SOA from wood burning appliances in a simplified total carbon measurement

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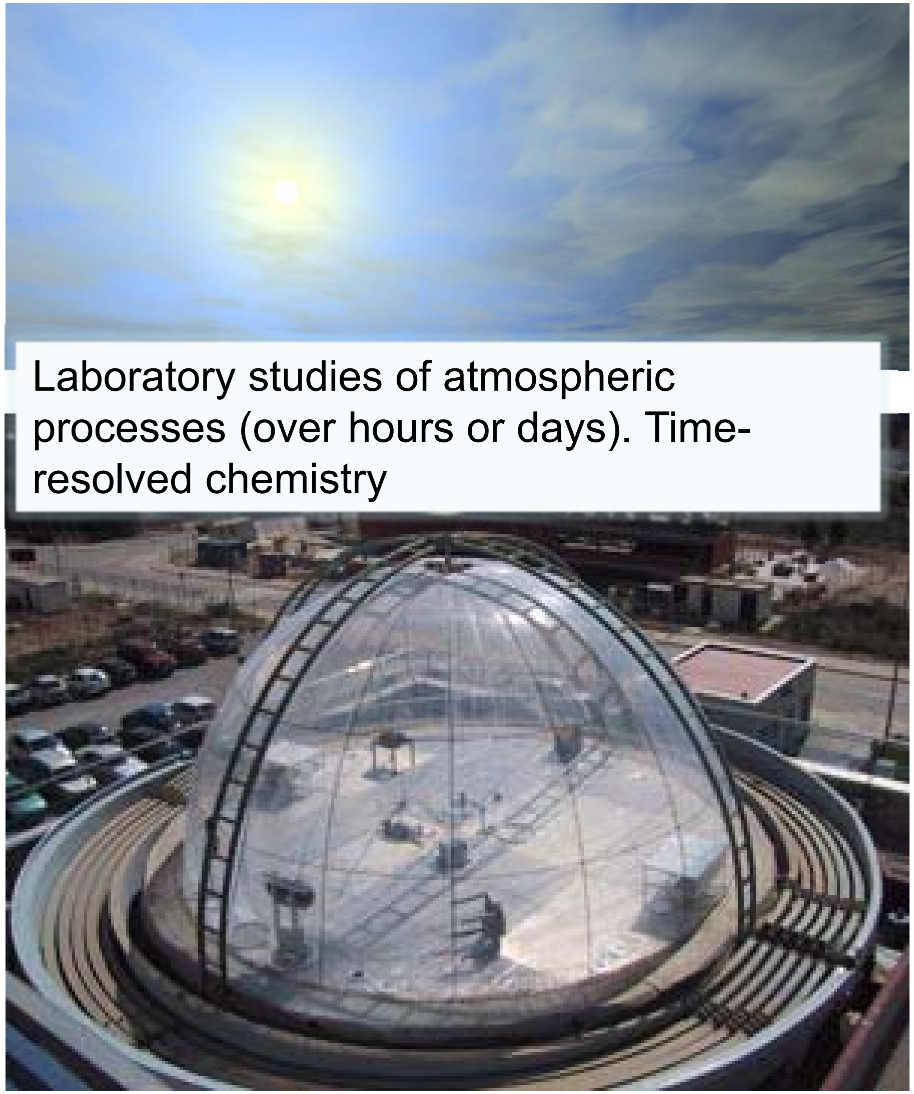
Motivation

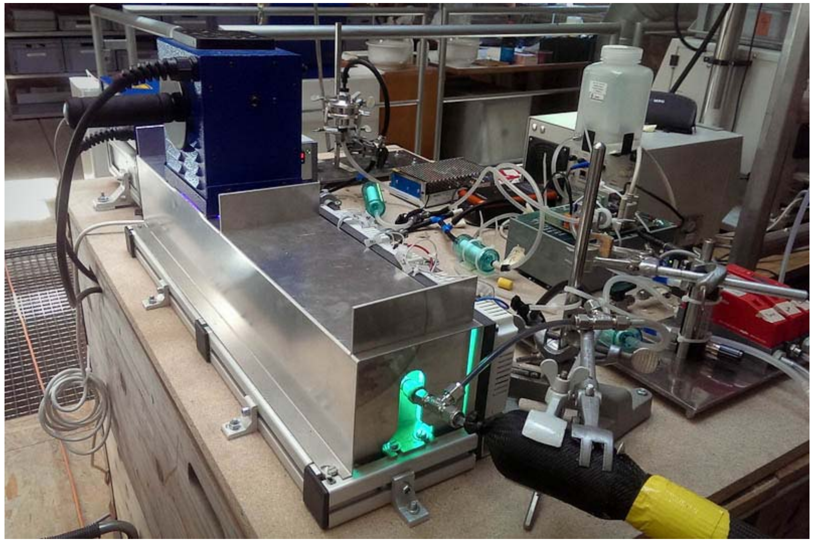
- Primary PM gives an incomplete picture of the contribution of wood burning to ambient aerosol as well as of the quality of the combustion.
- The emission of organic gaseous carbon (OGC) varies over 2 orders of magnitude for what is *legally defined* as a clean wood burning appliance (see, e.g., Johansson, Atmos. Environ. 2004); OGC is the source of Secondary Organic Aerosol (SOA).
- (on the test bench) Freshly emitted particles have an organic-carbon-to-elemental-carbon ratio typically around 0.1 and 0.3. In the atmosphere this ratio can be close to 10 for wood burning particles (see e.g. Szidat GRL 2007).
- “Organic material may have significant health effects” (R. Zellner, ETH-NPC 2014).
- The potential for SOA production should be included in standard measurements, and should also be accounted for as part of the PM emission limits.



Laboratory studies of atmospheric processes (over hours or days). Time-resolved chemistry

