provided by the Swiss Federal Office for the Environment (FOEN) and by Global Atmosphere Watch and the World Meteorological Organization through MeteoSwiss

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Development of coating unit within the framework of the EMPIR 18HLT02 AeroTox project

http://empir.npl.co.uk/aerotox/

METAS

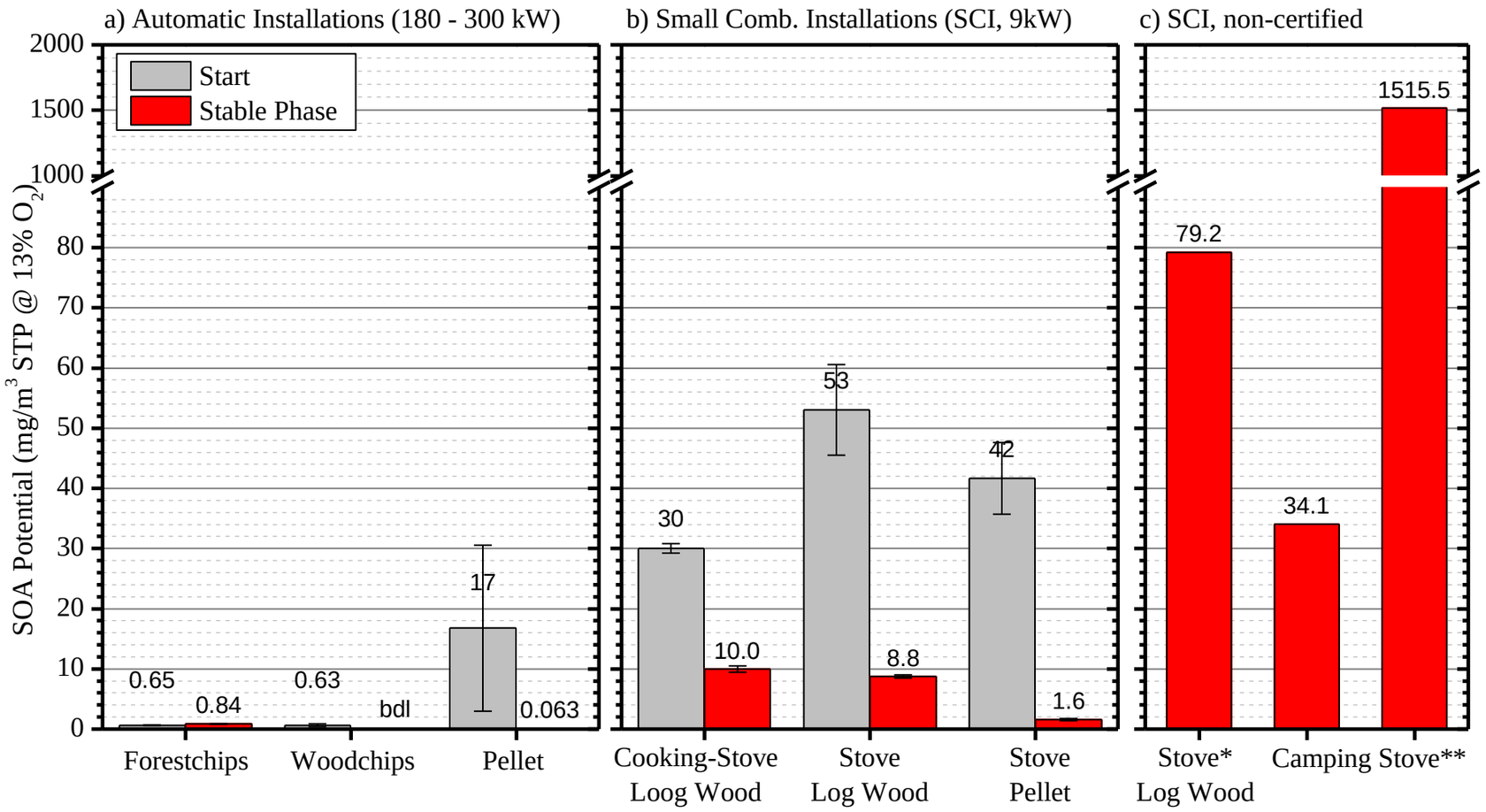
We gratefully acknowledge the collaboration from the Swiss Federal Institute of Metrology (METAS) for the characterization of the coating unit

