

# On-line measurement of secondary organic aerosol from wood burning using a continuous flow photo-oxidation reactor

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## Introduction

Wood-burning emissions, especially emissions from small combustion installations (SCI), contribute largely to the environmental particulate matter pollution. Current SCI legislation considers only the control of particulate matter (PM) and carbon monoxide. These parameters are relevant, but they give an incomplete picture of the contribution of wood burning to ambient aerosols as well as of the quality of the combustion. Beside PM and carbon monoxide, wood burning also contributes to the formation of secondary organic aerosols (SOA, Grieshop et al., 2009; Heringa et al., 2011).

SOA particles originate from the photo-oxidation and aging of organic gaseous carbon (OGC). This process takes place in the atmosphere and requires hours or even days to complete, making SOA impossible to measure at the emission point. However, its relevance becomes clear by looking at the organic-carbon-to-elemental-carbon ratio of wood-burning particles, which can be as high as 10 for atmospherically aged particles (see e.g. Szidat, 2007) but is typically lower than 1 for freshly-emitted material. Furthermore, it has been shown that organic material significantly contributes to the toxicity of wood-burning PM (Klippel et al. 2006).

Future legislation should account for OGC emissions and, ideally, regulate them based on their SOA production potential. However, there is currently no standard tool for this. Smog-chamber experiments (e.g. Paulsen et al., 2005), for instance, are a valuable tool for studying SOA formation or other atmospheric processes. But their size, complexity and high cost make them far from ideal for emission monitoring or type-approval testing.

In this work, we present a simple continuous-flow tube reactor that can be used as a conditioning system to oxidize OGC and form SOA. The idea behind our reactor is not to predict the actual atmospheric contribution to SOA from a single appliance, which depends among other things on the actual atmospheric conditions. Rather, the reactor is intended as a standard and reproducible method for comparing the emissions from wood-burning devices while taking the SOA-formation potential into account.

## Continuous flow photo-oxidation reactor

The continuous-flow tube reactor as described in detail by Keller et al. (2012) consists of three identical quartz tubes arranged in series. The first two tubes are the photo-oxidation chambers, where the sample is exposed to high intensity UV light. In our standard configuration, the sample is first exposed to 20 W of UVC light from five low pressure mercury lamps (254 nm and 185 nm emission lines) and then, on the second tube, to 30 W of UVA from a high pressure halogen lamp. The third tube is held at room temperature and is used as a condensation/nucleation stage. The volume of the tubes is very small, only 76ml each, and the residence time in each of them is of the order of a few seconds (1 to 5 seconds depending on the selected sample flow).

## Results and discussion

So far, we have evaluated our reactor using three different types of experiments:

1. First, a setup to test the reactor using model hydrocarbons was used. This setup demonstrated that the OGC can be transformed into SOA at a much faster rate than in the atmosphere or in a smog chamber experiment. Using our short residence time, we were able to oxidize relatively high concentrations of OGC (up to hundreds of ppm) in our reactor and form SOA. The upper limit for the OGC concentration is defined by the intensity of the UV light as well as by the residence time in the oxidation stages. The limit can thus be extended by increasing any of these two parameters.
2. A series of experiments using undiluted emissions from residential combustion appliances (a pellet stove and a logwood cooking stove, both with 9kW of heating power). Here, the sample was extracted from the chimney using a probe with ceramic particle filter and a sampling line, all heated to 160°C. The undiluted sample was first exposed in the reactor and diluted afterwards in order to reach adequate levels for our aerosol measurements devices. With these experiments, we were able to obtain a time resolved picture of the SOA emission for these devices at several operating conditions. Our results, expressed as a ratio between SOA production and emitted CO<sub>2</sub>, closely match the results from smog-chamber experiments with a residence time of 5h (Heringa et al., 2011). For the pellet stove, we observed SOA production at levels 5 times lower than the lowest detectable value reported by Heringa et al. (2011), which corresponds to the SOA from the stable phase of a modern logwood stove. Additionally, we did not find any correlation between the emissions of CO or OGC and SOA produced by our reactor.
3. The final set of experiments was done in slightly diluted (1:8) emission from residential combustion appliances (a logwood stove and a pellet stove, both 9kW of heating power). The goal of these experiments was to determine if the change on dilution would affect the production of SOA. This is not a trivial question since a change in the vapor pressure could affect the nucleation and condensation of the oxidized gaseous species. Additionally, we added several measurement devices to these experiments, among them a non-methane FID, two mass spectrometers (an Aerosol Mass Spectrometer, AMS, from Aerodyne Research Inc., and an Aerosol Time-Of-Flight Mass Spectrometer, ATOFMS, from TSI Inc., USA), and a gravimetric sampling system. This setup was used with filtered- as well as unfiltered-emissions to understand the contribution of SOA to the total PM emission factor. Finally, the mass spectrometers will deliver important information about the chemistry of the SOA as well as of the primary PM.

While setups 1 and 2 have already been described in detail under Keller et al. (2012), setup 3 is presented here for the first time. Once again, we were able to obtain a time resolve picture of the SOA production. Figure 1, for instance, shows the emission of SOA for a specific operating point of a logwood stove compared to the emission factor of other relevant pollutants. The dilution of the sample does not seem to have an influence on the production of SOA when expressed in terms of the emitted CO<sub>2</sub>.

We also confirmed the results found using setup 2: SOA does not seem to correlate with the primary PM, CO, OGC or non-methane OGC. The production of SOA, when compared to the OGC (both total and non-methane) seems to be the lowest during the start phase of the logwood cycle or the start and cleaning phases of the pellet stove. As can be seen in figure 2, the SOA-to-OGC ratio is highly variable even at the constant conditions of the pellet stove.

Finally, our preliminary results from the AMS suggest that, for this particular modern logwood stove, the SOA results in a 40% to 60% increase of the total organic mass of the PM emissions. However, when including a single batch of logwood that did not burn under optimum conditions, the average increase of organic mass can be a factor 5 or more. The bad combustion was not achieved on purpose; it was part of the variability of the standard test procedure.

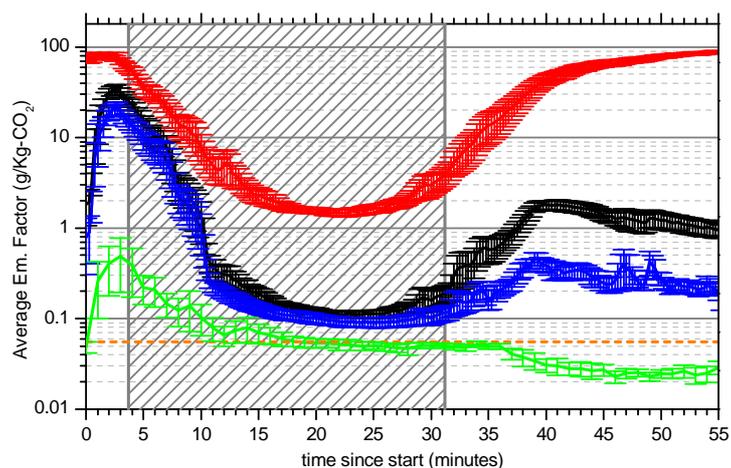


Figure 1 Average emission factor for CO (red), OGC (black), non-methane OGC (blue), and SOA (green) for the warm start cycle of a residential log-wood stove (9kW of heating power). The SOA was produced in our tube reactor using diluted (dilution factor 1:8) and filtered emissions and a sample flow of 1 lpm. The dashed line (orange) shows the SOA formation for the stable phase of a similar stove as calculated using a smog-chamber and a residence time of 5h (Heringa, 2011). The filled area shows the region where the gravimetric sampling for the type-approval test takes place. The error bars represent the standard error.