EUPHORE Smog Chamber, Valencia

Micro Smog Chamber

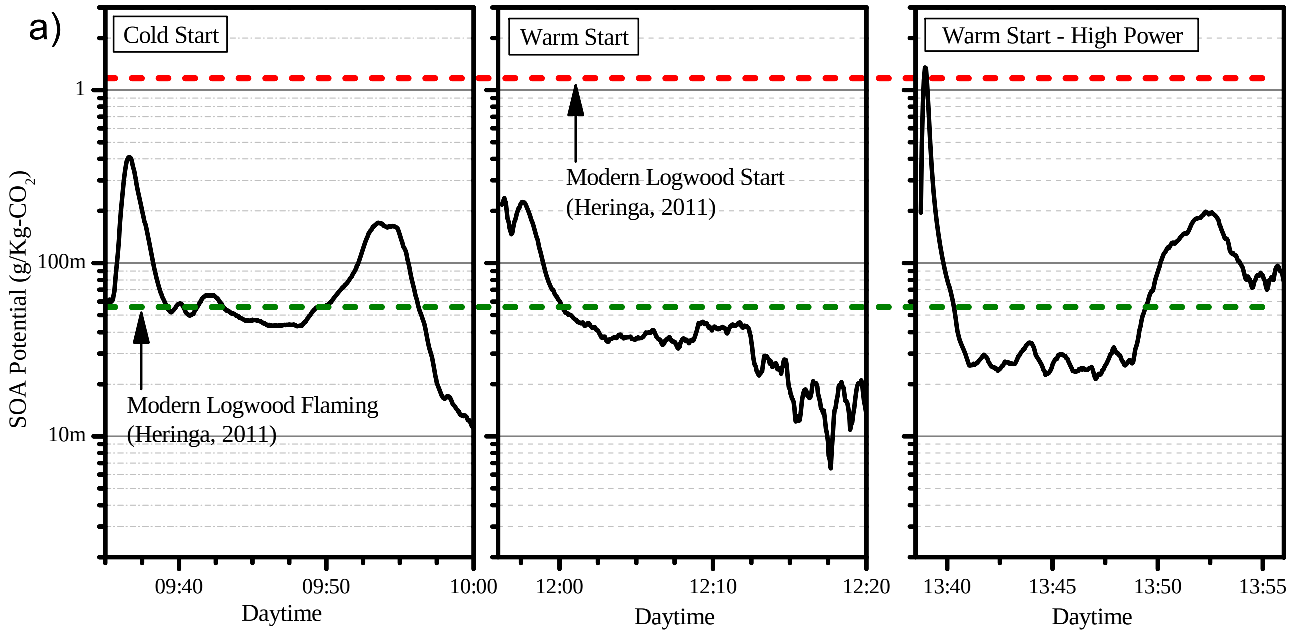


Volume: 2 or 3 76ml-tubes
Flow: 1 lpm
Residence time: ~10 Seconds
O_3: up to 100ppm (atmosphere < 60ppb)
Light: UVC (20W) and UVA (30W)

- Dimensioned for slightly diluted emissions (e.g. 1:10) from wood burning appliances.
- Focus on final state
- Oxidation degree can be adjusted through flow, length, or light intensity.

Keller & Burtscher, 2012, Aerosol Sci. 49 pp. 9-20

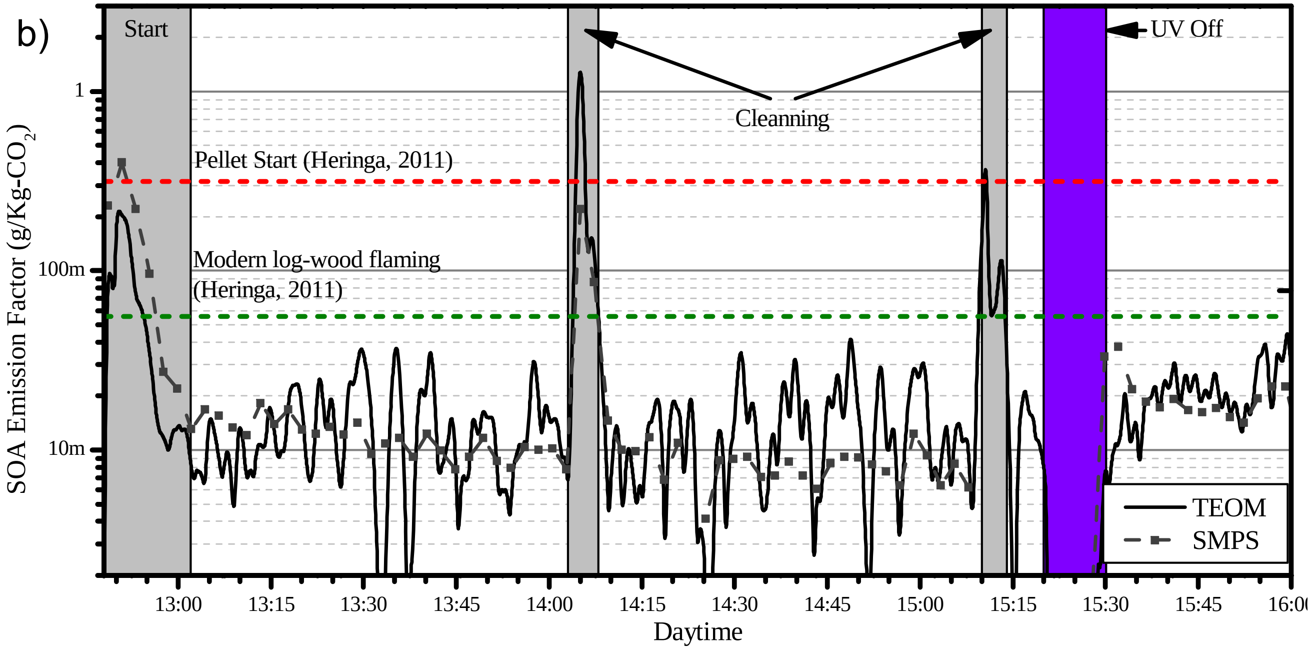
Example 1 (2012): On-line measurement of filtered emissions after UV-conditioning



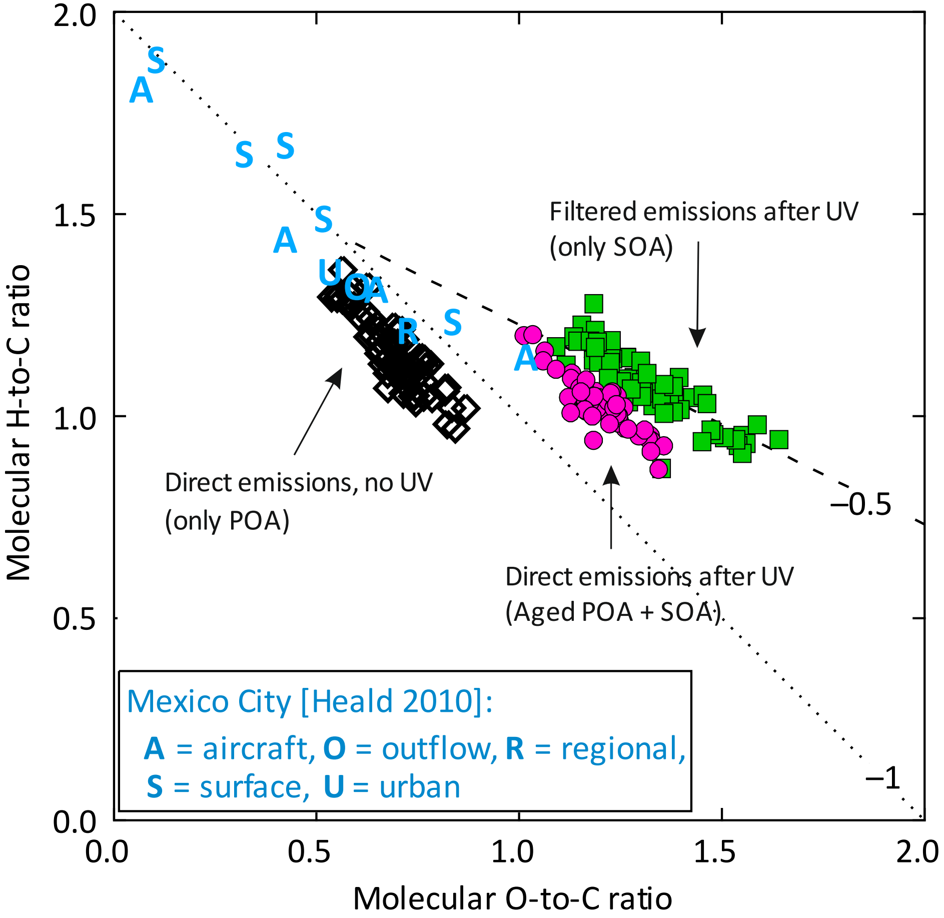
Pure Secondary Organic Aerosol, a) Log-Wood Cooking Stove and b) Pellet Stove.