# Backup Slides

# Comparison of measurement methods

| | Current (Mass) | Number | TC |
|---|---|---|---|
| Avoid large particles | - | + | + |
| Correlate with toxicity | - | - | (+) |
| Reflect the quality of the combustion | o | - | + |
| Online or semi-online | - | + | + |
| Suitable for test bench as well as field measurements | o | + | + |
| Include primary as well as secondary emissions | - | - | + |

# Ranges for secondary organic aerosol (SOA) production potential (primary emissions not shown)

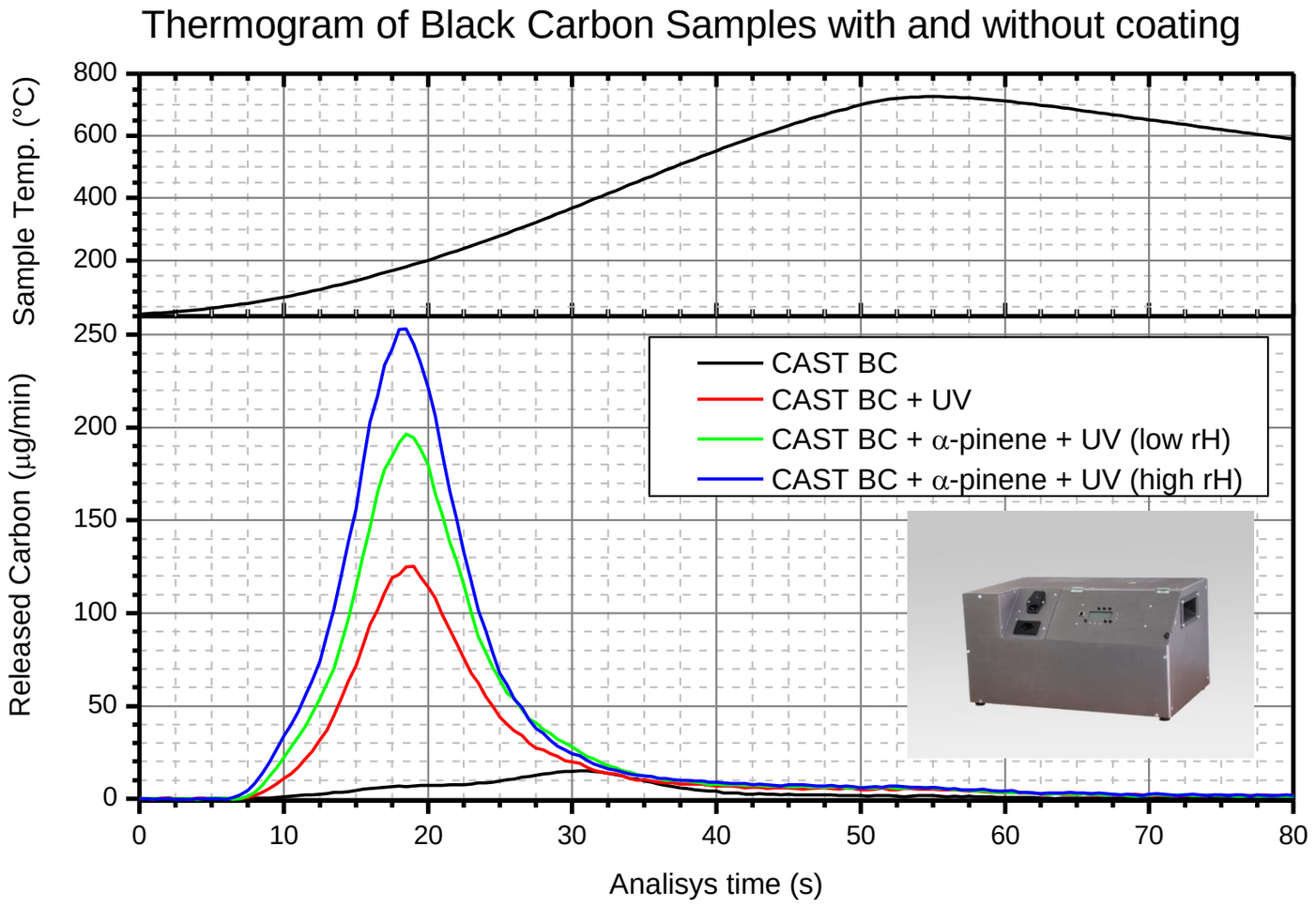



Source: Keller & Burtscher, 2017 (https://doi.org/10.1016/j.jaerosci.2017.08.014)

# Coating Propane Soot

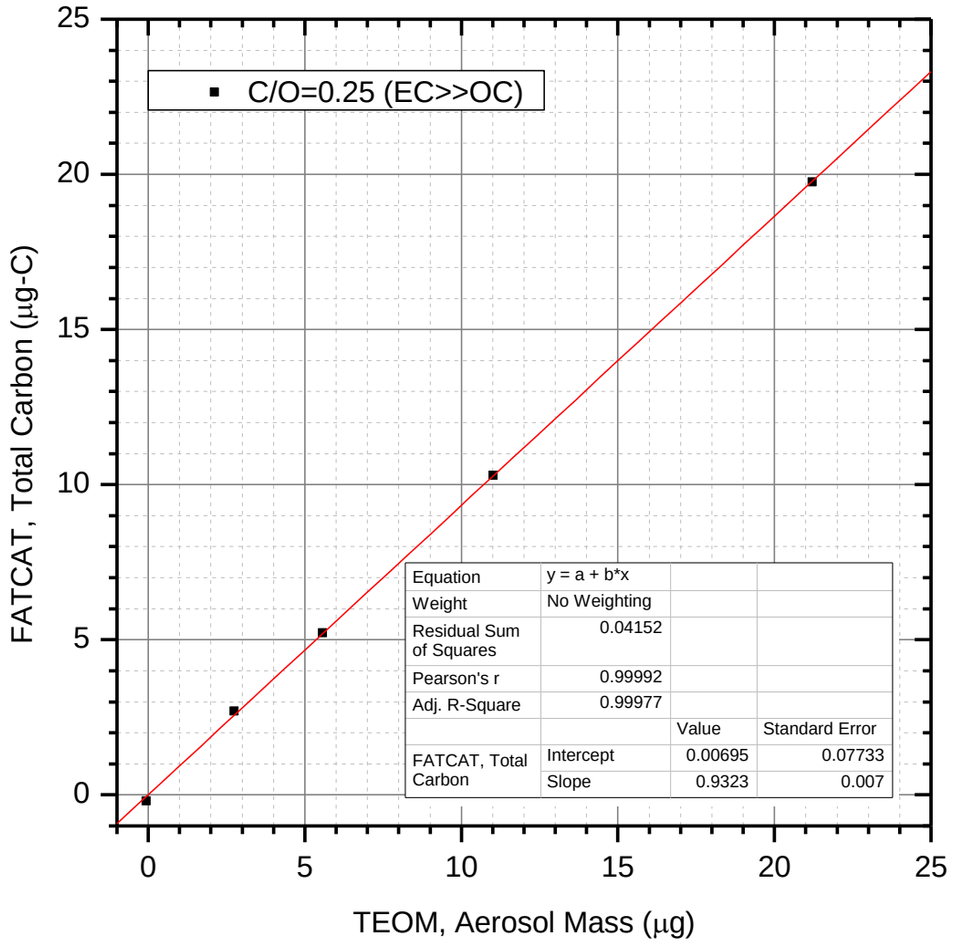
- The coating unit can be used to study the potential formation of SOA from specific sources (by disabling the VOC dosage)
- Requirement is simply to keep the source related VOC precursors