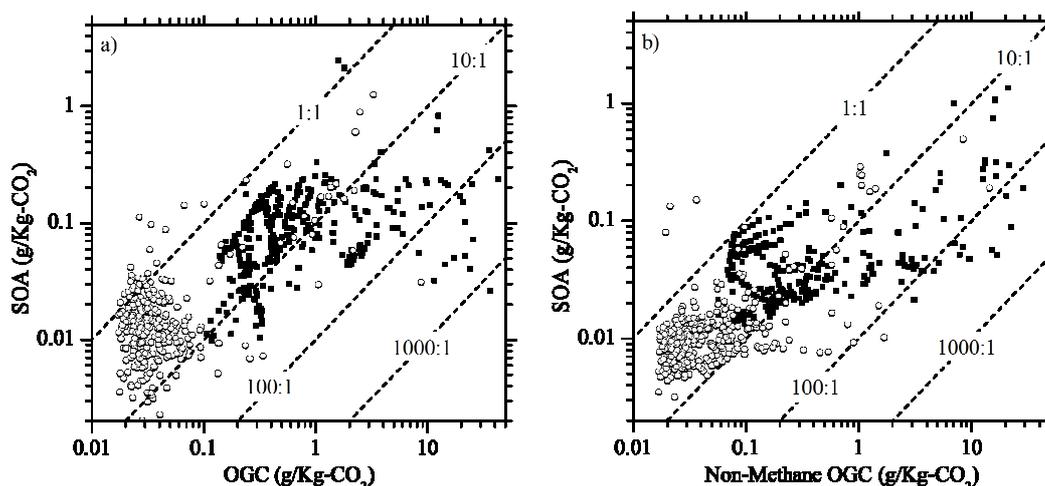


Figure 2 Comparison of the SOA production in terms of the emission of OGC for logwood appliances (black squares) and a pellet stove (open circles) during two different experiments on filtered emissions: a) shows the production of SOA against total OGC when exposing the undiluted emissions to UV light in our reactor tube, whereas b) shows the SOA against the non-methane OGC for diluted emissions (dilution factor 1:8). The pellet stove was operated at 70% of its nominal power on experiment a) and at 100% on b); the logwood stoves were not the same in the two experiments.

## References

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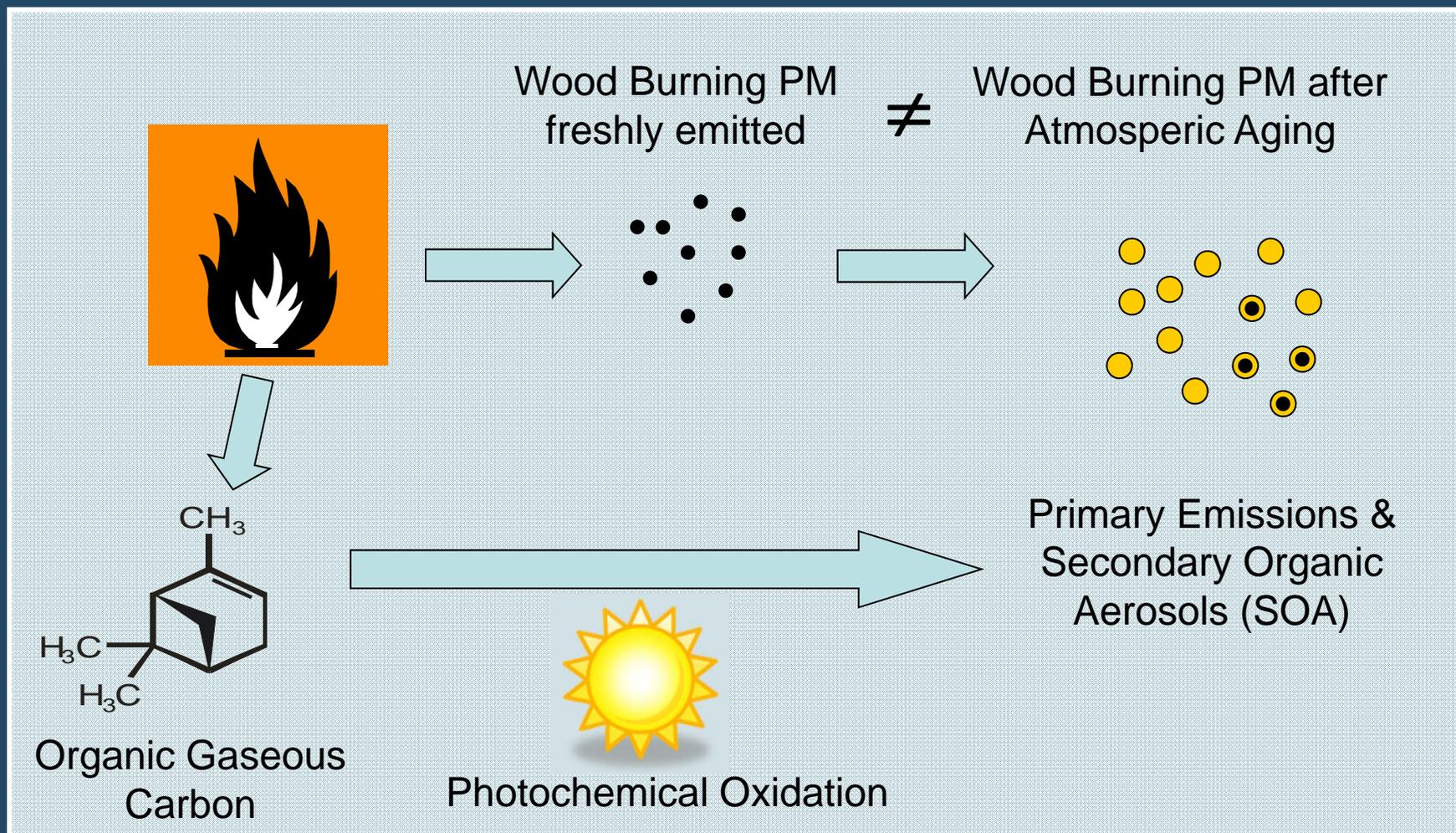
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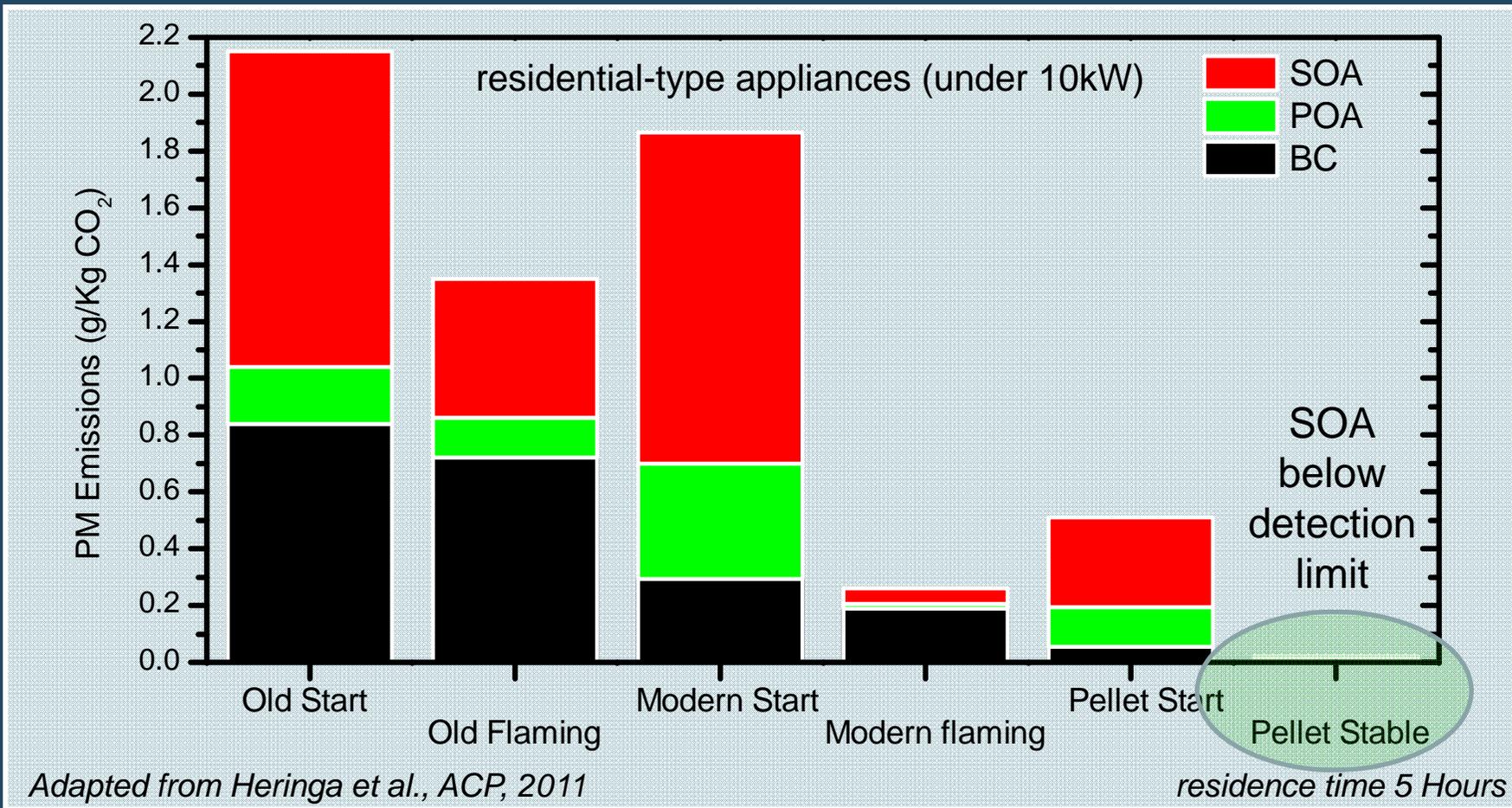
# Primary/Secondary Emissions



