On-site estimation of secondary organic aerosol production potential from wood burning appliances

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Organic aerosol (OA) can be the dominant component of ambient particulate matter (Szidat et al., 2007). However, not all OA is formed at the emission point. An important fraction, called secondary organic aerosol (SOA), forms after emitted organic gaseous carbon (OGC) undergoes atmospheric chemistry, in a process that can take hours or even days to complete. Lee et al. (2008) inferred an enhancement as high as 6-fold for the OA in a forest fire plume 3 to 4 hours after emission. Smog-chamber experiments show that similarly high OA enhancement factors are possible even for modern, residential-type, small combustion installations (SCI; Grieshop et al., 2009; Heringa et al., 2011).

We propose the use of a compact continuous-flow tube-reactor with a short residence time as a conditioning system for an on-line estimation of the SOA production potential (SOA-PP). The UV conditioning can be done on filtered as well as unfiltered emissions. Previous experiments demonstrate that our reactor can oxidize OGC emissions from SCI, resulting in a SOA-PP between 0.01 and 1.28 g/kg-CO_2 (Keller and Burtscher, 2012). The lowest potential correspond to the steady state operation of a 9kW pellet stove. The largest SOA-PP was measured during the start phase of a log-wood cooking stove. The typical SOA-PP for batch operated log-wood SCI was found to be around 0.06 g/kg-CO_2 during steady state conditions. This is a considerable amount of additional PM-material, specially in the light of new emission-limits in European countries (e.g. the German PM emission-limit will be set to a value equivalent to 0.25 g/kg-CO_2 by 2015 for batch operated SCI). Non-certified or badly operated stoves can have an even higher SOA-PP. SOA emissions close to 10 g/kg-CO_2 have been reported by Grieshop et al. (2009) for a log-wood stove during a smog-chamber experiment.

We have also performed field measurements on state-of-the-art automatic boilers (250 to 400 kW) burning woodchips or pellets. When properly designed and operated, these systems achieve a very good combustion with no measurable OGC emissions and have, accordingly, no measurable SOA either. In general, the contribution of SOA to the total PM emissions for these boilers is negligible. These sources present a challenge for our measurement setup. The SOA-PP has to be estimated using only the gas-phase components of the raw gas. However, primary particles that penetrate the filter can cause a positive artifact. The emissions from these boilers were always close or below the detection limit of our system. The lowest still-measurable SOA-PP during this field campaign was $4\text{x}10^{-4}$ g/kg-CO_2 and corresponds to the steady-state operation of an automatic pellet boiler (300kW).

Finally, we performed a chemical analysis of the emissions from a manually operated wood stove by means of an Aerodyne aerosol mass spectrometer (AMS) run by ETH Zurich. When using our reactor, the resulting SOA, or the combination of aged primary organic aerosol (POA) and SOA, is more oxidized than typical ambient aerosol or SOA from smog-chamber experiments (see, e.g., Kroll et al., 2011; Donahue et al., 2012). Pure SOA experiments using a log-wood stove resulted in an average carbon oxidation state of about 1.5. This higher oxidation state does not come into conflict with the purpose of our reactor. We do not want to predict an ambient outcome, which is influenced by atmospheric conditions and the contribution of other local sources. Instead, we want to provide a system for the evaluation and the inter-comparison of wood burning appliances that takes the SOA production potential into account. A high oxidation state of carbon is associated with heavily aged SOA, and corresponds to organic species with low or extremely-low volatility. Thus, the UV treatment promotes an efficient nucleation/condensation of OC.

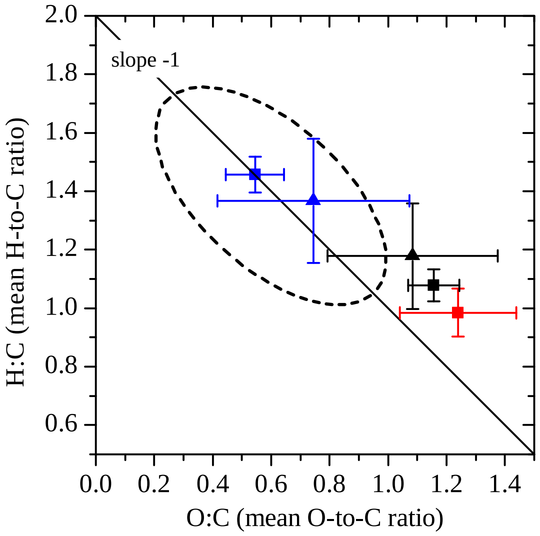

Figure 1: Van Krevelen diagram of the elemental ratios of organic aerosol emitted by a log-wood stove (■) and a pellet stove (▲) measured by AMS run by ETH Zurich. The colors represent POA (blue), aged POA and SOA (black), and pure SOA (red). Aged POA and/or SOA were obtained by conditioning the emissions by means of the UV reactor tube. The dashed line shows the area comprising ambient data from the MILAGRO C-130 aircraft campaign over and near Mexico City (Heald et al., 2010).

