

Considering potential secondary organic aerosol in wood combustion emission measurements

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Wood burning is a major contributor to particulate matter (PM) pollution. The regulatory offices of several countries, including Switzerland, have already recognized this and are in the process of introducing lower PM emission limits for wood burning devices. However, limiting only the emissions of particles is not enough; an important part of the ambient PM pollution related to wood combustion is originally emitted in the form of Organic Gaseous Carbon (OGC). These gaseous compounds are then transformed into particles known as secondary organic aerosols (SOA) in the atmosphere. Whereas primary particles are easily measured at the combustion site, SOA exists only after a complex chemical process that requires solar radiation and takes hours or even days for completion.

Current legislation for small combustion installations imposes no emission limits for the precursor substances of SOA. This can be understood since, on the one hand, it is only recently that the importance of SOA has become apparent (see, e.g., Szidat 2006 and Grieshop 2009) and, on the other hand, there is no standard way to calculate the SOA production potential of a combustion device. Most of our knowledge about these particles comes from smog-chamber experiments (Heringa *et al.*, 2011). Smog chambers are however large (tents of cubic meters), slow and expensive to run. They are, therefore, far from being an acceptable tool for emission monitoring or type approval tests. In this work, we present a simple conditioning system that could be used for this task. The system is based on a continuous-flow tube-reactor, with a volume of less than 100mL, where a sample gas is irradiated with UV light of a several mercury lamps (20W of UVC in total). During this stage the OGCs undergo photo-oxidation. Afterwards, the sample cools down in absence of UV light on a second identical tube where the gaseous species condense forming SOA.

Our results show that it is possible to transform OGC into SOA in just a few seconds at yields comparable to traditional smog-chamber experiments. The SOA yield, Y , is the ratio of the mass concentrations of formed aerosol against the reacted OGC. Figure 1 shows the SOA yield for two model hydrocarbons after a residence time of only 15 seconds. The yield for toluene is comparably lower than for α -Pinene. This is due to the fact that ozone is the oxidant predominantly produced by UVC radiation. Toluene has higher yields under the presence of other oxidants like the hydroxyl (OH) or nitrate (NO₃) radicals or under photo-oxidation with longer wavelengths (Hildebrandt 2009). In future experiments we will include longer wavelengths to promote also these reaction paths.

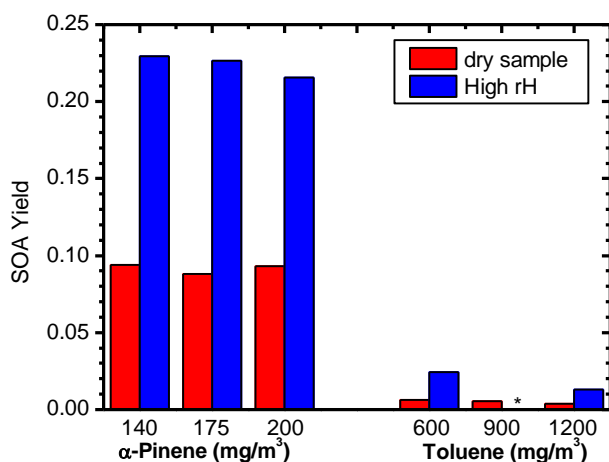


Figure 1. SOA Yield after 15 seconds residence time for two precursor species. The high rH corresponds to a humidity of approximately 80% rH. (* no data for the high rH case of toluene at 900mg/m³).

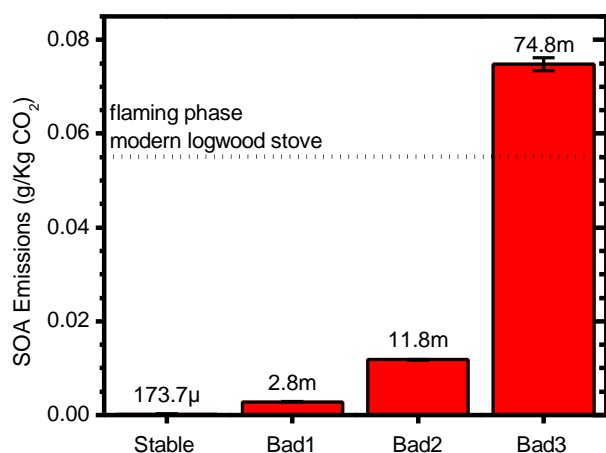


Figure 2. SOA emission factors after 15 seconds residence time for emissions at different operating points of a modern pellet stove. “Stable” corresponds to the standard operating conditions, whereas the points labelled “bad1” through “bad3” correspond to non-standard operating points. The dotted line shows the SOA emission-factor for a modern logwood stove on a traditional smog-chamber experiment after 5 hours residence time (Heringa, 2011).