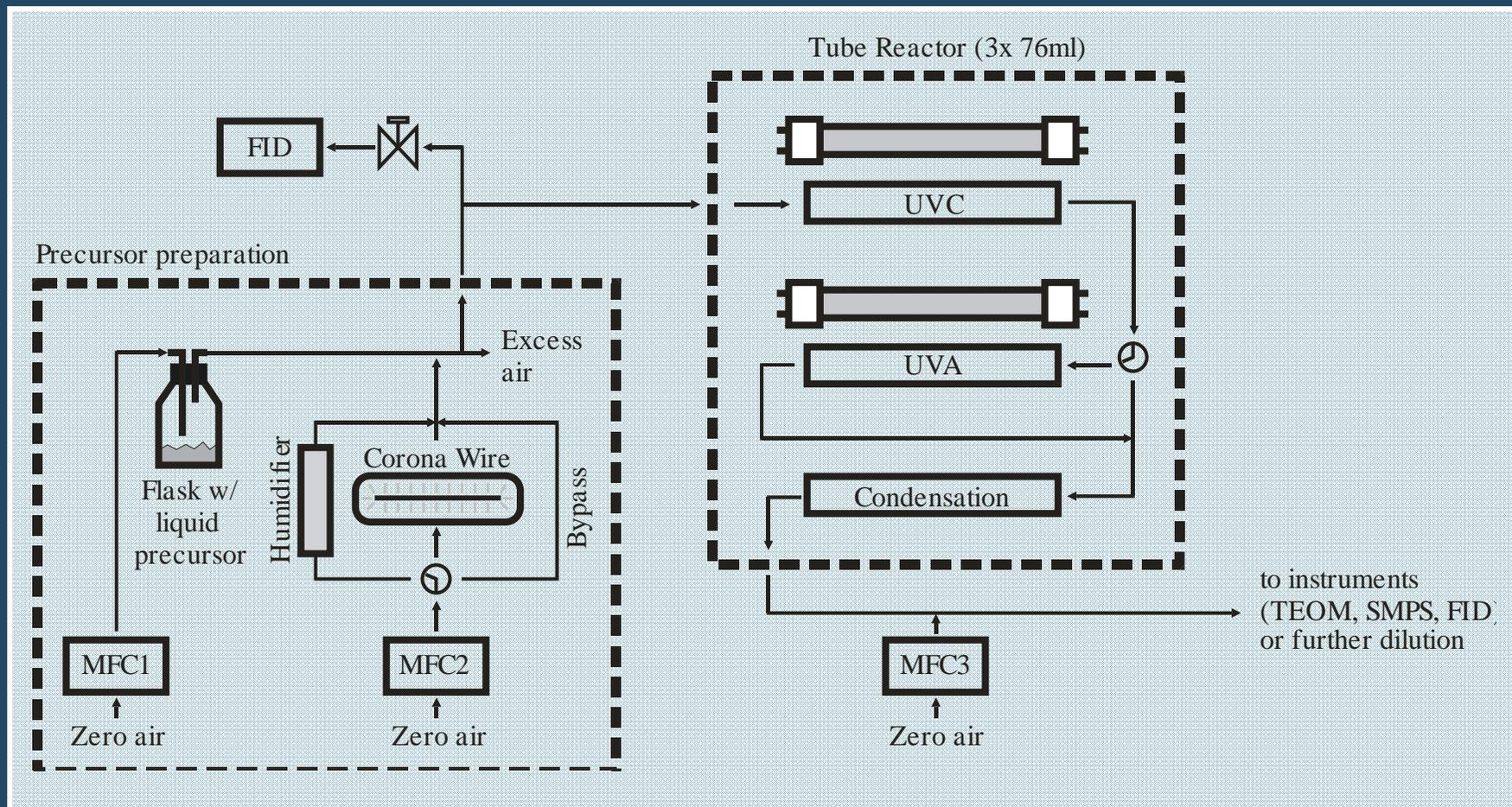
# Motivation

- 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 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. But once 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.

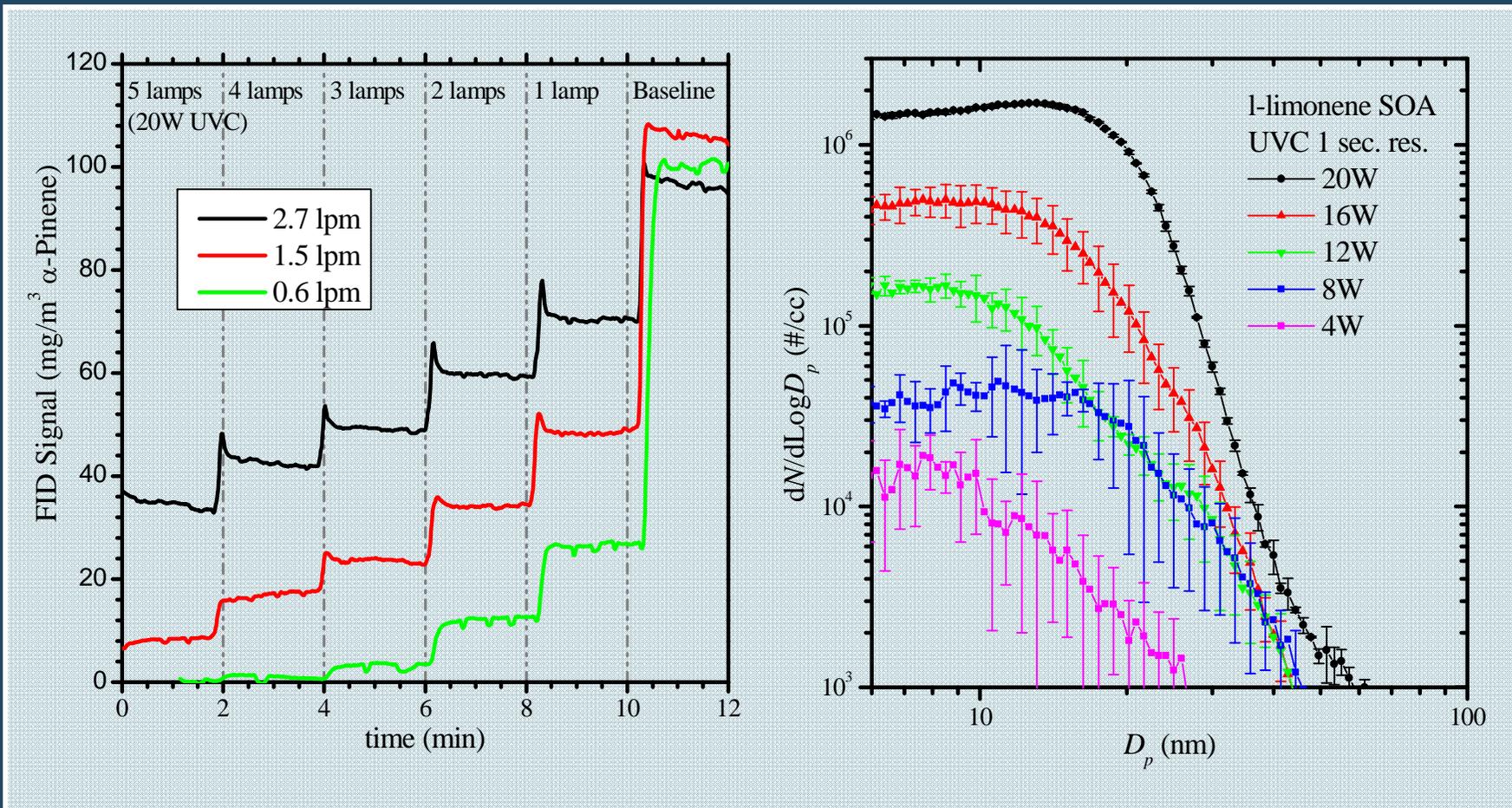
# Wood-Burning Emissions (Smog Chamber)