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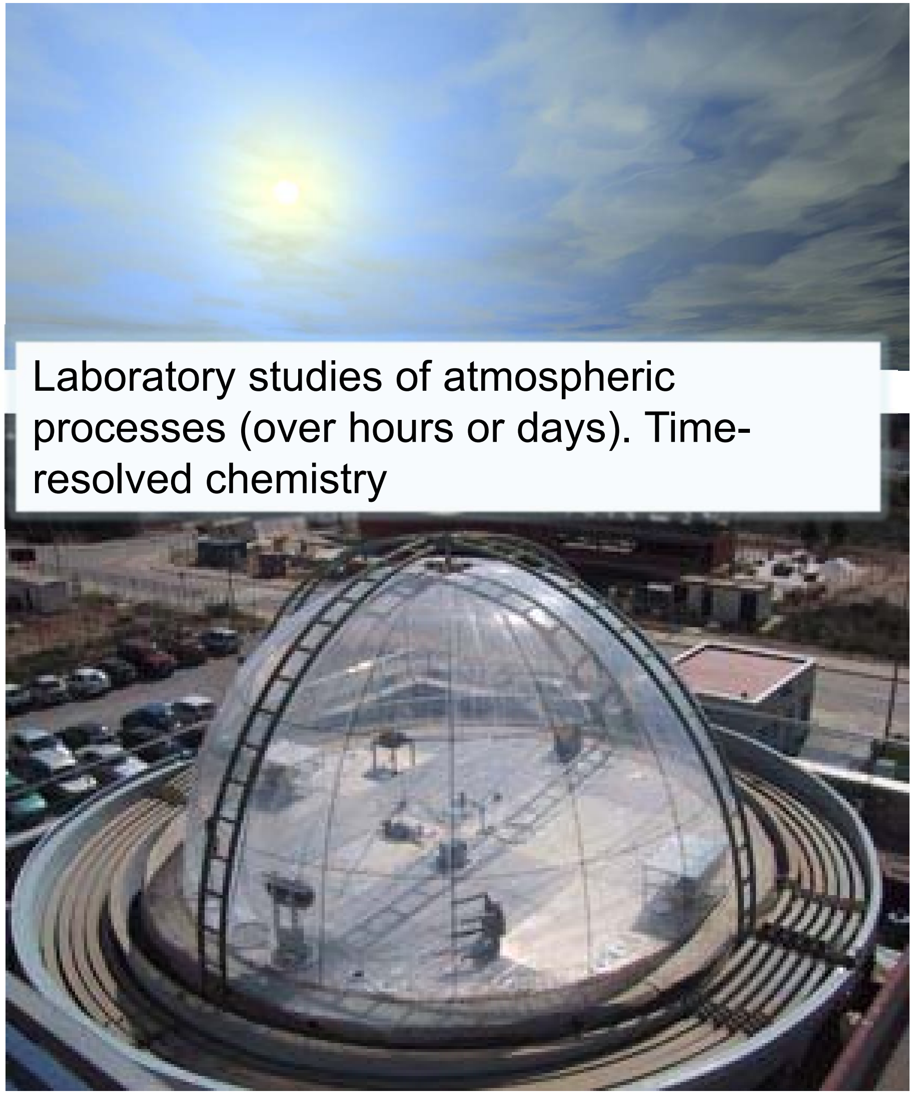
Motivation

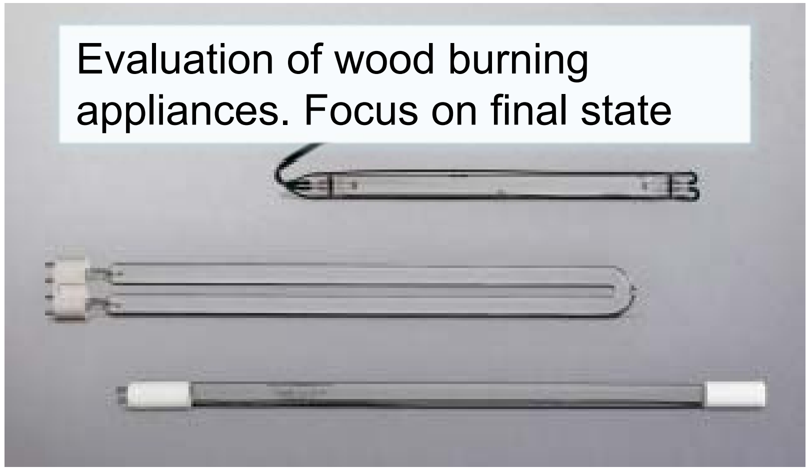
- Primary PM gives an incomplete picture of the contribution of wood burning (WB) to ambient aerosol as well as of the quality of the combustion.
- The emissions of organic gaseous carbon (OGC) vary over 2 orders of magnitude for what is *legally defined* as a clean wood burning appliances (examples under Johansson, Atmos. Environ. 2004); OGC is the source of Secondary Organic Aerosol (SOA).
- Freshly emitted particles have an organic-carbon-to-elemental-carbon ratio lower than 1. In the atmosphere this ratio can even be close to 10 for WB particles (see e.g. Szidat GRL 2007).
- Organic material significantly contributes to toxicity.
- Future legislation should contemplate the hydrocarbon emissions and, ideally, regulate them based on their SOA Production Potential. However, there is currently no standard tool for this.