Our reactor-tube can also be used to estimate the SOA emission factors for wood combustion appliances. Figure 2 shows an example using a modern residential pellet stove (Rüegg KEA, Switzerland, P_{\max} 9kW). As a reference, the SOA emission factor for a modern logwood stove is also included in the figure. It can be seen that the standard, optimized operating point produces practically no SOA. Traditional smog-chamber experiments did not show any SOA formation for a similar stove (Heringa, 2011). However, in the traditional experiments, the low SOA concentration may have been under the detection limit of the instruments or masked by the primary organic aerosol (POA) signal. In any case, it can be said that our result is in agreement with their findings considering that the SOA yield for a stable pellet-combustion is 300 times lower than their lowest SOA yield (i.e. that of a modern logwood stove).

As is to be expected, the SOA yield increased for the non-optimized combustion points (cases “bad1” through “bad3” in figure 2). The increase in the SOA emission factor was always higher than the increase in the emission-factors for CO or OGC. This suggests that it is not enough to measure the gas-phase species to estimate the potential SOA contribution to atmospheric particulate matter. On top of that, similarly to the toluene case, the SOA emissions may be even larger than what we are measuring at the moment since our results consider only ozone chemistry.

Conclusions

SOA is an important source of ambient particulate matter that must be considered when doing emissions characterization and included in emission-limit legislation. The present work shows that a continuous-flow tube-reactor with a short residence time is a viable alternative for evaluating the SOA production potential. The reactor can be used to evaluate even low emitting sources that are difficult to measure using traditional smog chamber experiments. However, the formation of SOA is a complex chemical process. The present study should be extended to include other oxidative species or radiation wavelengths.

This work was supported by the Swiss FOEN and by the IMBALANCE project of the CCES of the ETH Domain.

References

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Potential Secondary Organic Aerosol in Wood Combustion Emissions

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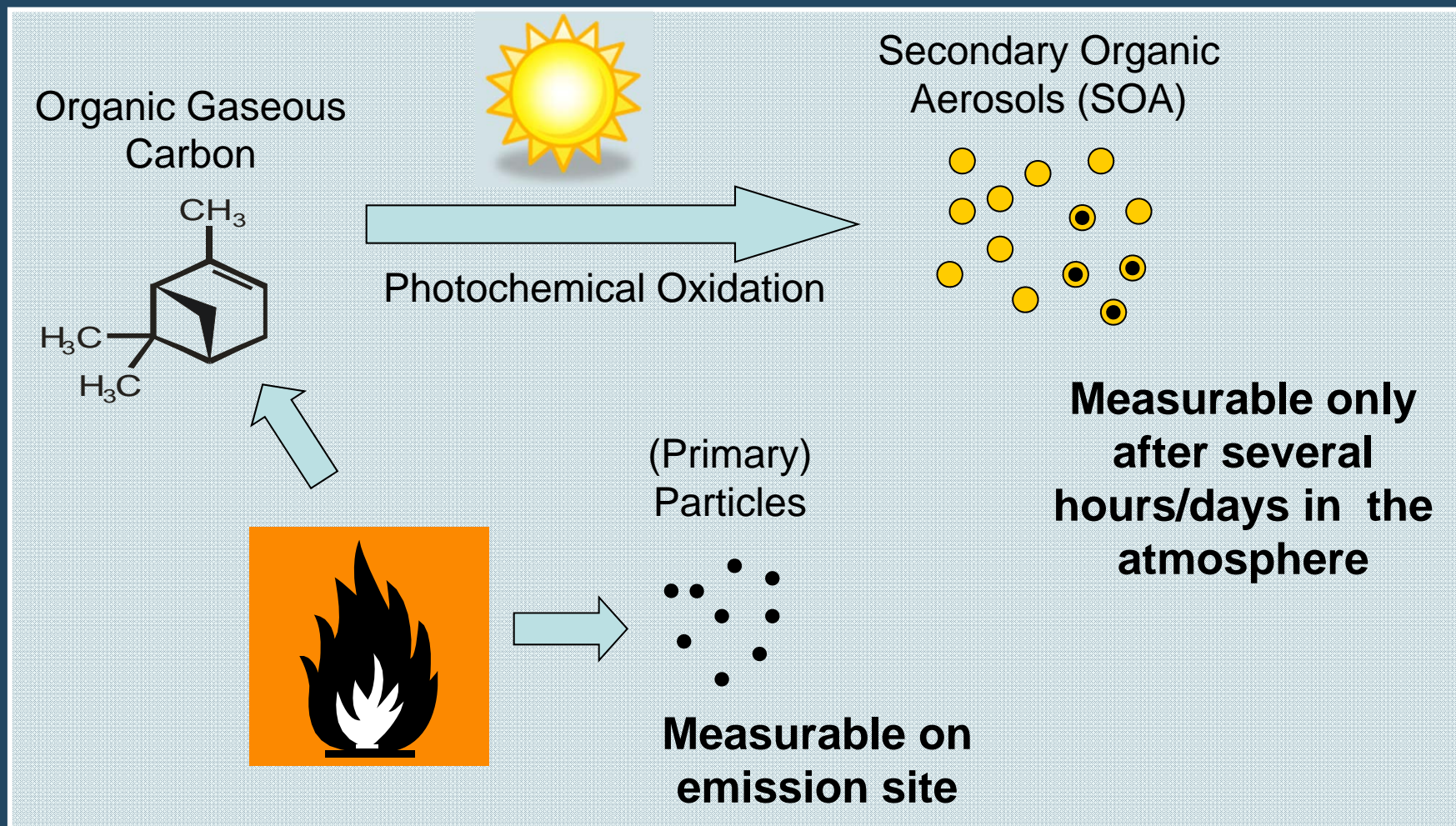
Fachhochschule Nordwestschweiz