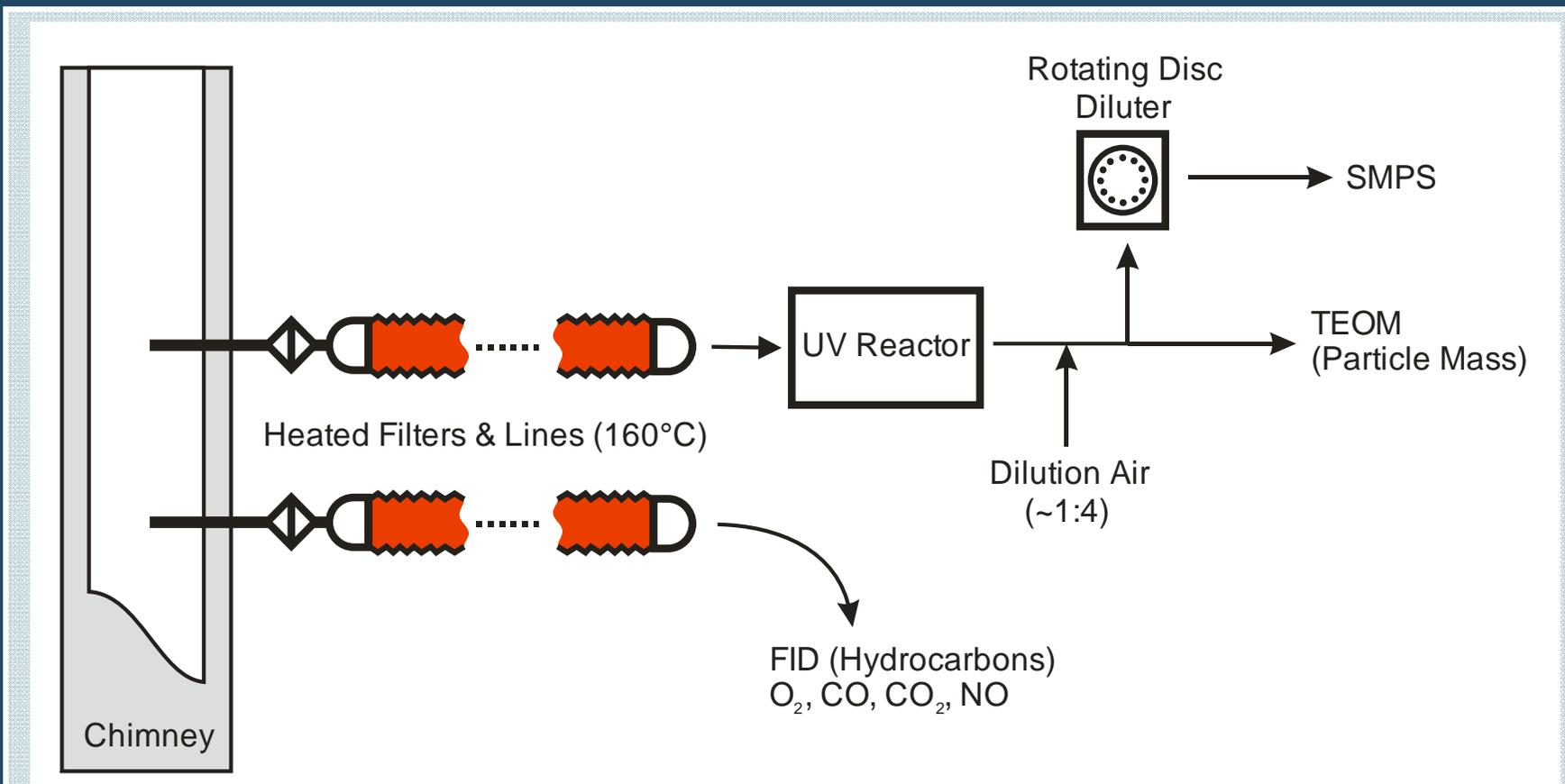
# Setup 1: Model Hydrocarbons



# SOA from Model Hydrocarbons

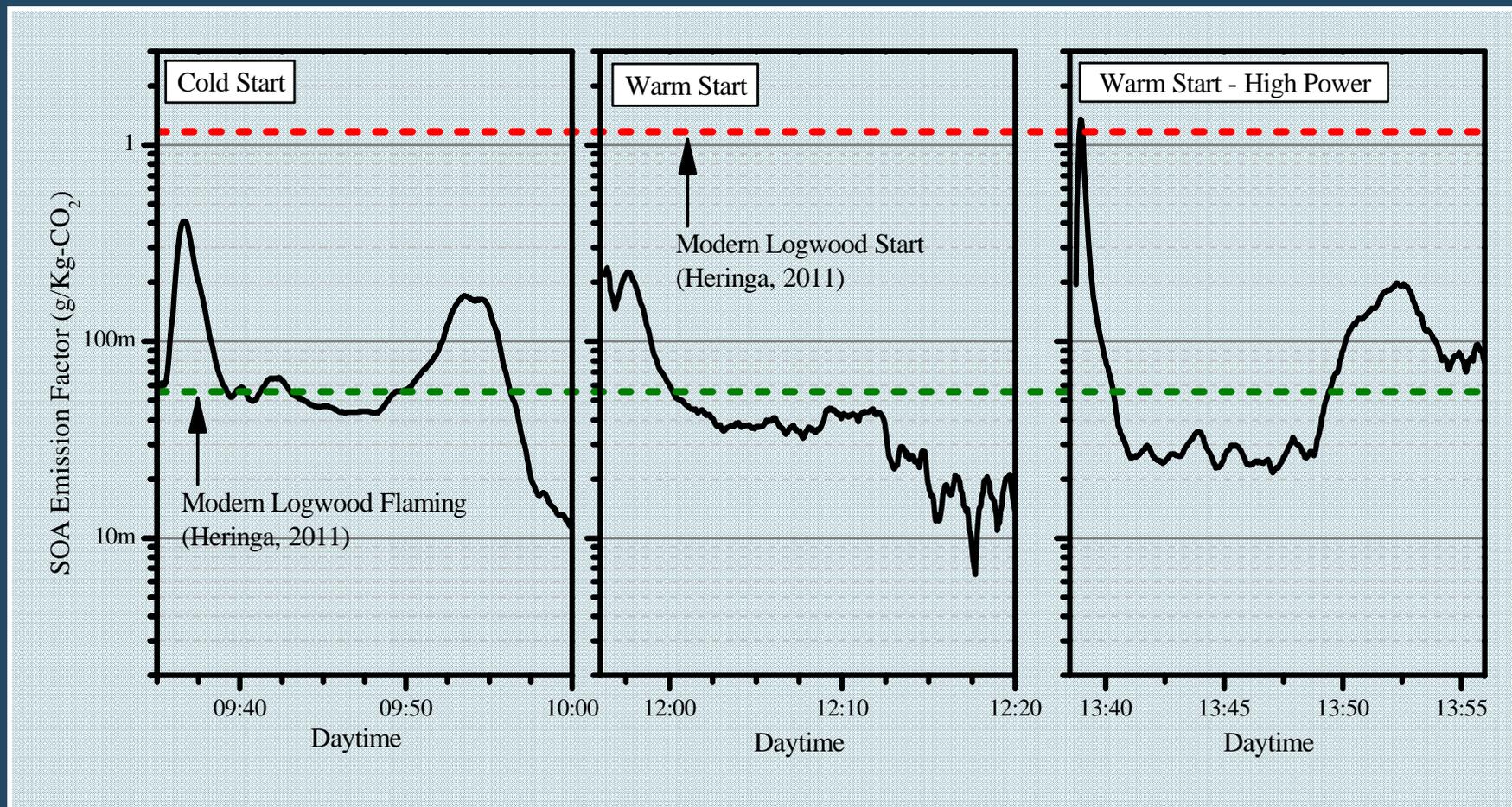