Keller & Burtscher, 2012, Aerosol Sci. 49 pp. 9-20

From ETH NPC 2012: The emission factor for SOA produced by means of the reactor does not correlate with other pollutants like primary PM, CO, Organic Gaseous Carbon (OGC) or even Non-Methane OGC.



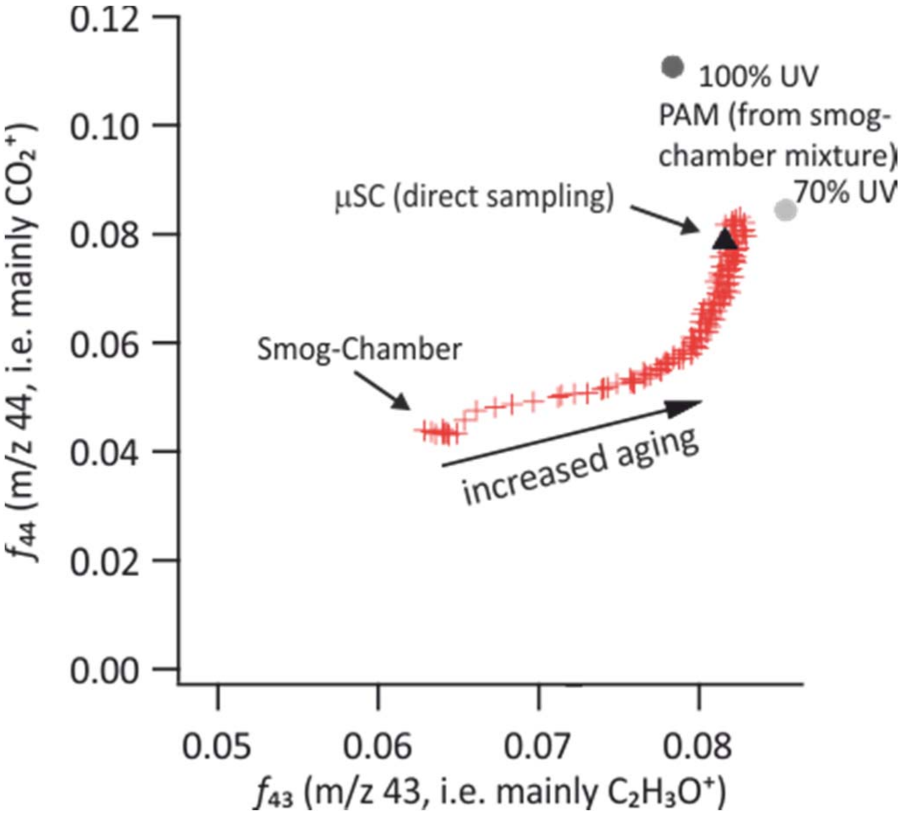
Example 2 (2013-2014): Oxidation degree after UV-conditioning in the (3 tubes, 225ml) µSC. AMS and SP-AMS Analysis



Van Krevelen representation of log-wood stove emissions in comparison to ambient observations from Mexico City.
Figure adapted from: Corbin *et al.* book of abstracts of the International Aerosol Conf. 2014, September 2014, Korea.

- **O-to-C ratios are at the upper limit of atmospheric observations.**
- Better understanding of the processes that contribute to secondary organic aerosol (SOA) formation.
- New results show that AMS measurements with the standard assumptions (i.e. for an average ambient mixture) underestimate O-to-C and overestimate H-to-C for the case of wood burning.
- Manuscript under preparation by Corbin *et al.* **(see also poster 12 downstairs)**

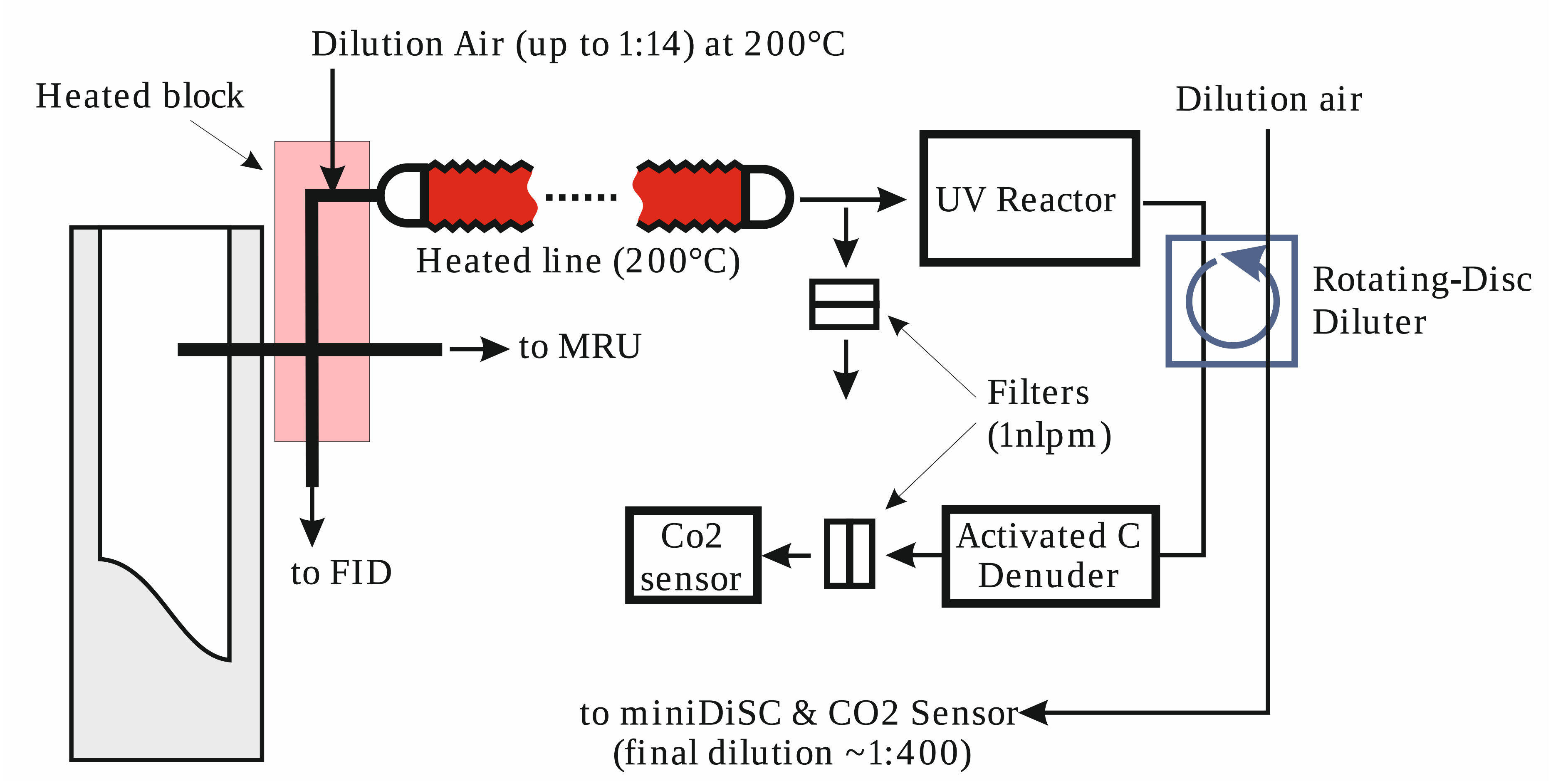
Example 3 (2014), unfiltered emissions: Inter-comparison between Smog-Chamber (5m^3), μSC (150ml) and PAM Chamber (10 litters). AMS Analysis