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

EUPHORE Smog Chamber, Valencia

μSOA Chamber

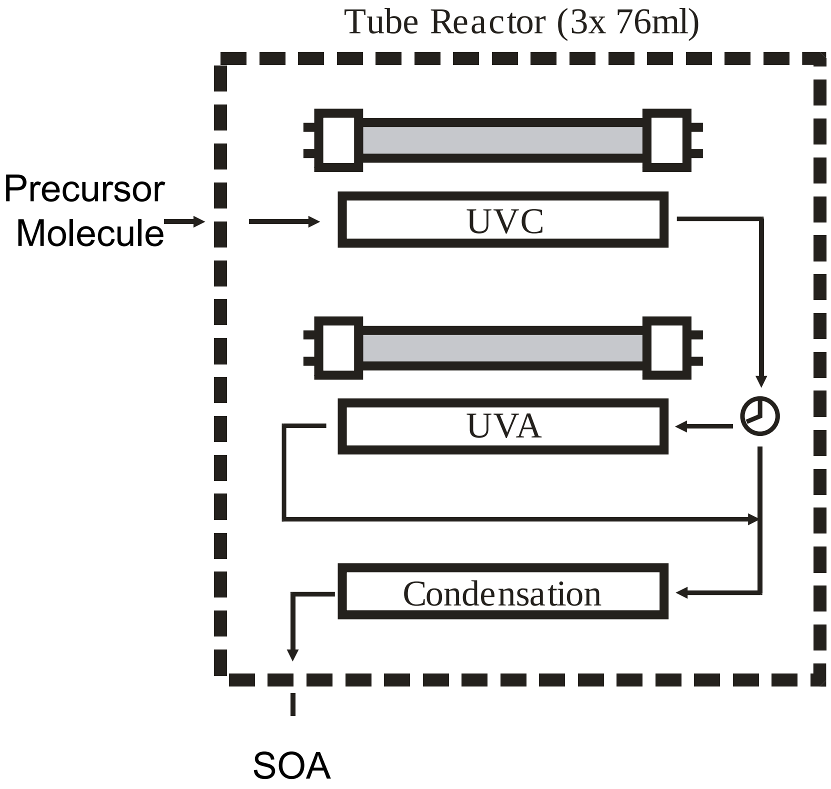


Evaluation of wood burning appliances. Focus on final state

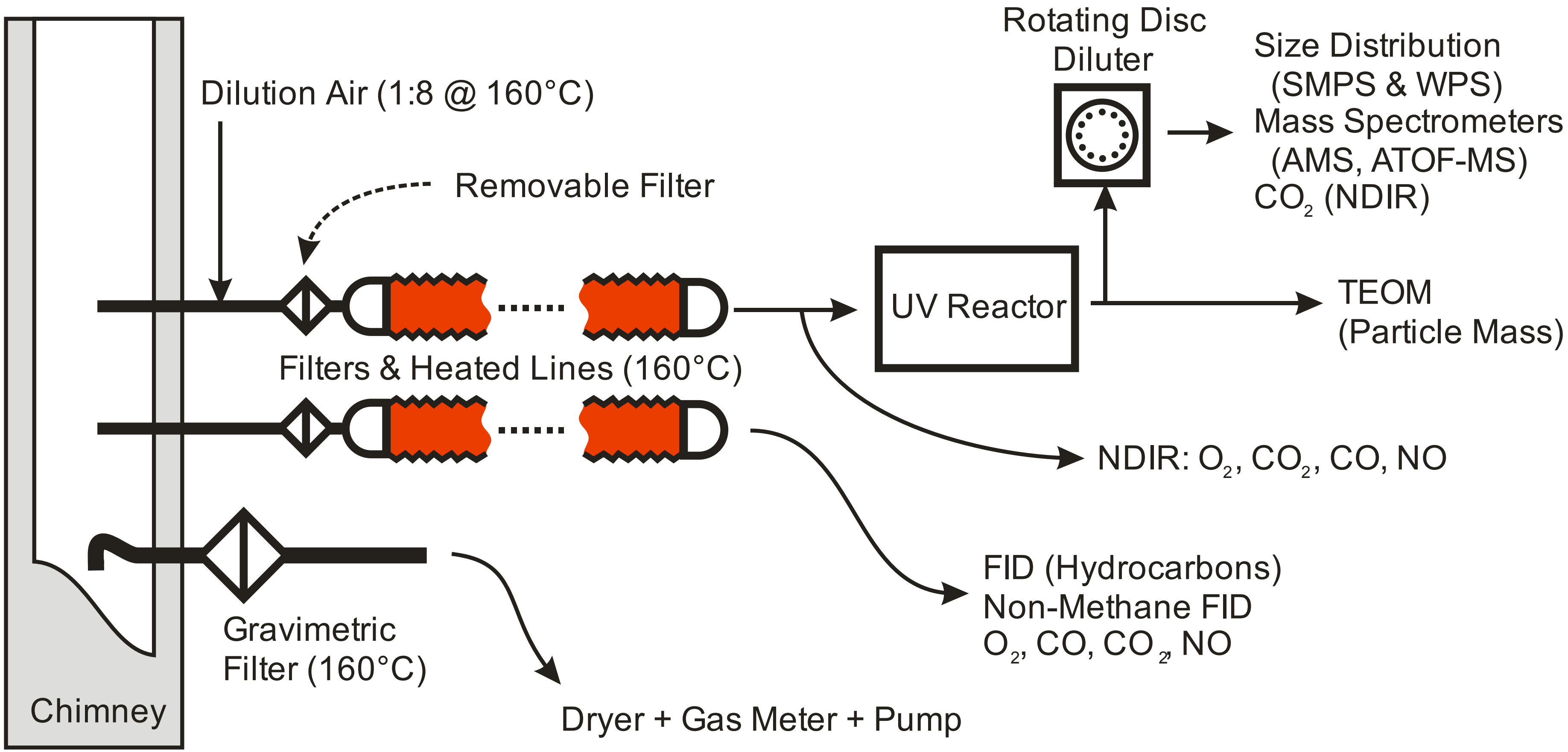
Light: UVC and UVA
Volume: 3x 76ml
Residence time: ~10 Seconds