# Setup 2: Emission Measurements

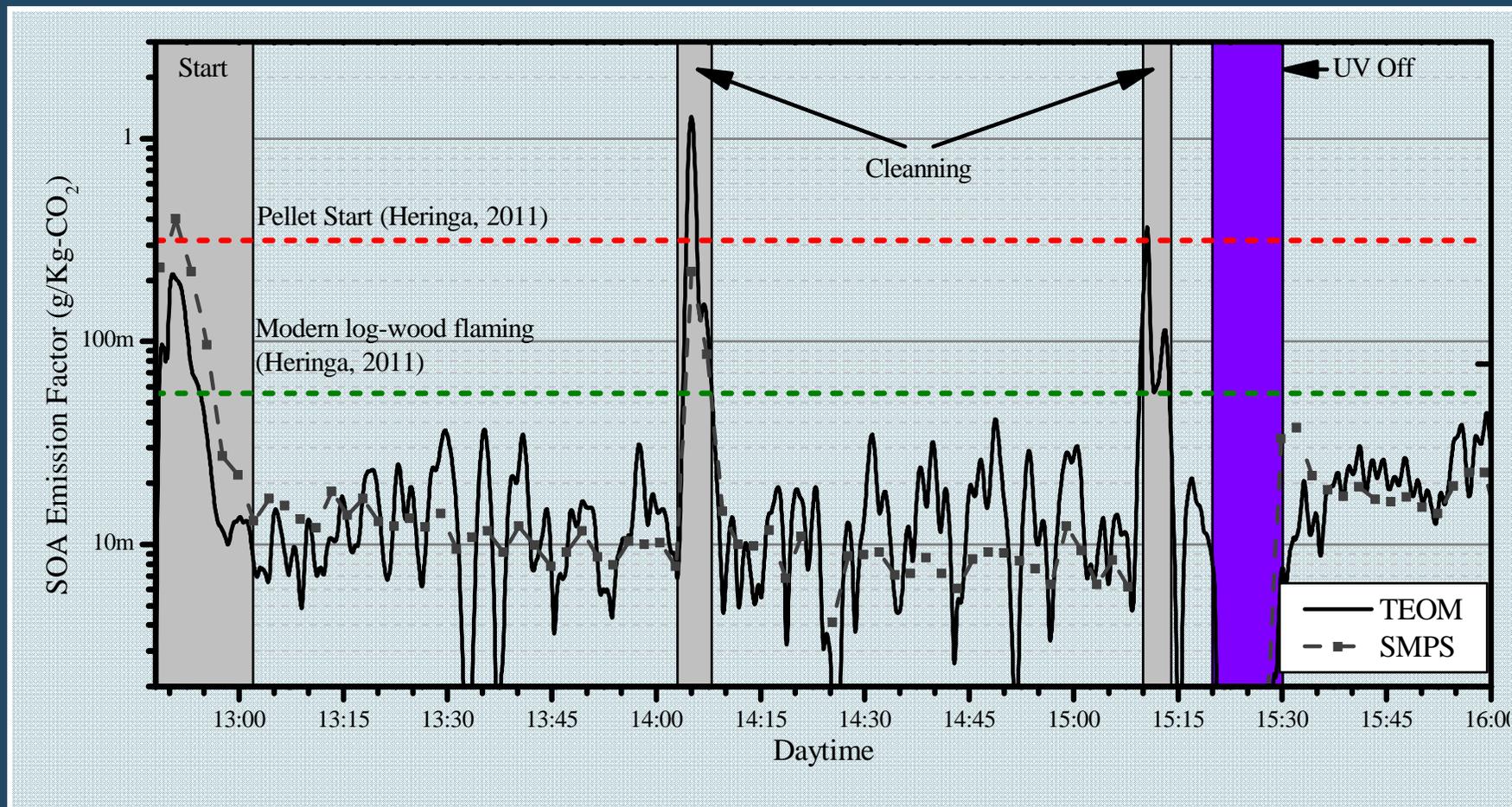


Keller & Burtscher, J. Aerosol Sci. 49, pp 9-20, 2012

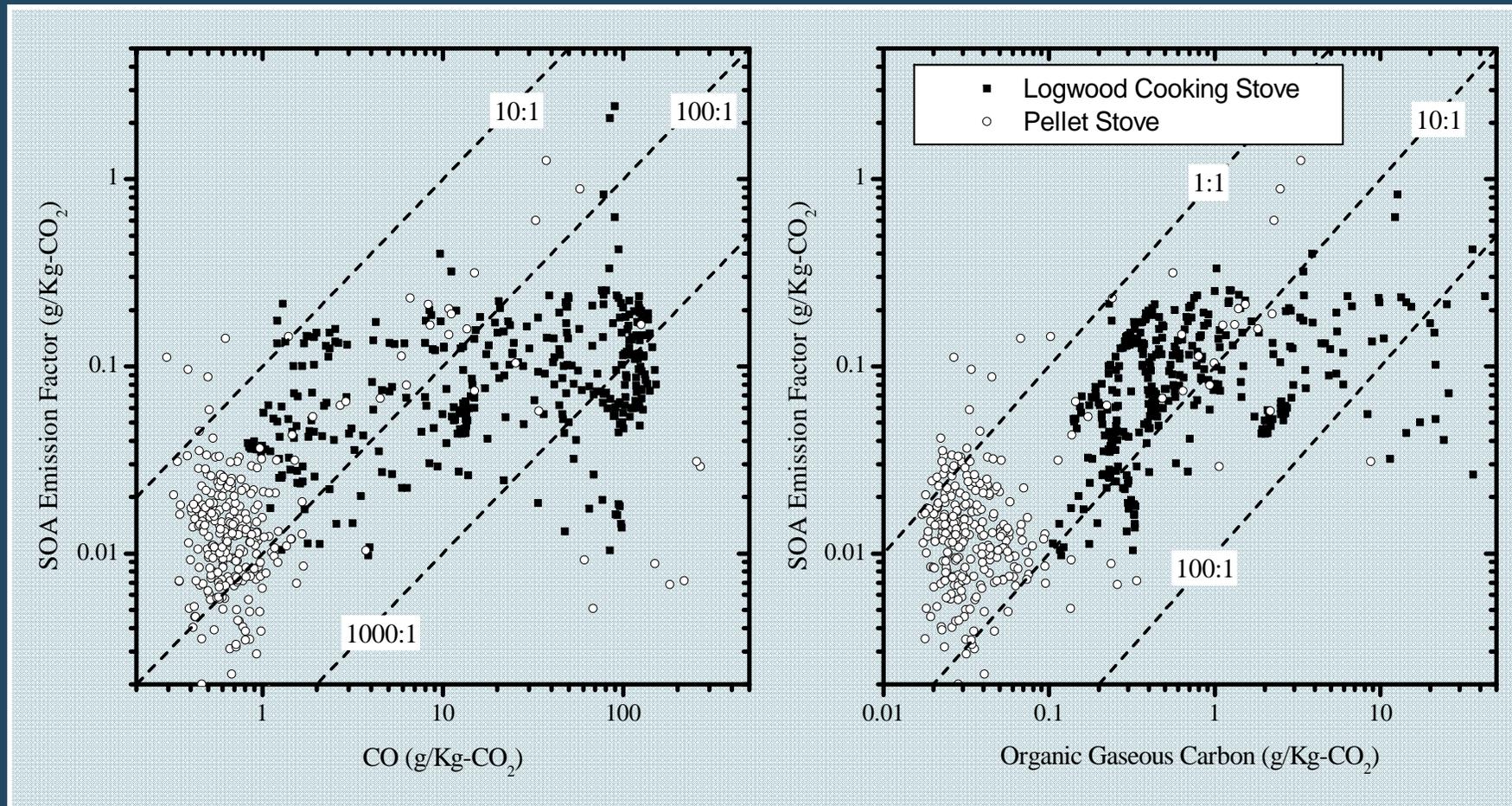