Comparison of oxidation in terms of the fraction *m/z* 44 and *m/z* 43 to the total organic signal for a single log-wood combustion experiment.
Figure adapted from: Bruns *et al.*, book of abstracts of the International Aerosol Conf. 2014, September 2014, Korea.

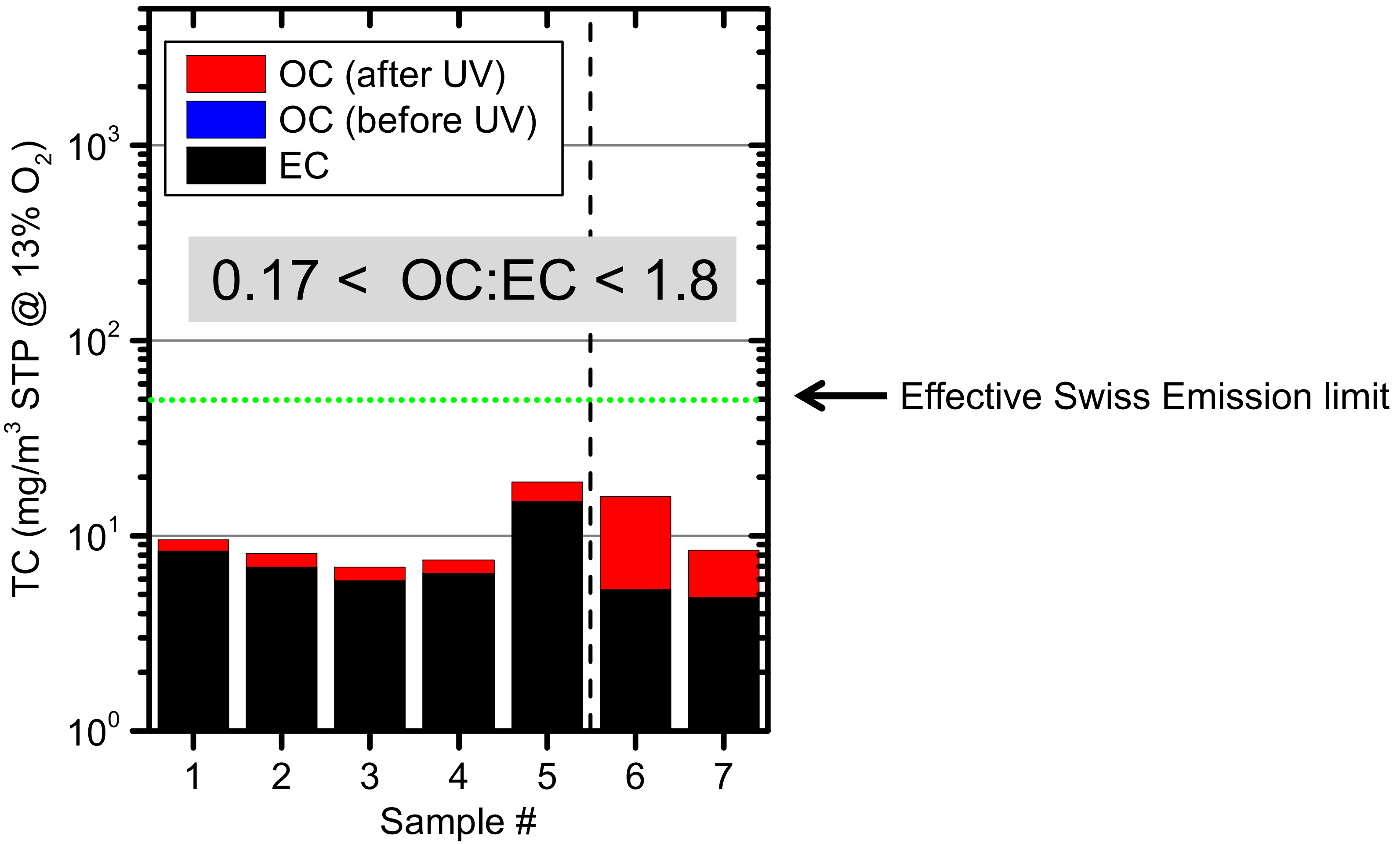
«Good agreement was also observed between the μSC and SC at similar OH exposures when sampling direct emissions»