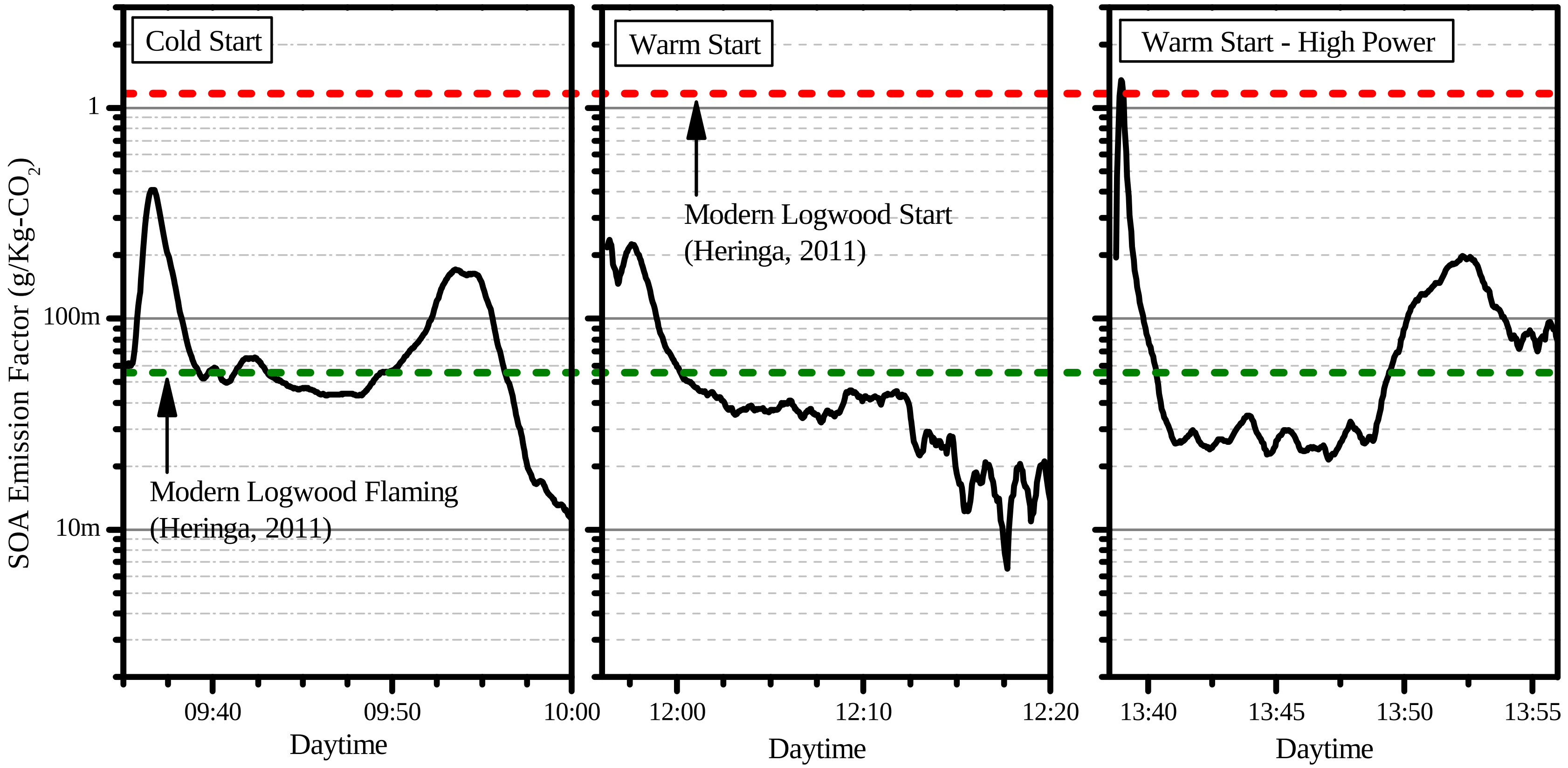
Continuous-Flow UV Reactor Tube

- Three stages: UVC (20 W mercury lamp), UVA (30 W high pressure halogen lamp) and Condensation.
- Each stage consists of a 76ml quartz tube.
- Total residence time in the reactor ~13 seconds.

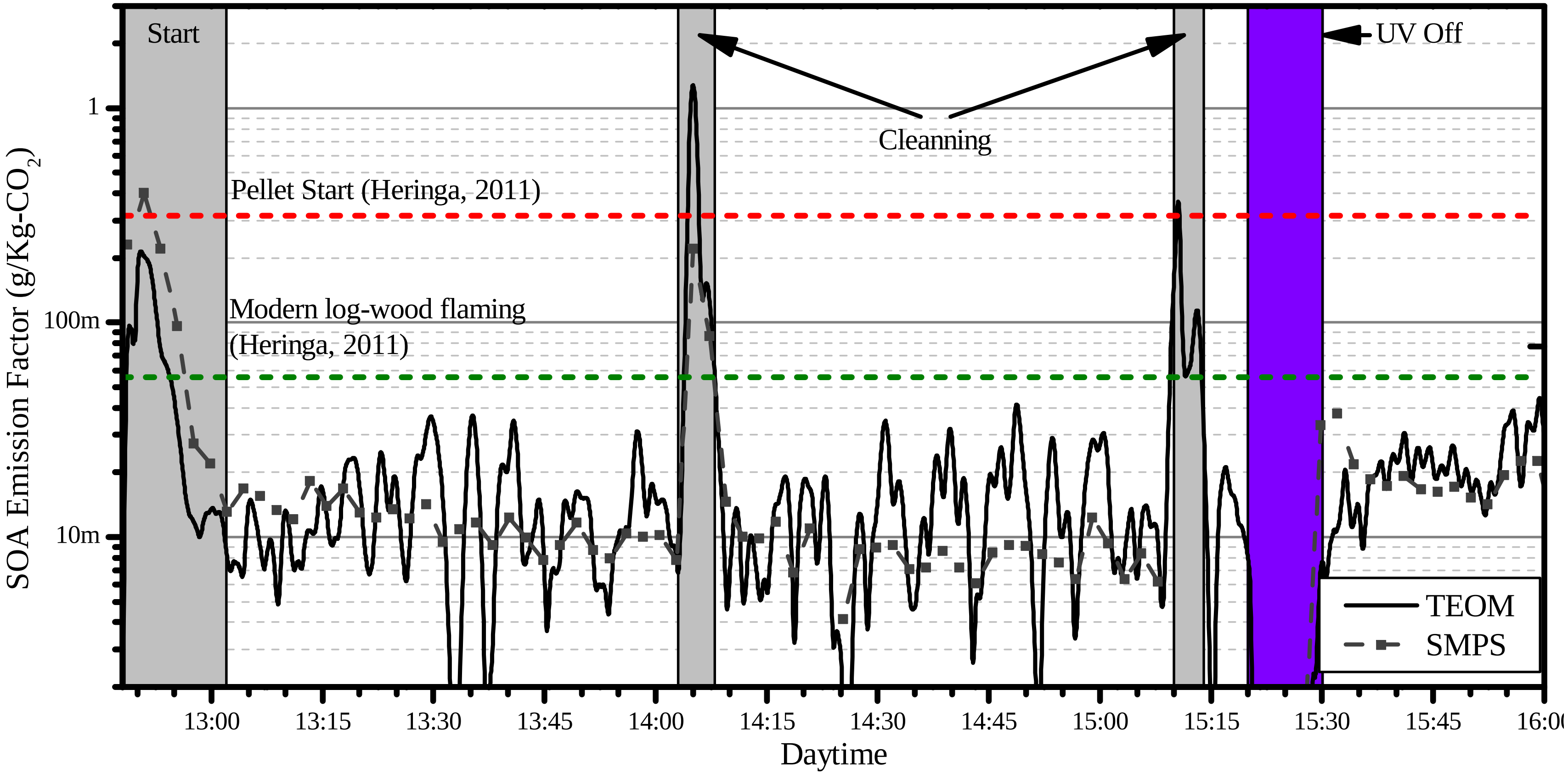


Emission Measurements (on-line data)