# Example 1: Logwood Cooking Stove



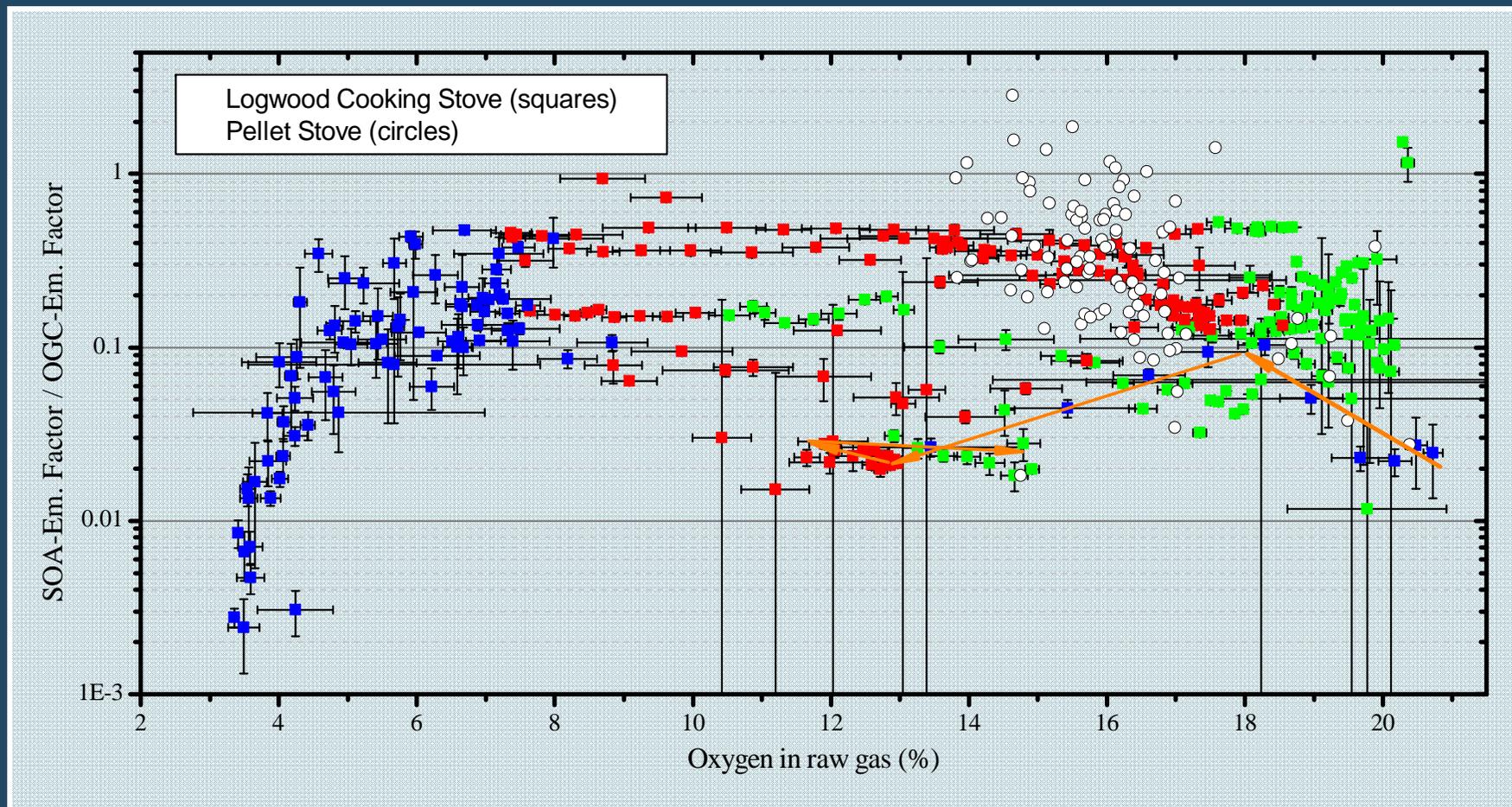
# Example 1: Logwood Cooking Stove



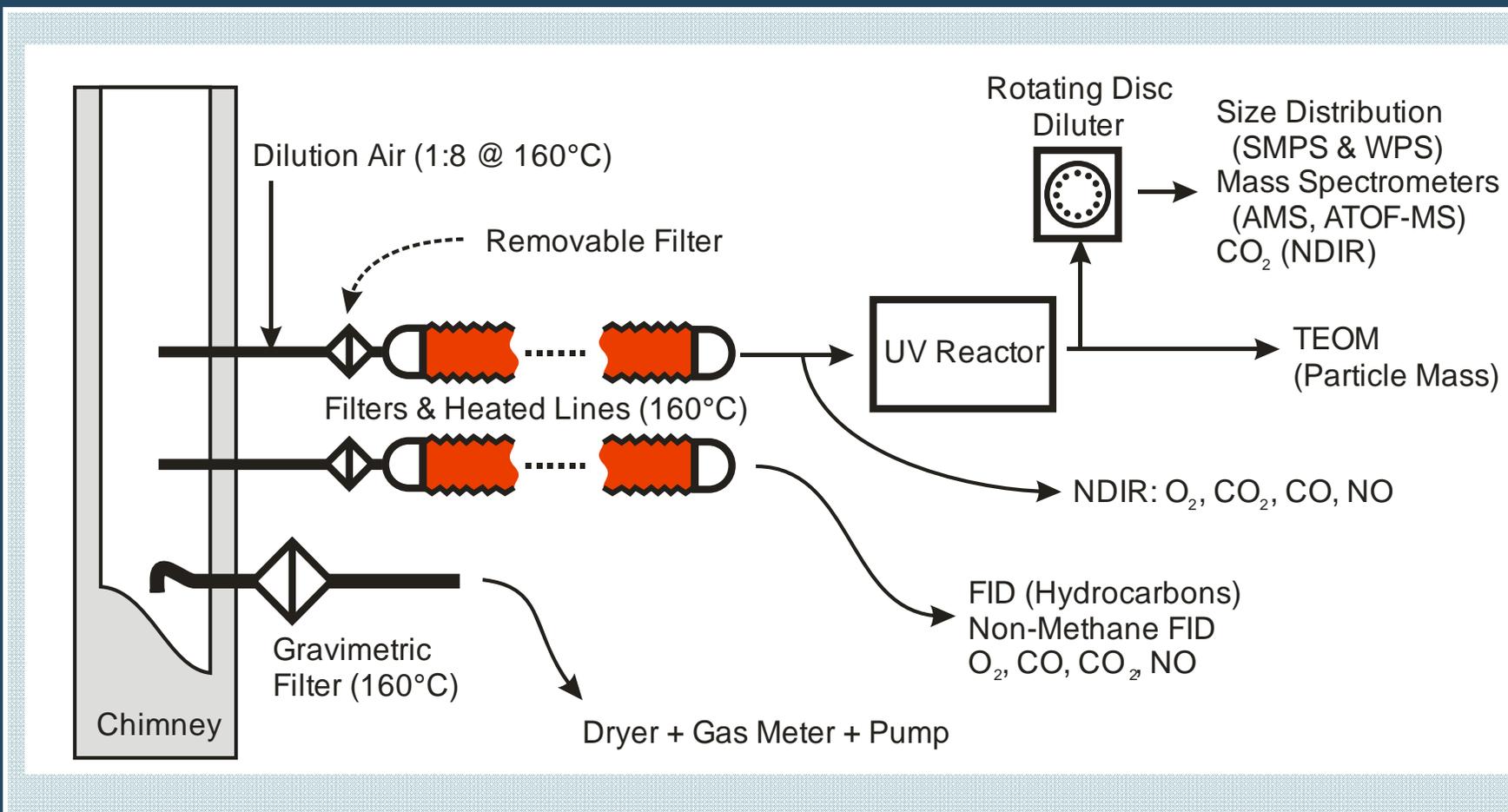
# SOA vs Other Pollutants (Gases)