Setup for filter analysis experiments



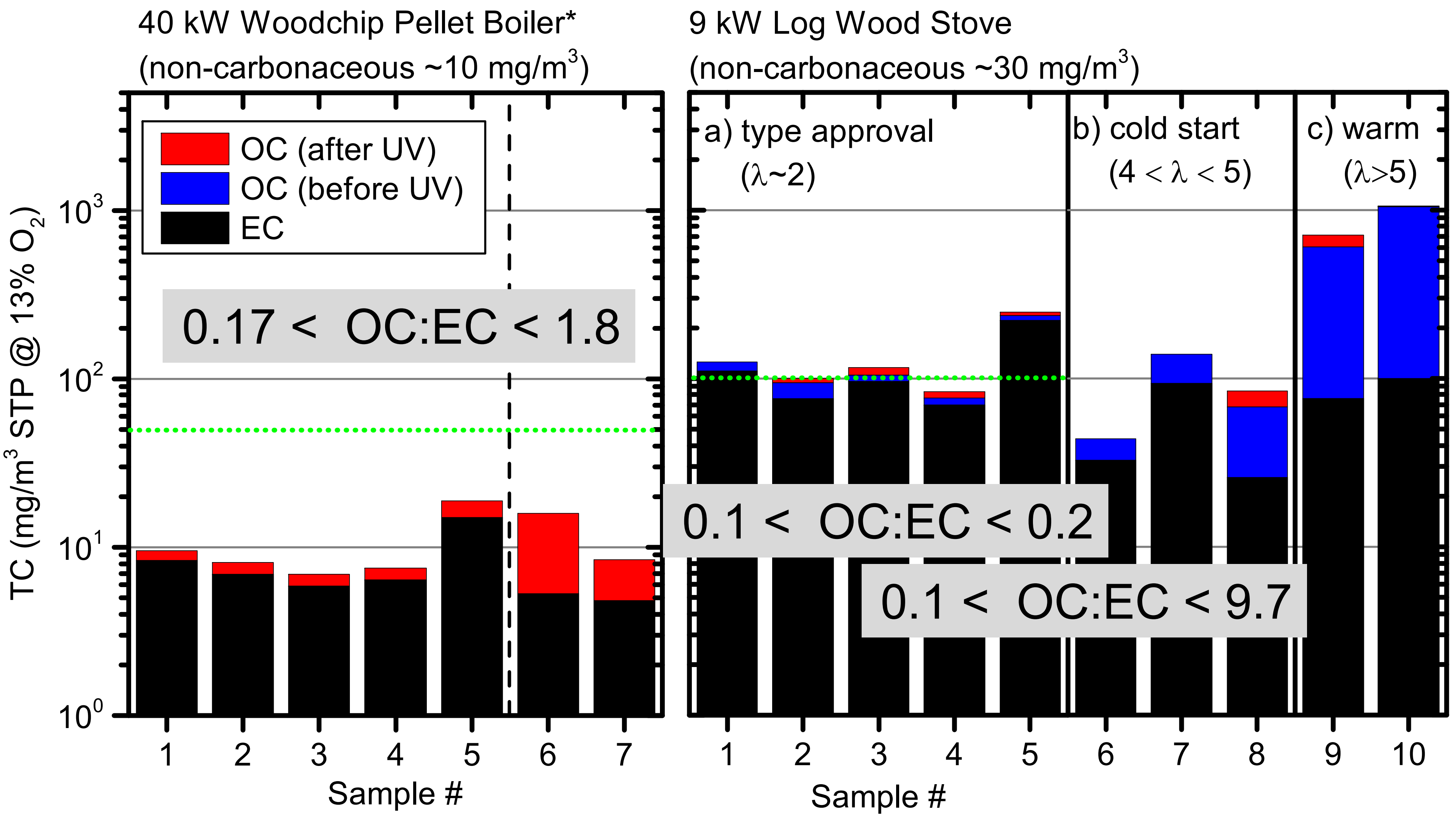
- On a first step, [particle bound] organic carbon (OC) and elemental carbon (EC) measurements by means of thermo-optical analysis (EUSAAR 2 protocol). Total Carbon, TC = OC + EC
- In a future, the analysis may be substituted by a relatively simpler thermal analysis for TC.

40 kW Woodchip Pellet Boiler*
(non-carbonaceous ~10 mg/m^3)



← Effective Swiss Emission limit

* "before UV" data not available for pellet boiler samples



40 kW Woodchip Pellet Boiler*
(non-carbonaceous ~10 mg/m^3)

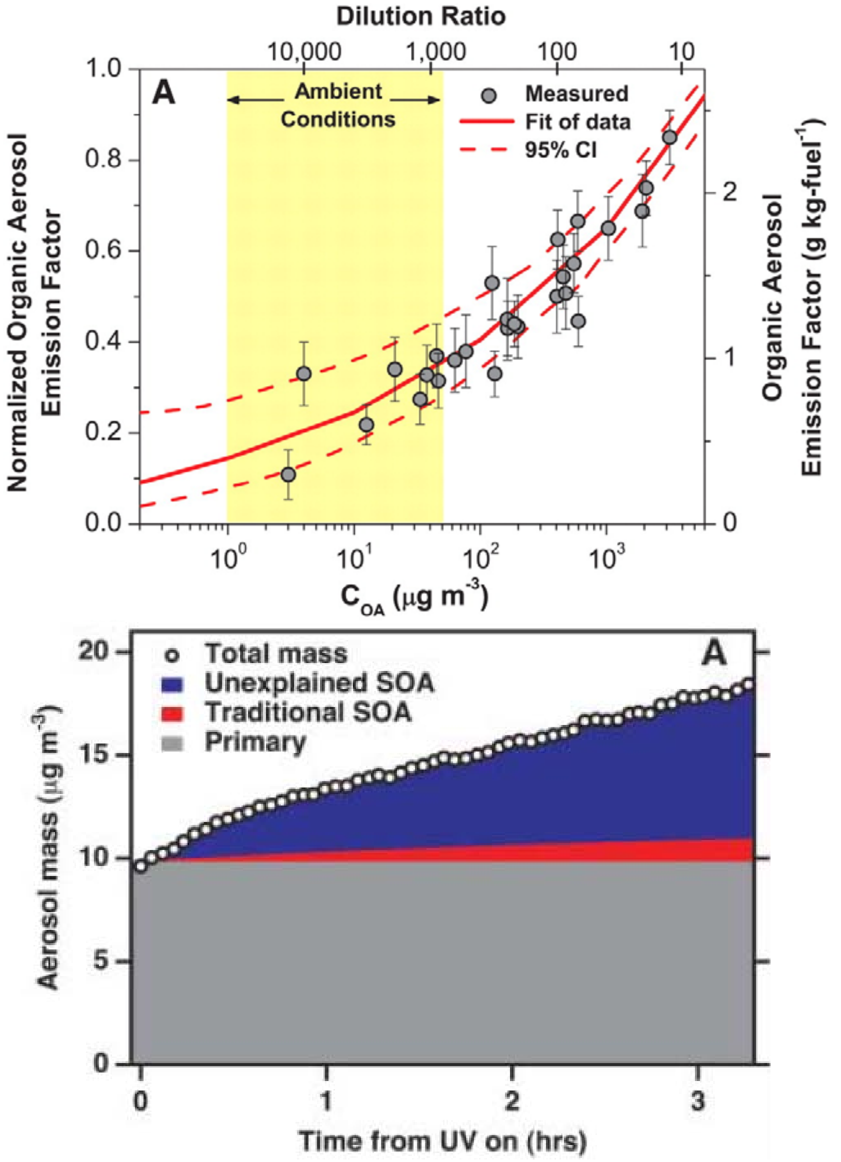
9 kW Log Wood Stove
(non-carbonaceous ~30 mg/m^3)

* "before UV" data not available for pellet boiler samples

- Under test-bench conditions the combustion is generally “good”. However, deviations of the combustion protocol/settings may severely alter the composition as well as the emission-factor.
- Filter sampling (room temperature and low dilution) shows minimal formation of secondary organic aerosol (SOA).