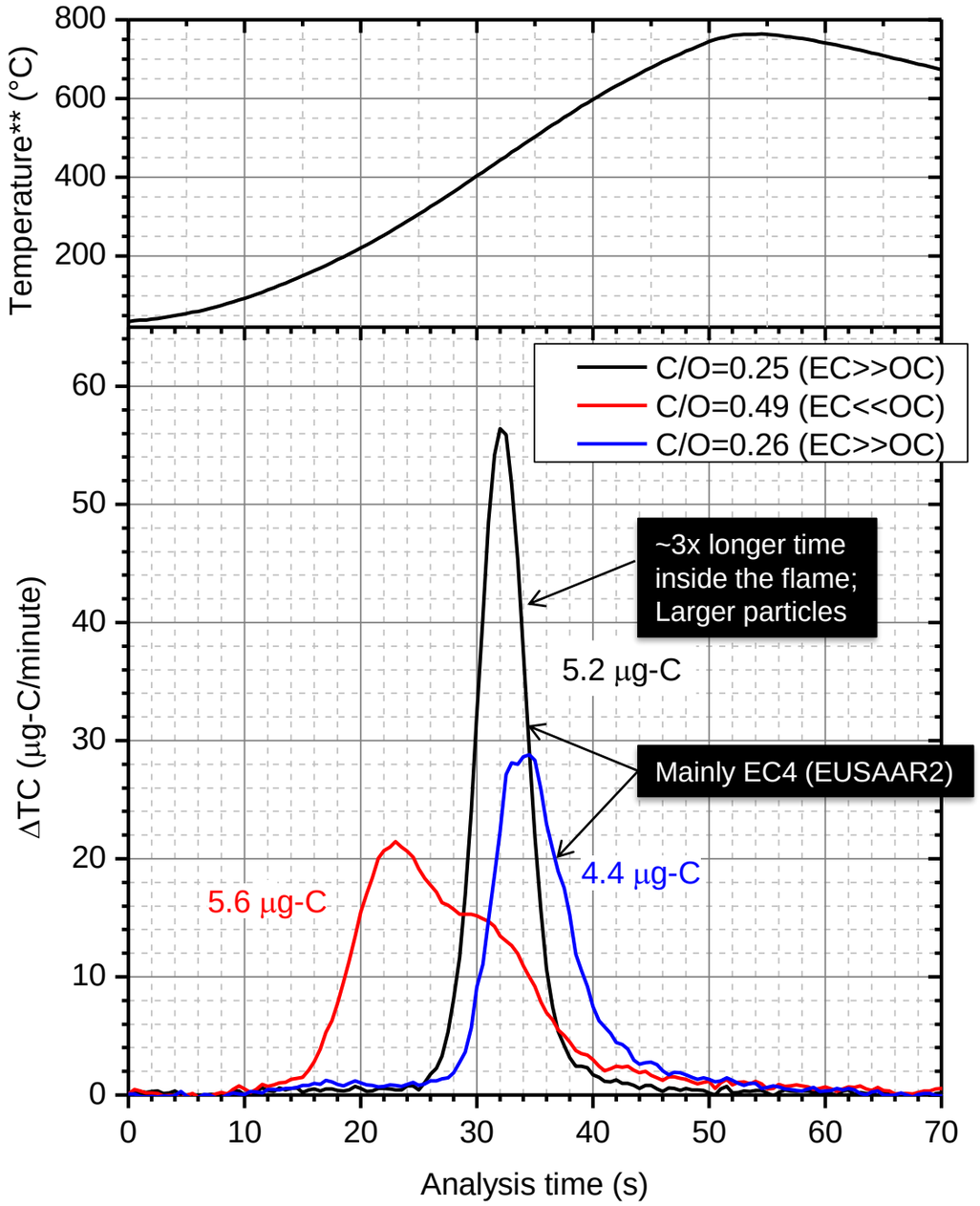
**Other interesting applications:**
- Lab-based study of health effects (Health)
- Lab-based calibration of, e.g., absorption photometers (Air quality)
- New test aerosols for, e.g., filter testing (Industry)