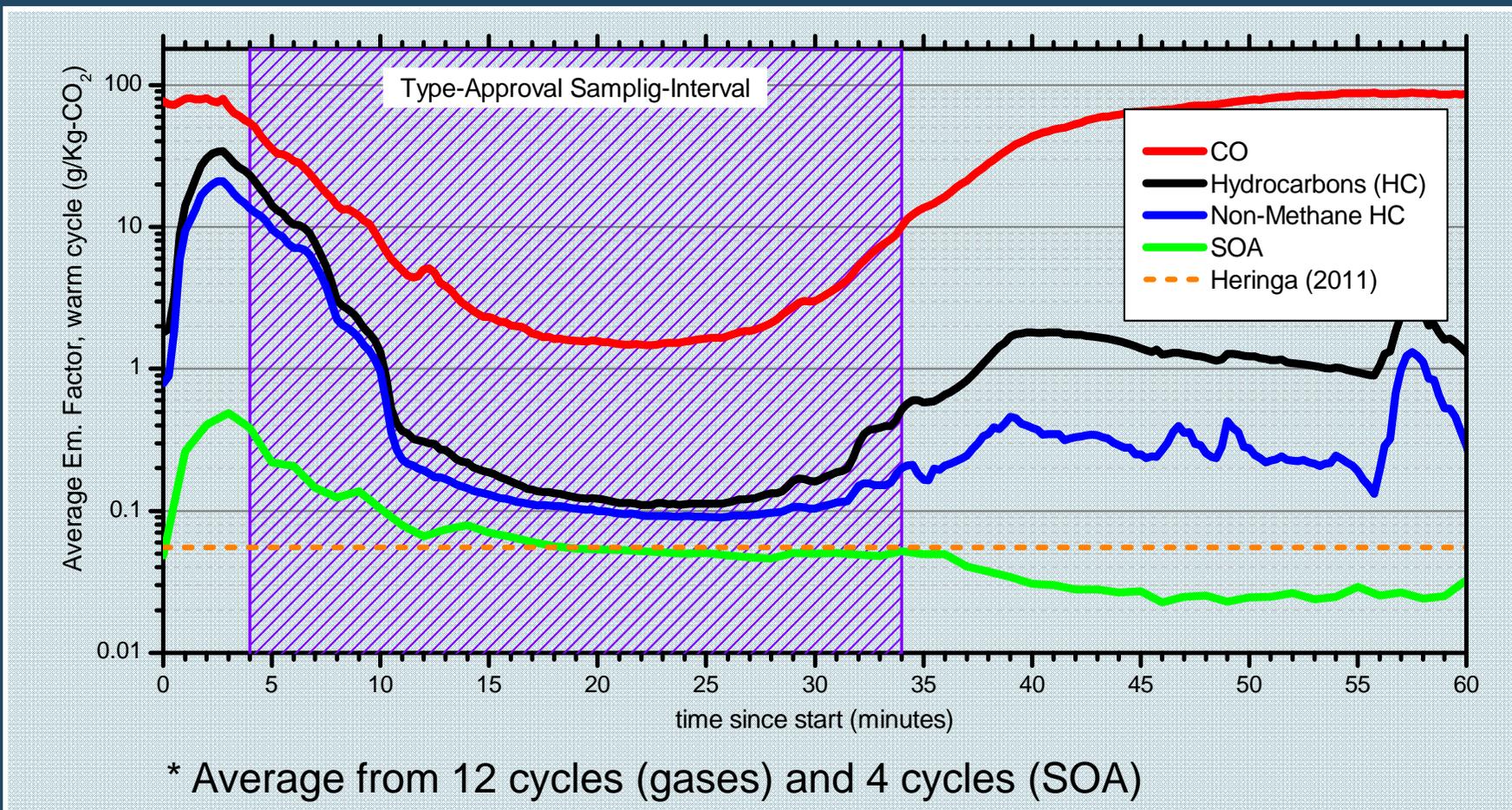
# SOA Yield During Combustion Cycle



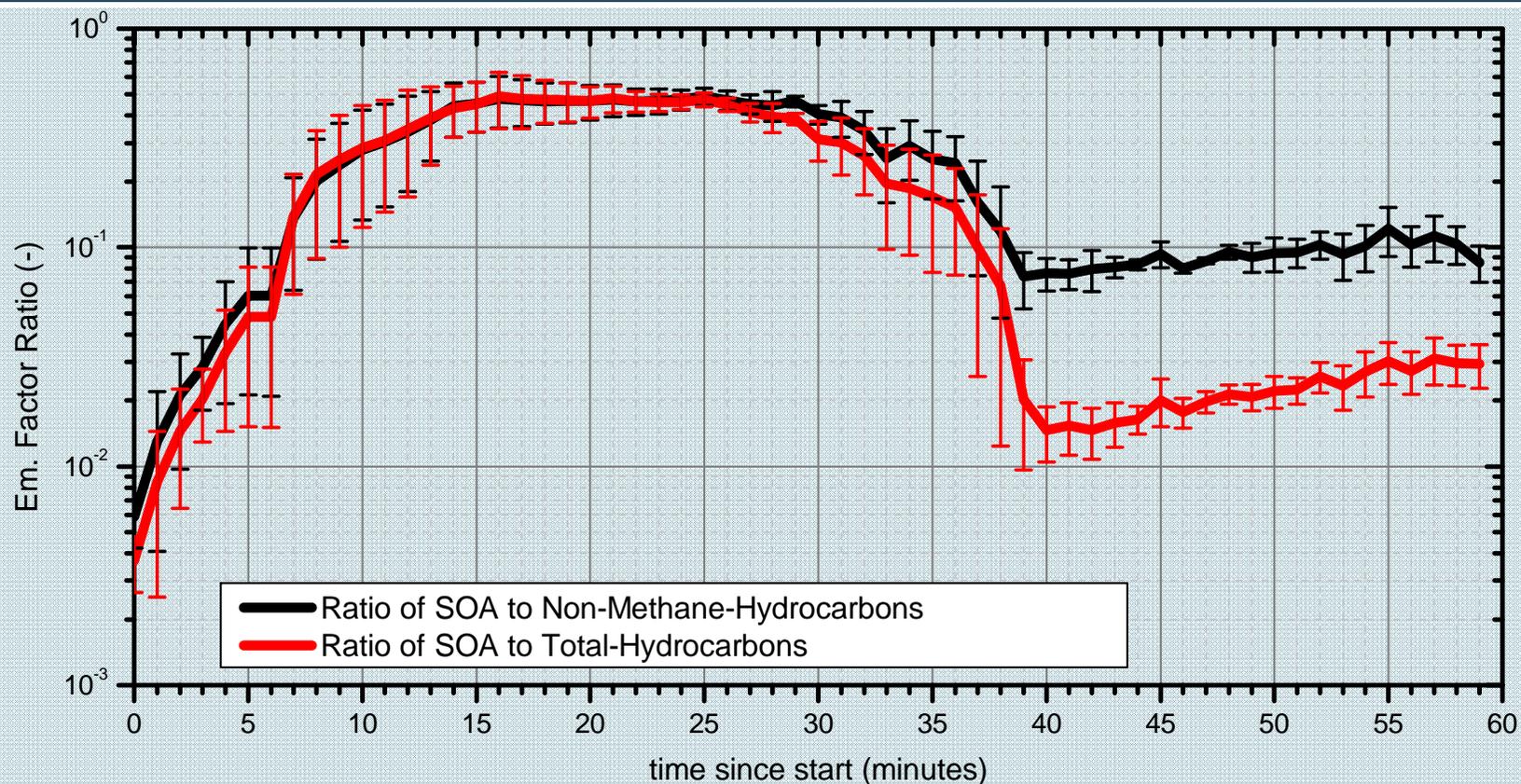
# Setup 3: Modified Em. Measurements



# Warm Cycle, Modern Logwood Stove\*

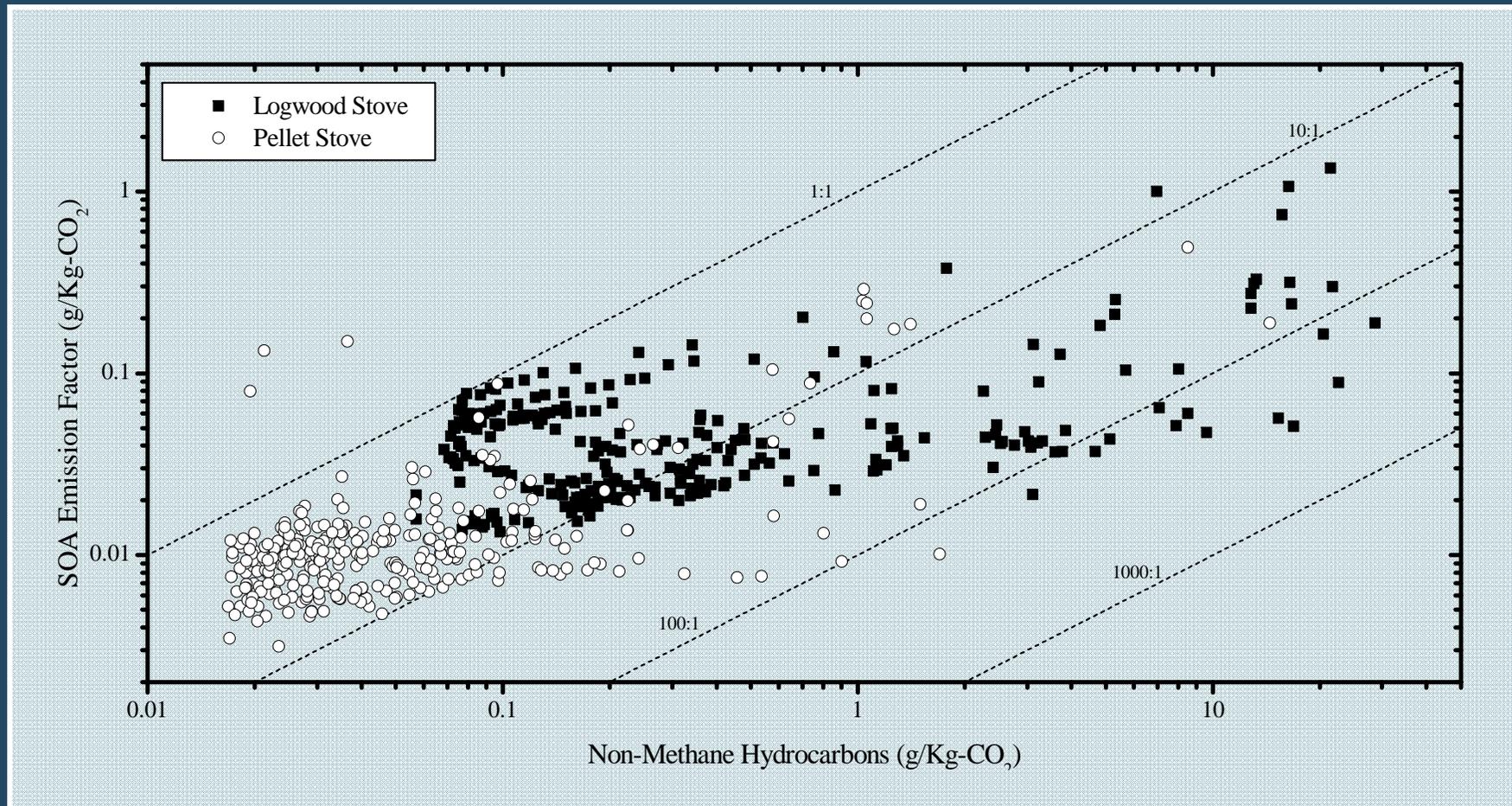


# Warm Cycle: SOA-to-Hydrocarbons\*

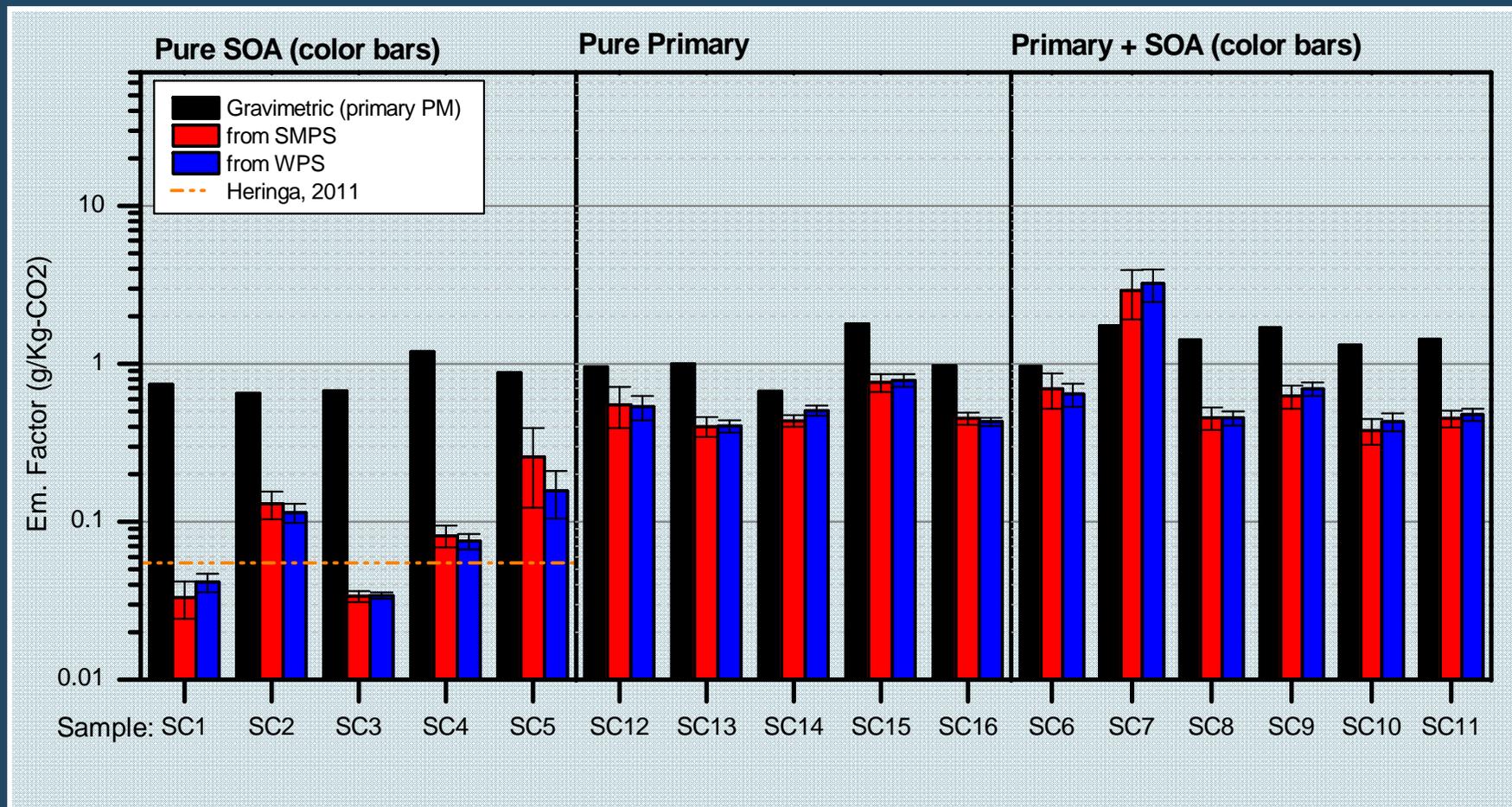


\* Average from 4 warm cycles

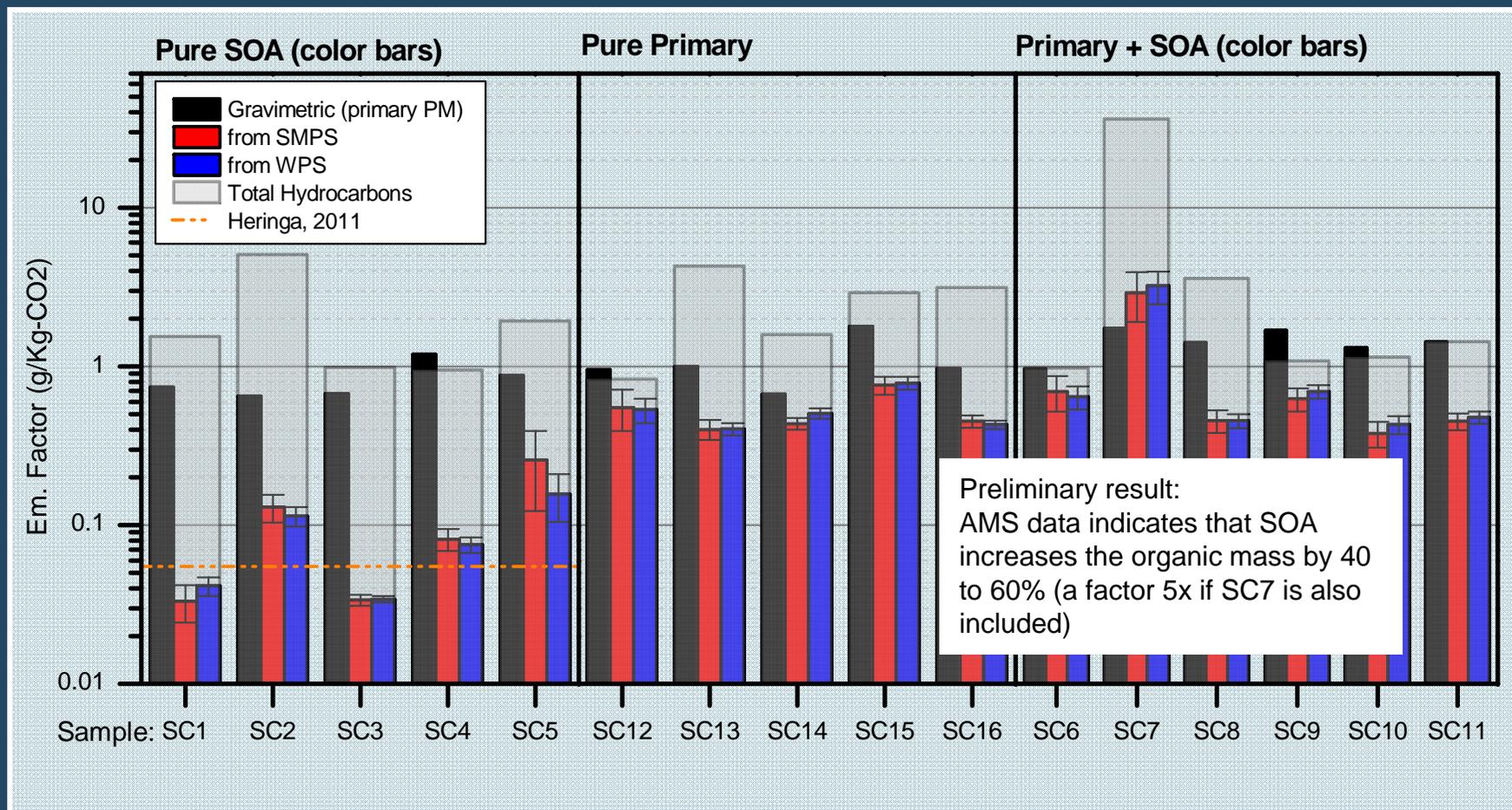
# SOA vs Non-Methane Hydrocarbons



# Logwood Stove: Primary Em. + SOA



# Logwood Stove: Primary Em. + SOA



## Summary and outlook

- A continuous flow reactor with short residence time is a viable alternative for evaluating the SOA production potential.
- This reactor can be used to evaluate even low emitting sources that are difficult to measure using *traditional* smog chambers.
- The emission factor of 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. In particular, the OGC from the start phase of the combustion cycle (logwood stove) has a lower SOA production than the rest of the cycle.
- We tested the system using undiluted- as well as slightly diluted (1:8) emissions. This change did not affect the SOA emission factor.
- Combustion conditions are important; during suboptimal operation, the emission factor for SOA can be larger than for primary PM even on a modern stove.
- An important next step is to test the reactor side by side to a a smog chamber.

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# Hydrocarbons vs Carbon Monoxide