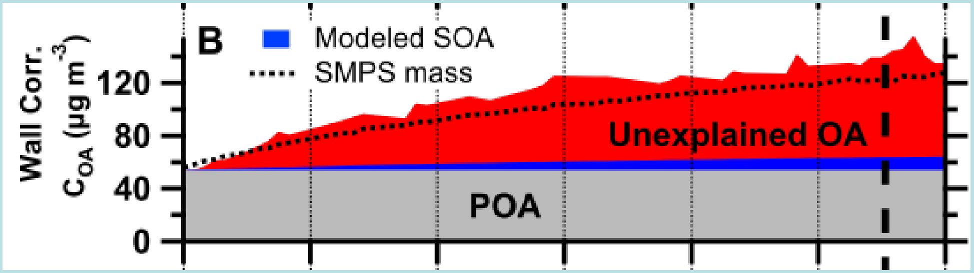
Partitioning of organic species (Diesel)

- Semivolatile species evaporate with atmospheric dilution, creating substantial amounts of low-volatility gas-phase material.
- Laboratory experiments show that photo-oxidation of diesel emissions rapidly generates organic aerosol (i.e. SOA) from low- and intermediate-volatility gas-phase species.

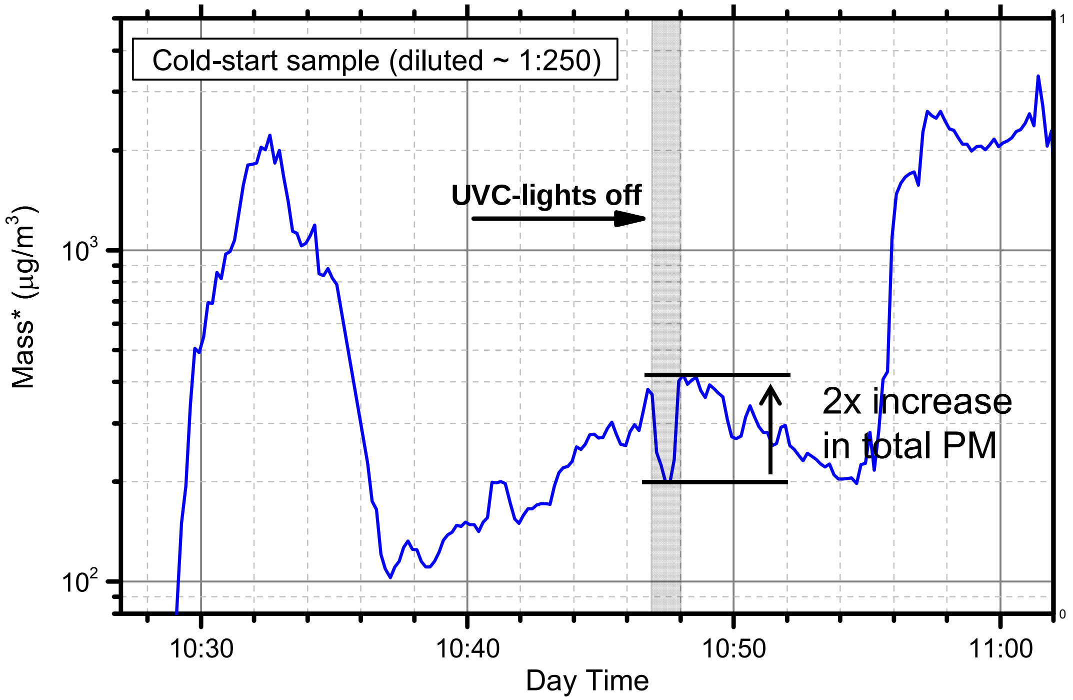


Graphics: Robinson et al. (2007), *DOI: 10.1126/science.1133061*

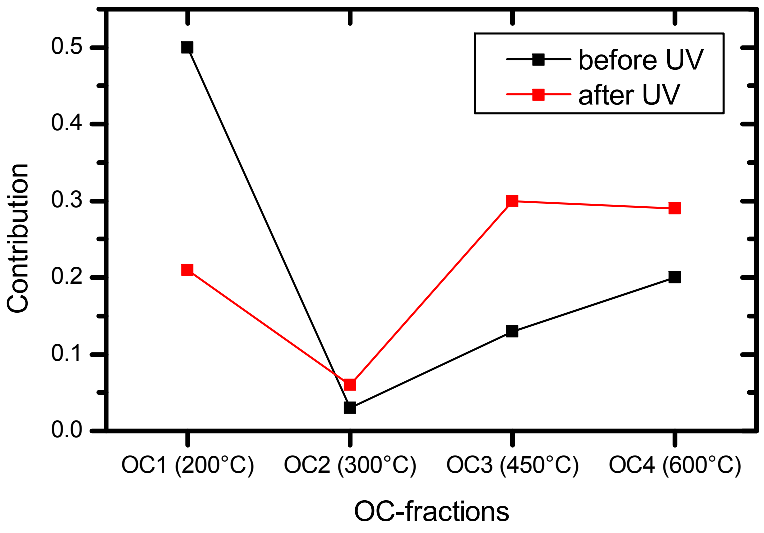
Similar unexplained OA for wood burning under far worst conditions than our experiments (i.e. modified combustion efficiency, MCE = $CO_2/(CO_2+CO)$, between 0.58 and 0.93). Grieshop *et al.*, 2009, doi:10.5194/acp-9-1263-2009



Partition of organic species (log-wood stove)



*on-line mass derived from miniDiSC data using σ_g=1.9 and ρ=1.2 g/cc



- The effect of oxidation (i.e. formation of SOA) can be observed at higher dilutions (thus also in the atmosphere).
- The difference with the filter measurements is due to the lower of volatility of oxidized sample.
- Gravimetric sampling is done on undiluted emissions, but the high sampling temperatures (typically 120°C) and the filter conditioning (1 h at 160°C after sampling) eliminate potential SOA.

Summary and Conclusions

- A continuous-flow reactor with a short residence time can be used as a tool for on-line estimation of the SOA production potential or, alternatively, to threat unfiltered emissions and simulate aging.
- The aerosol is similar to what is produced by means of traditional smog-chamber experiments (in quantity and composition), and has an oxidation degree (i.e. molecular O-to-C ratio) comparable to the upper limit of atmospheric observations
- Type approval testing is probably not representative of the real-world emissions of a wood burning appliance. (Specially on manual operated devices) Small changes in the combustion protocol can heavily affect the emissions specially in regard to the organic fraction (in particular, SOA during high lambda operation can multiply them several-fold).
- The partition of OC during measurement is very relevant. (Heated) Gravimetric measurements exclude the OGC-fraction which seems to contribute the most to SOA formation. UV-treatment reduces the volatility of the emissions and therefore makes the particle fraction robust against dilution or temperature changes.
- Our current thermo-optical analysis (OC and EC separation) could also be substituted by a less elaborated total carbon measurement. This can be used to include the potential SOA formation into PM emission measurements.