Example 1: Pure SOA (filtered emissions), Log-Wood Cooking Stove (Keller & Burtscher, 2012, Aerosol Sci. 49 pp. 9-20)

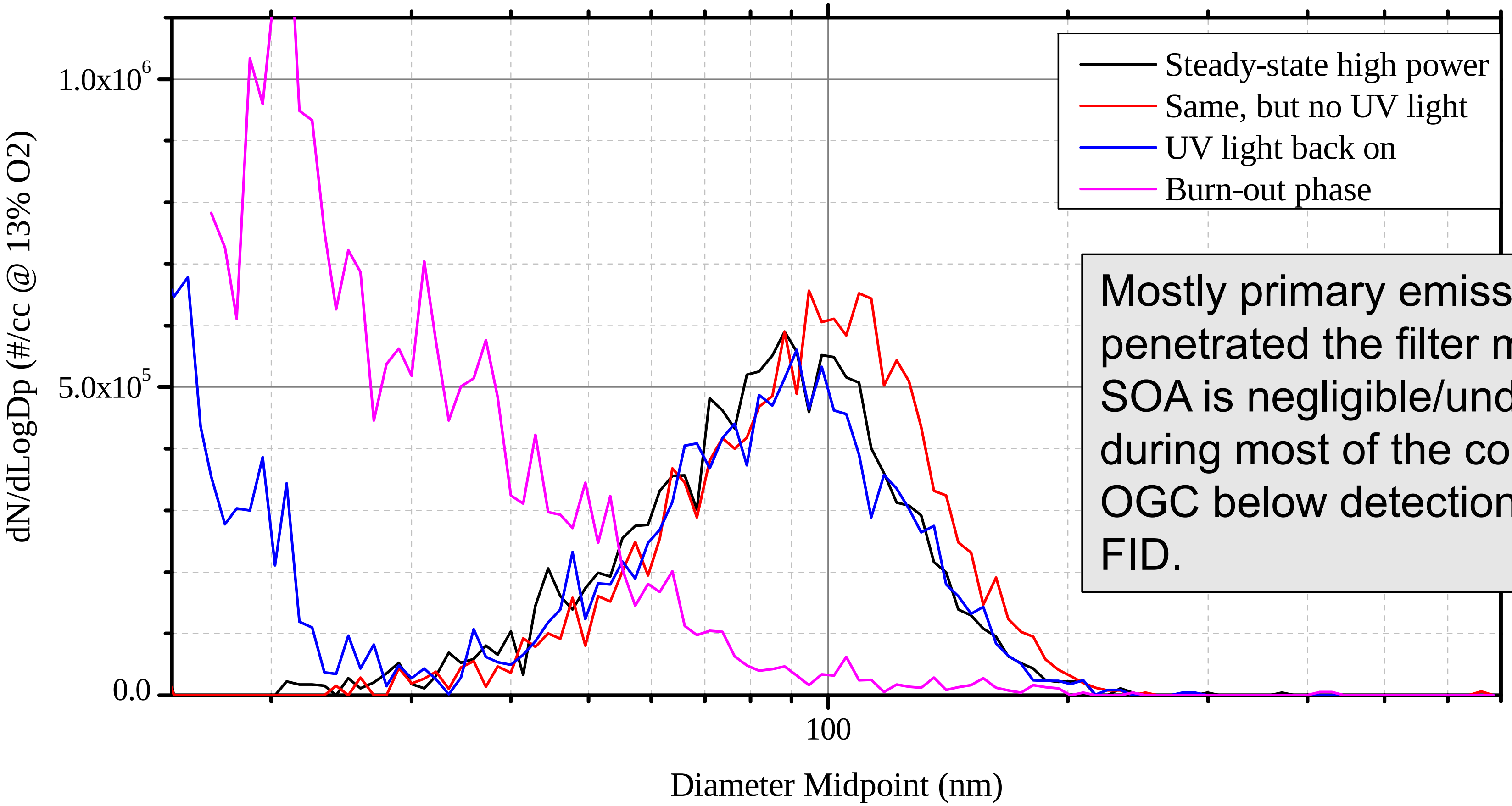


Example 1: Pure SOA (filtered emissions), Pellet Stove (Keller & Burtscher, 2012, Aerosol Sci. 49 pp. 9-20)

Is there a limit?