Thermogram produced through $CO_2$ measurements using our semi-online total carbon measurement system (i.e. FATCAT; an in-house development)

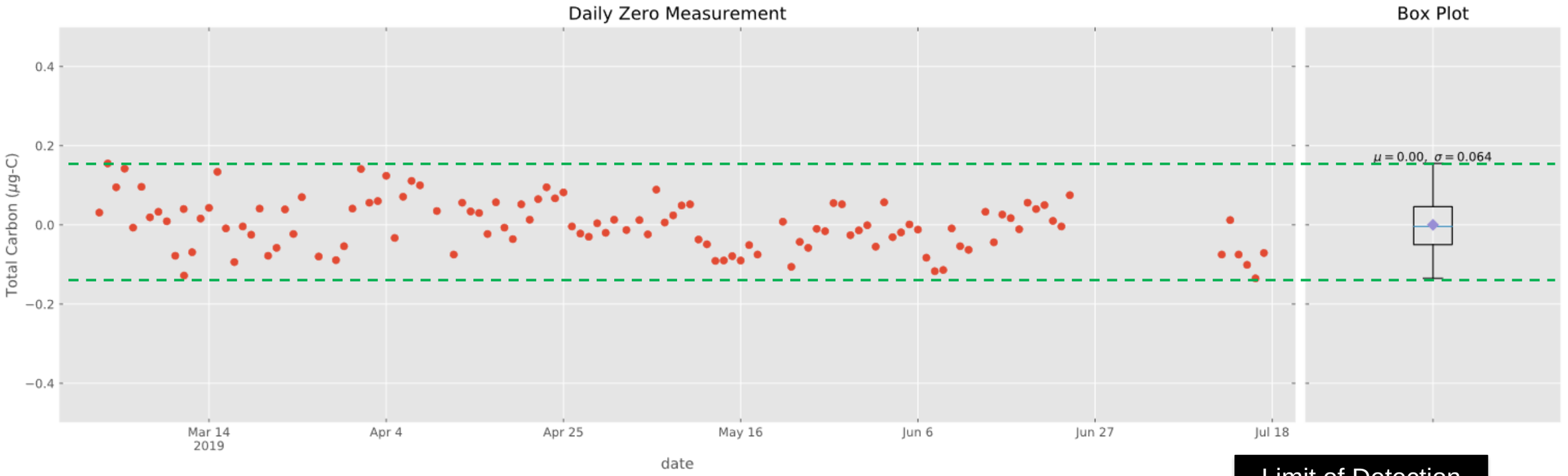
# Characterization: Standard Soot*



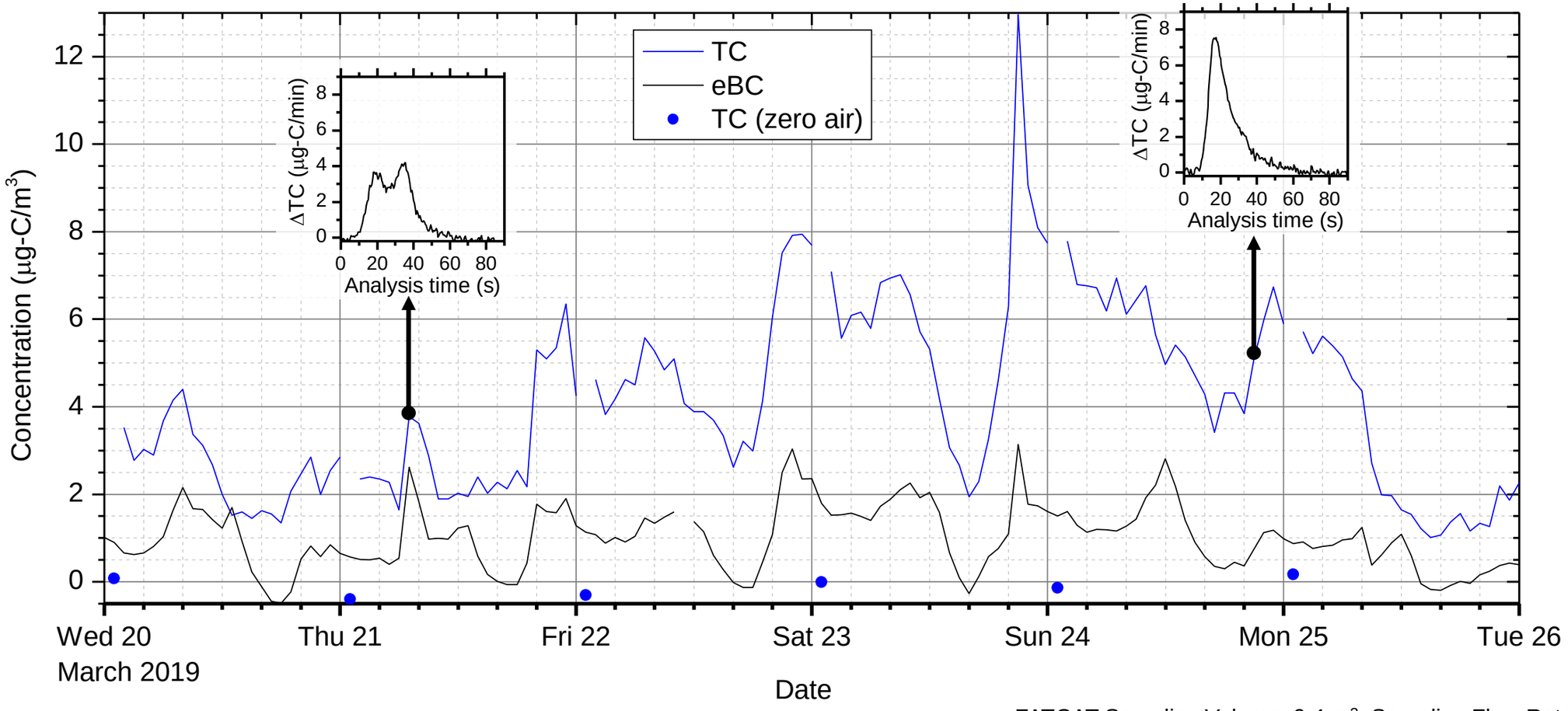

*Synthetic aerosol generated by means of a CAST (Jing, ag) diffusion flame generator.
**Temperature measured behind sampling filter. Actual filter temperature is higher.

# FATCAT characterization: Zero measurements (preliminary results)




Limit of Detection
LoD = 0.19 µg-C
(Using 3σ criterium)

# FATCAT characterization: Ambient air at Windisch (Aargau), Switzerland




FATCAT Sampling Volume: 0.4 $m^3$; Sampling Flow Rate: 8 lpm
eBC measured at λ=880nm (Aethalometer AE33, Magee Sci.)

# Characterization: Open Fire*

| Cycle | Total Carbon (TC) mg/m³ @ 13% $O_2$ | Gravimetric mg/m³ @ 13% $O_2$ | TC fraction |
|---|---|---|---|
| Cold start | 90.8 | 220 | 41% |
| Warm start | 118.8 | 538 | 22% |

*Sample undiluted, no aging. Preliminary data, do not cite!