Thanks to:

M. Bertschi and J. Wüest from the combustion laboratory at the Institute University of Applied Sciences Northwestern Switzerland.

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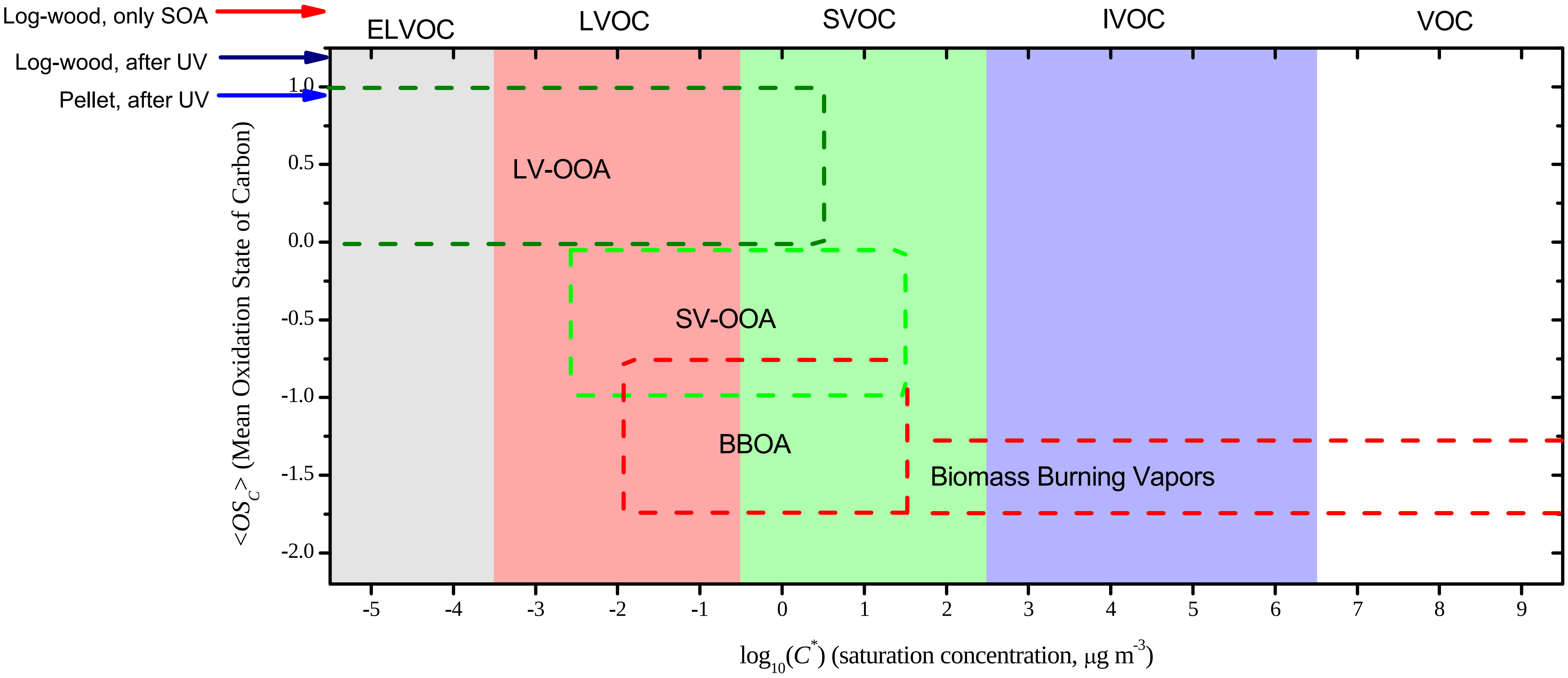
Some details about our experimental setup

	Pros	Cons
First dilution stage (1:4 to 1:14)	Prevents condensation of water.	Filters, specially before UV, do not reflect atmospheric partition.
Filter measurement before UV conditioning	Reference for EC (and OC) before aging. Can be used to calculate loses in the UV-reactor and denuder.	Requires backup filter to account for absorption of gas-phase organics.
Denuder after UV conditioning	Removes O_3 and prevents further oxidation on the filter. Also removes the remaining gas-phase organics (i.e. no blank filter required).	Causes losses. This can be partially compensated by comparing the EC-fraction with the filter before UV-conditioning.
Second dilution stage (final dilution 1:200-400)	Closer to atmospheric values and, thus, realistic partition. Concentration in range of commercial on-line instruments.	
UV conditioning	Reduces the volatility of the sample, thus making the measurement robust against variations in temperature or dilution ratio	Requires dilution if the filters are at room temperature. Without dilution it is not clear how well it would work under low O_2 conditions.
Thermo-optical analysis	Detailed (temperature resolved) data about the OC and EC content	Expensive and elaborated, requires inert gas for OC analysis. No standard protocol for emissions.

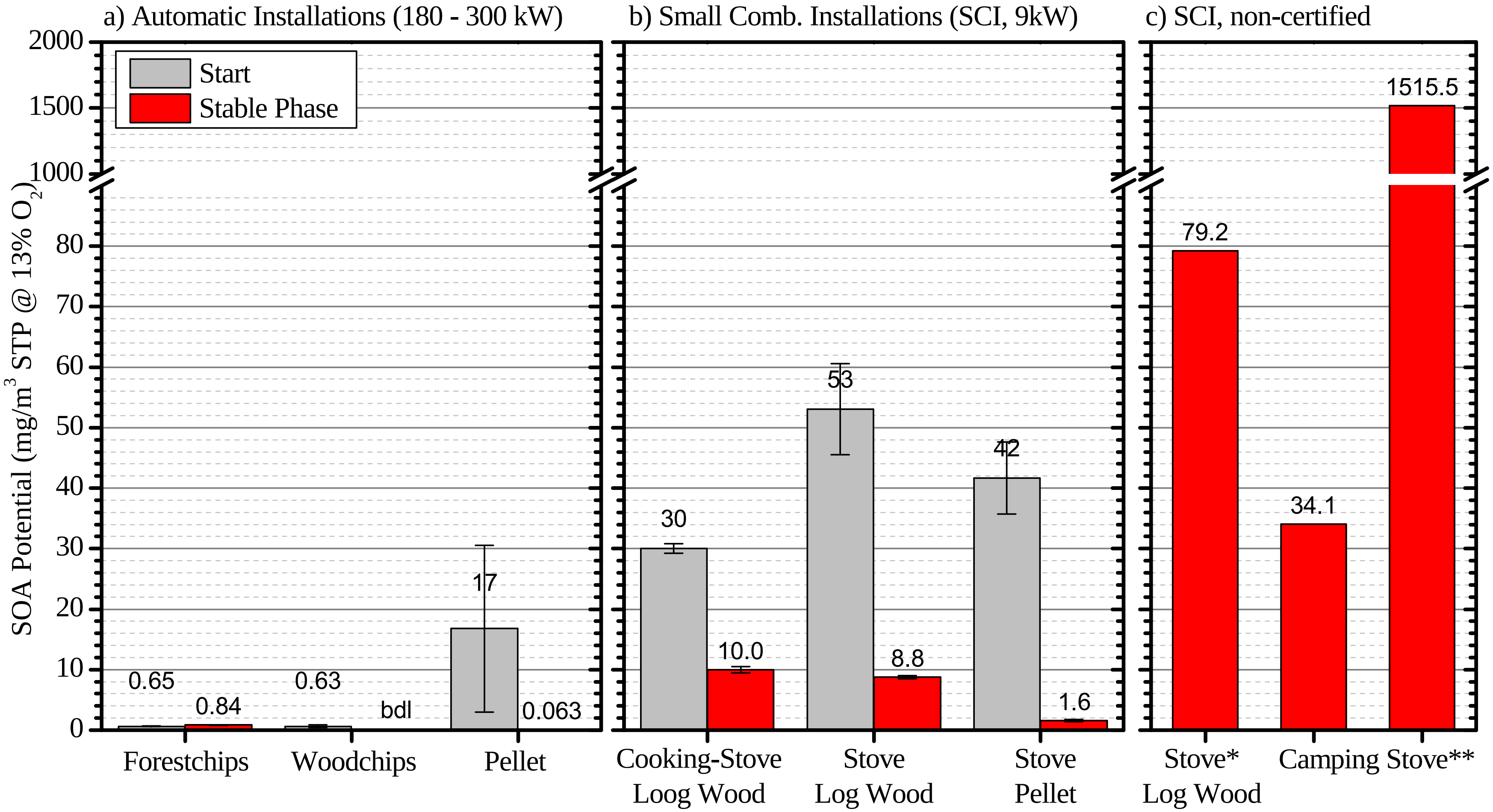
Is our oxidation degree enough to prevent desorption?