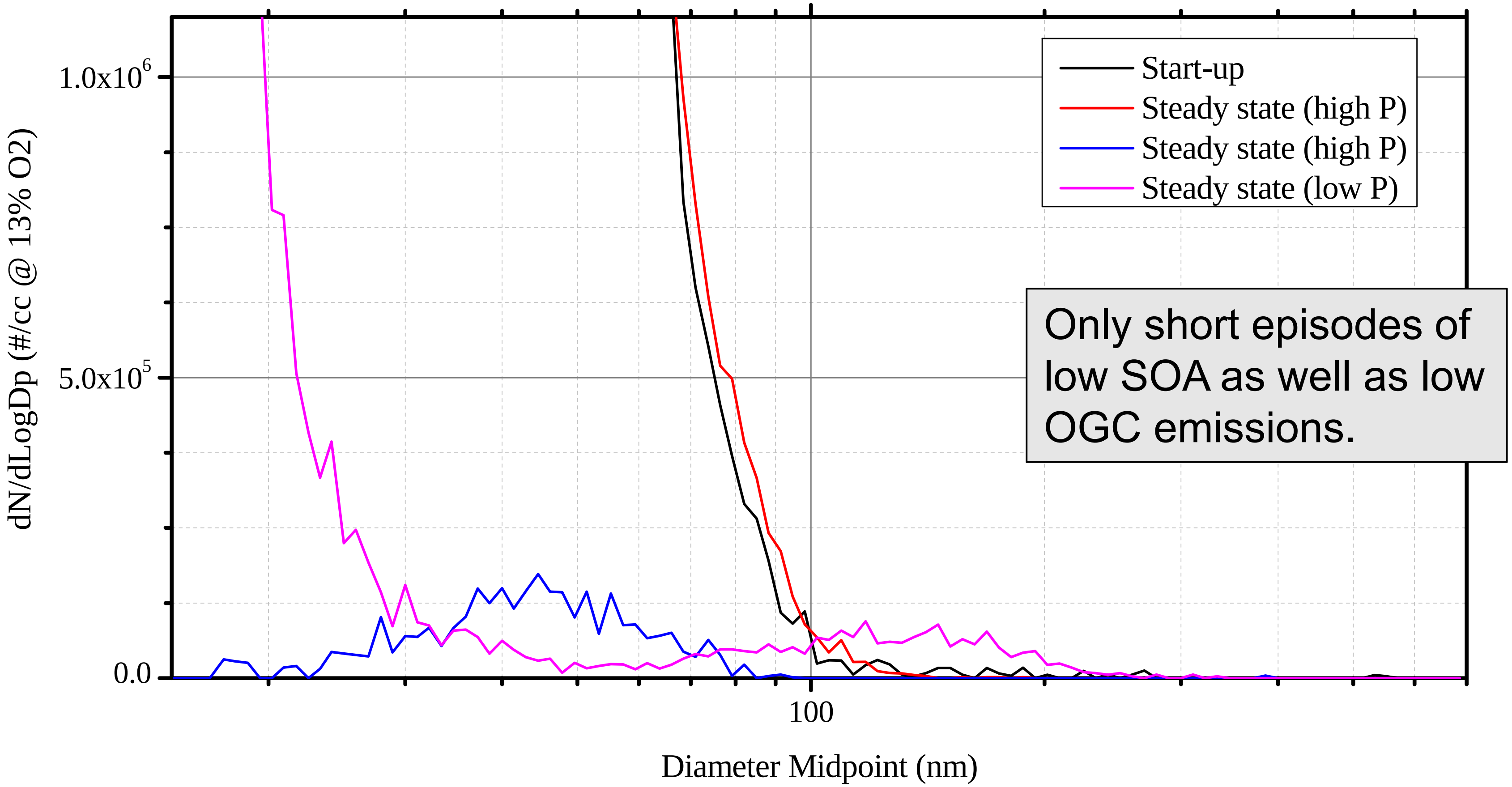
- We can measure SOA formation from low emitting sources. However, even pellet stoves emit several ppm of OGC. What happens when we take an even better combustion?
- Can we detect SOA formation from OGC concentrations in the sub-ppm range? (Traditional smog-chambers use the sub-ppm range for model experiments like, e.g., studies with a single precursor molecule)

Auto. Woodchip Boiler (in field, 250 kW)



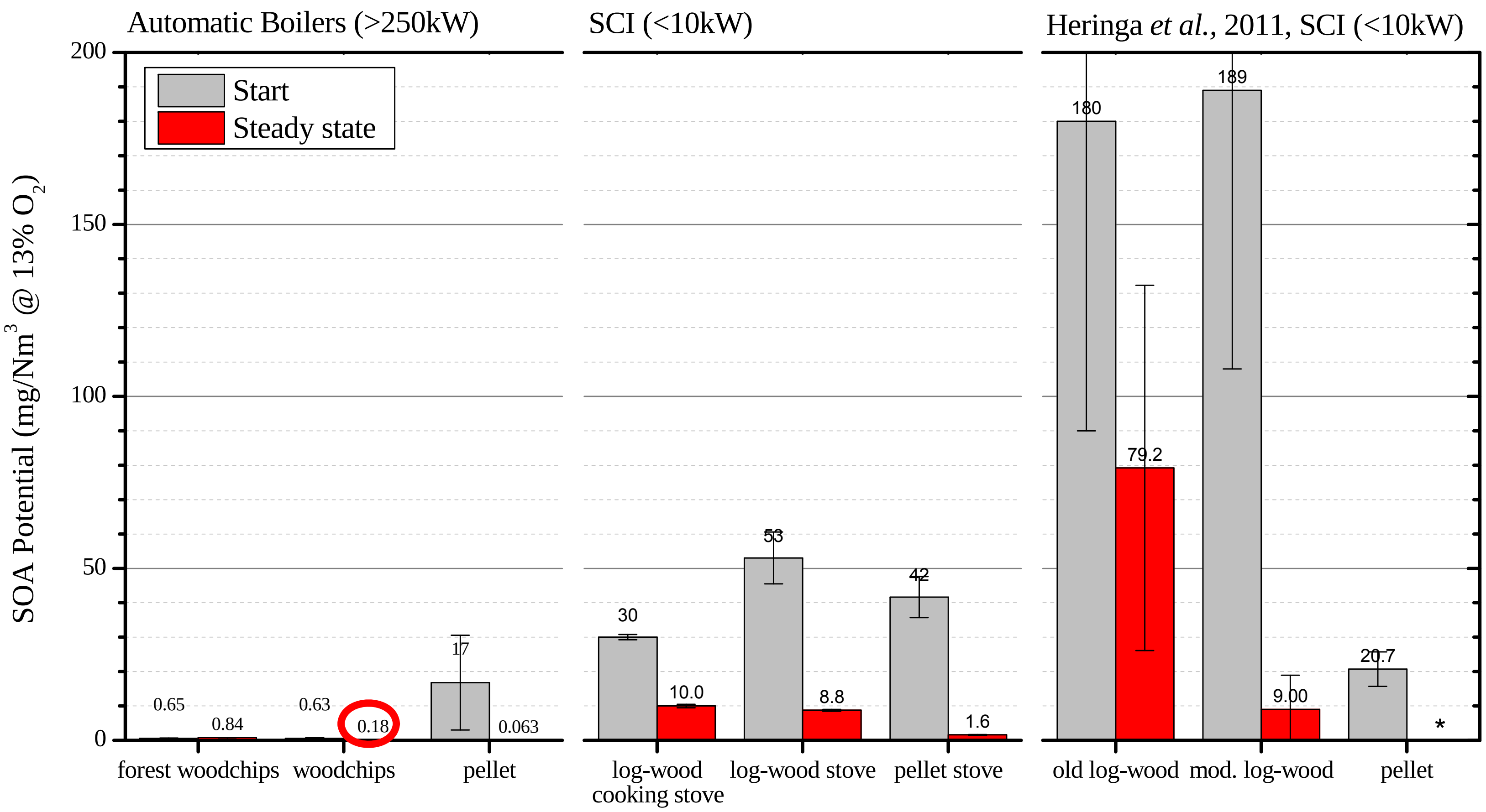
Mostly primary emissions that penetrated the filter material. SOA is negligible/undetectable during most of the combustion. OGC below detection limit of FID.