Oxidation State of Carbon= 2 O:C – H:C ; e.g. CH_4 → -4, Graphite → 0, CO_2 → 4
BBOA: Biomass Burning Organic Aerosol (freshly emitted)
SV-OOA: Semivolatile Oxidized Organic Aerosol (fresh SOA)
LV-OOA: Low-Volatility Oxidized Organic Aerosol (heavily aged SOA)



Volatility graphic adapted from: Donahue *et al.* (2012), DOI 10.5194/acp-12-615-2012

SOA production potential for different appliances

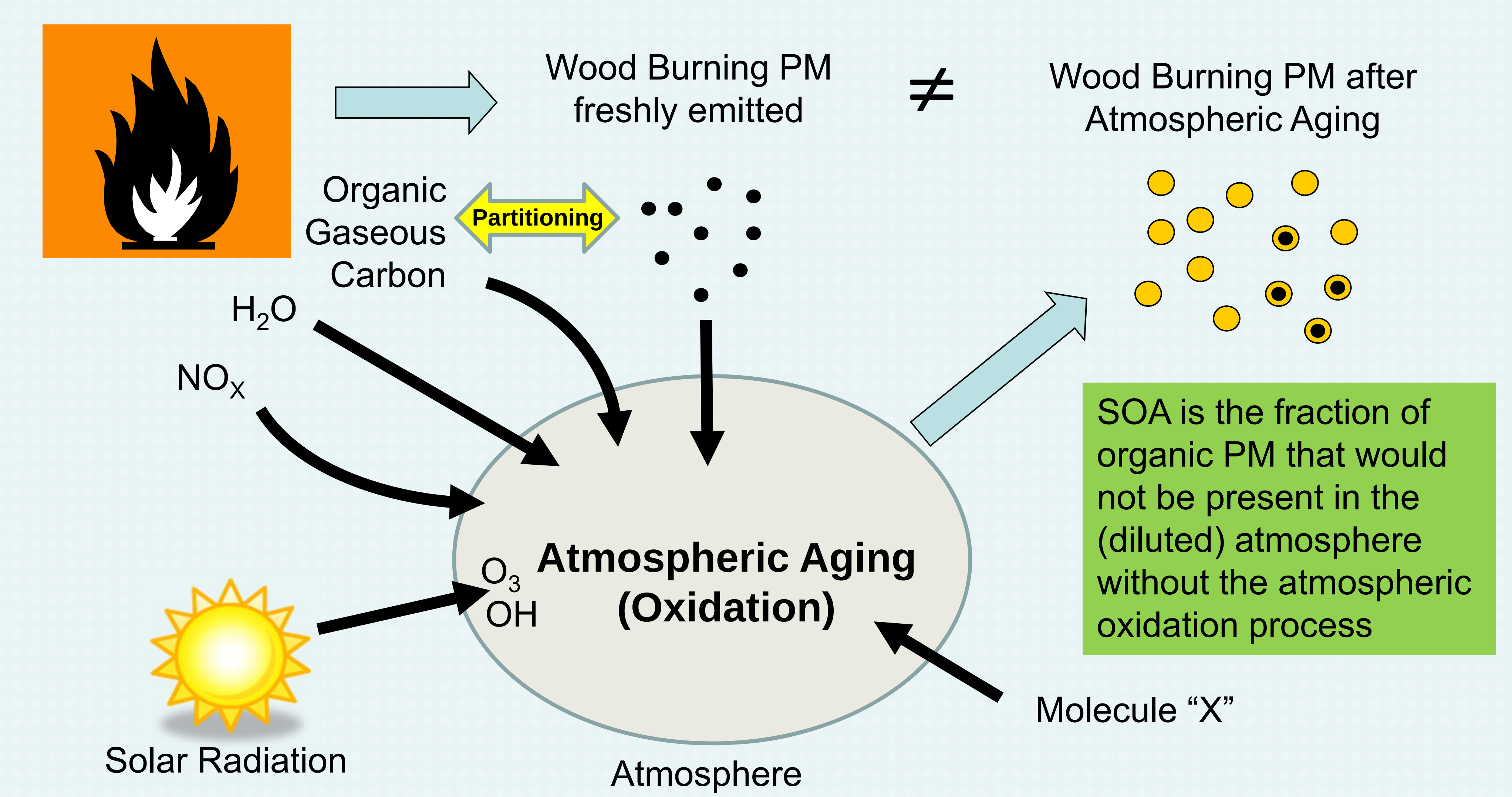


bdl: below detection limit

* Heringa *et al.* Atmos. Chem. Phys. 11, 5945, 2011

** adapted from: Grieshop *et al.* Atmos. Chem. Phys., 9, 1263, 2009

Emissions: Primary PM and Secondary Organic Aerosols (SOA)



Wood Burning PM freshly emitted ≠ Wood Burning PM after Atmospheric Aging

Organic Gaseous Carbon

Partitioning

H_2O

NO_X

O_3

OH

Atmospheric Aging (Oxidation)

Solar Radiation

Atmosphere

Molecule “X”

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

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