Auto. Pellet Boiler (in field, 300 kW)

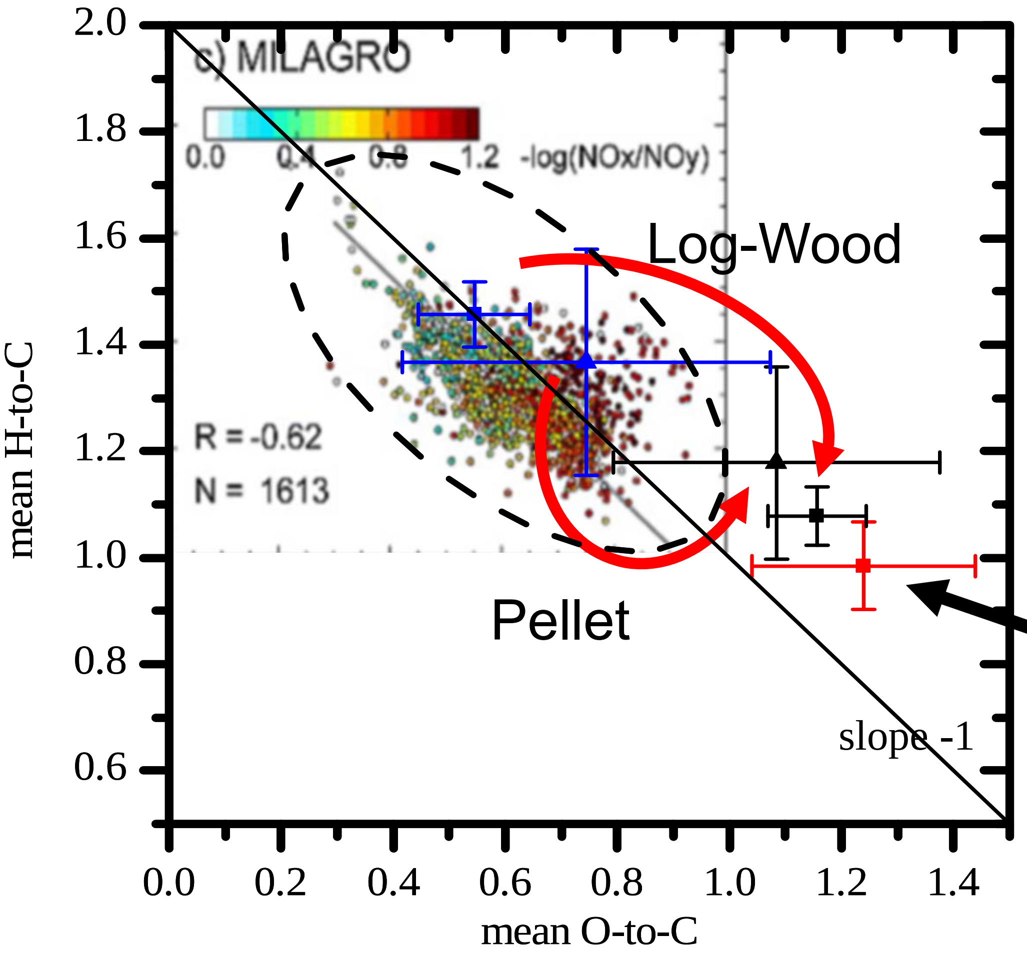


Only short episodes of low SOA as well as low OGC emissions.

SOA production potential for different appliances



Chemical composition (Aerosol Mass Spectrometer, AMS) of filtered and unfiltered emissions



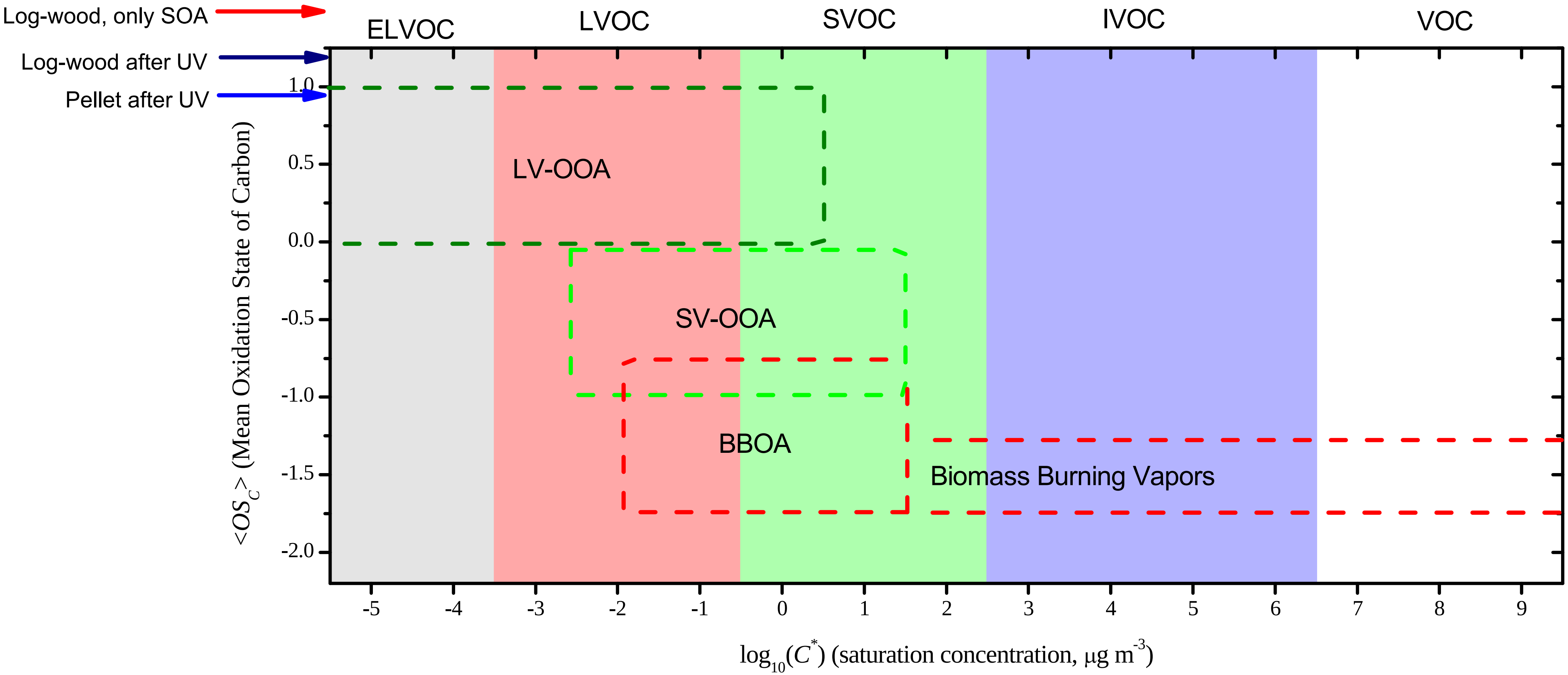
Detailed results will be presented on September by Corbin *et al.* at the EAC 2013 in Prag.

Only SOA (Log-Wood)

Milagro data: Heald et al., GRL, 37, L08803, 2010

Is our oxidation degree too high?

Oxidation State of Carbon= 2 O:C – H:C ; e.g. CH4 → -4, Graphite → 0, CO2 → 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

Summary

- A continuous-flow reactor with a short residence time is a viable alternative for on-line evaluation of the SOA production potential. The UV conditioning can be done on filtered as well as unfiltered emissions. Most of our work has been done with filtered emissions.
- Well design and **well operated** residential stoves (9 kw) have a SOA production potential comparable to primary PM emission limits (type approval). Automatic pellet stoves can achieve a very low SOA production potential during steady state operation.
- Medium-size (250 kw) state-of-the-art automatic-boilers can achieve OGC emissions factors below the detection limit of an FID. The contribution of SOA to the total PM emissions for these boilers is negligible. These sources present a challenge for our measurement setup. Primary particles that penetrate the filter cause a positive artifact.
- When using our reactor, the resulting SOA (or the combination of aged POA and SOA) is more oxidized than the typical ambient aerosol or the SOA from smog-chamber experiments.
- A high oxidation state of carbon is associated with heavily aged SOA (LV-OOA), and corresponds to organic species with low or extremely-low volatility. Thus the UV treatment promotes an efficient nucleation/condensation of OC. However, extreme oxidation could also transform some hydrocarbon into CO or CO_2.

Thanks to:

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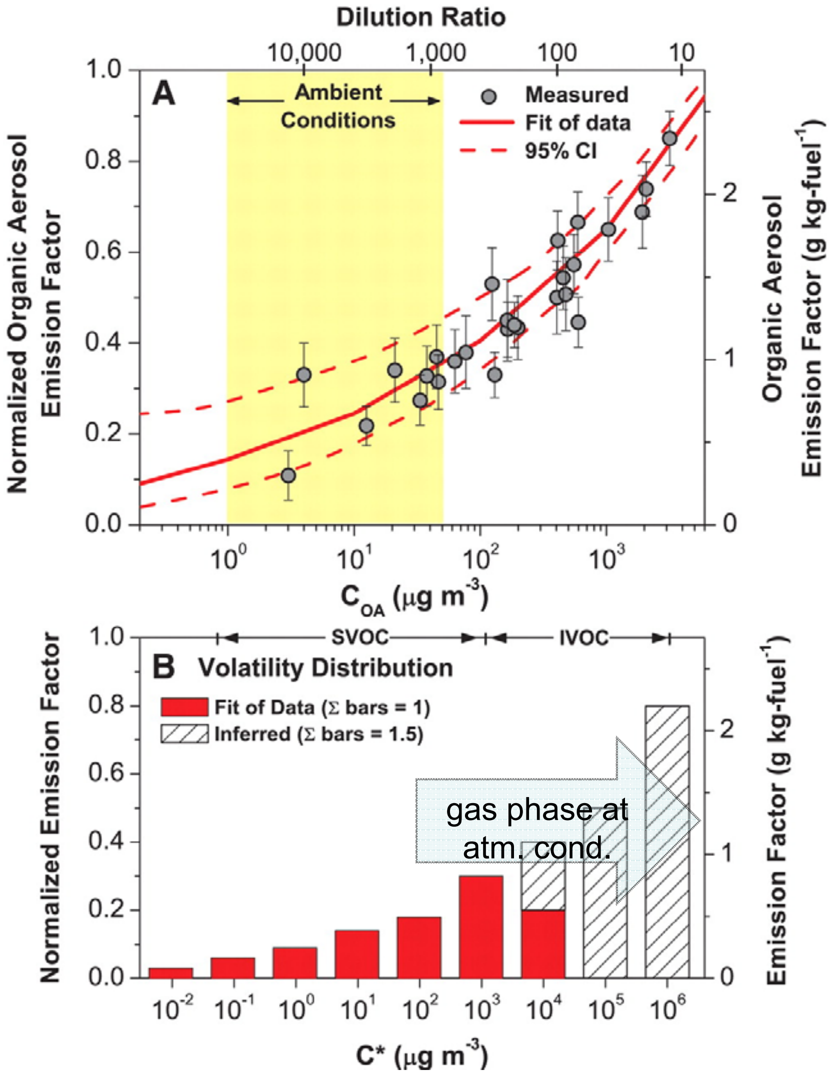
Can UV conditioning Solve the problem of condensables?



(ambient) saturation concentration

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

- Semivolatile species evaporate with atmospheric dilution, creating substantial amounts of low-volatility gas-phase material.
- Laboratory experiments show that photo-oxidation of diesel (as well as wood burning) emissions rapidly generates organic aerosol. (i.e. even in the atmosphere, low- and intermediate-volatility gas-phase species are transformed very fast into SOA)
- Wood Burning SOA: Grieshop et al. 2009, doi:10.5194/acp-9-1263-2009