Official view: wood burning emissions

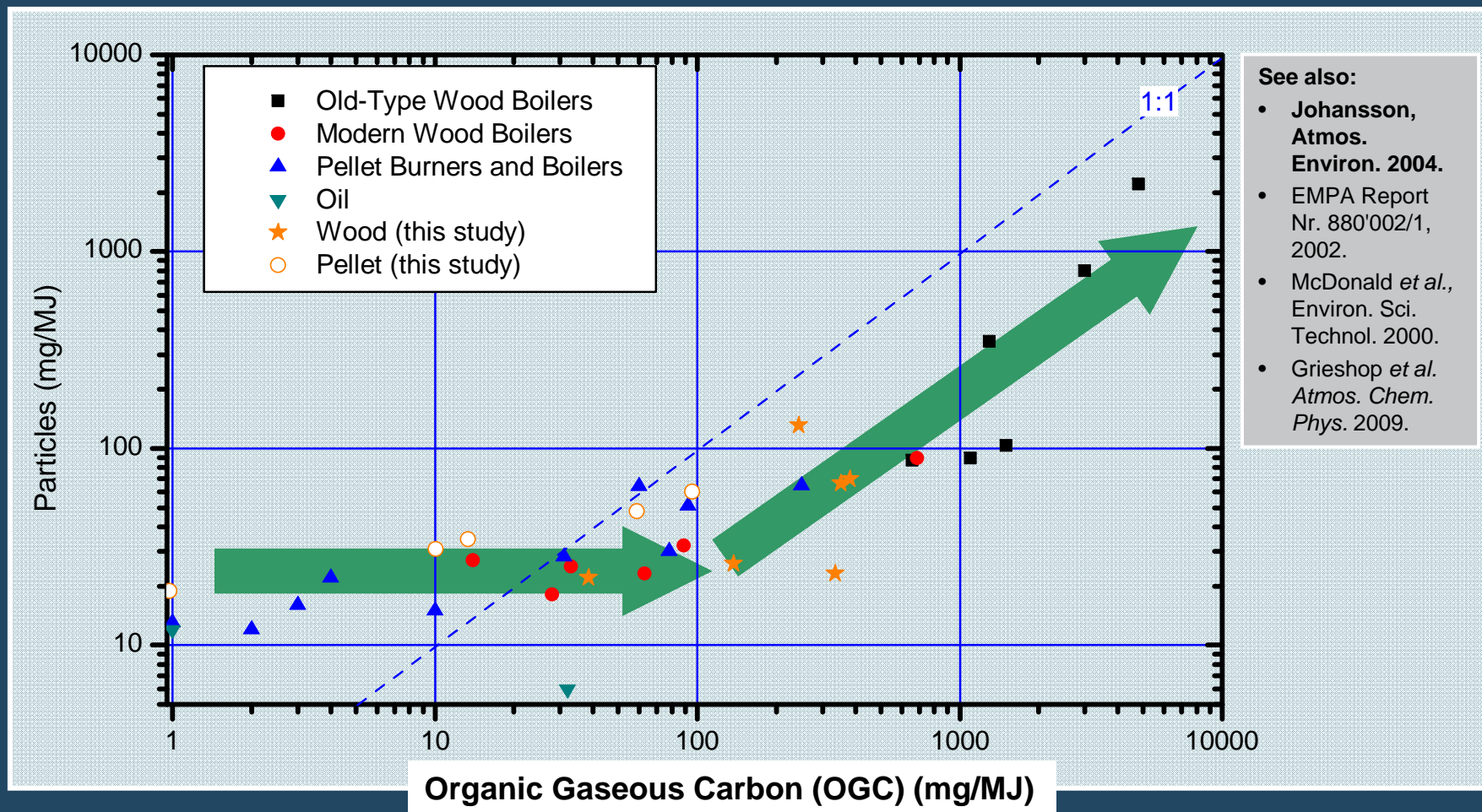
- PM emissions from wood burning are now officially recognized as a problem.
- In Switzerland, the amount of PM originating from wood burning is expected to duplicate within the next decade.
- As a reaction to this, lower emission standards have been introduced for small as well as for large combustion installations (starting 2011).

| Type of combustion installation (below 70 kW) | CO mg/m ³ @ 13% O ₂ | PM mg/m ³ @ 13% O ₂ |
|--|---|---|
| Log Wood Boilers | 800 | 60 -> 50 |
| Automatic Operation Boilers | 400 | 90 -> 60 |
| Pellet Boilers | 300 | 60 -> 40 |

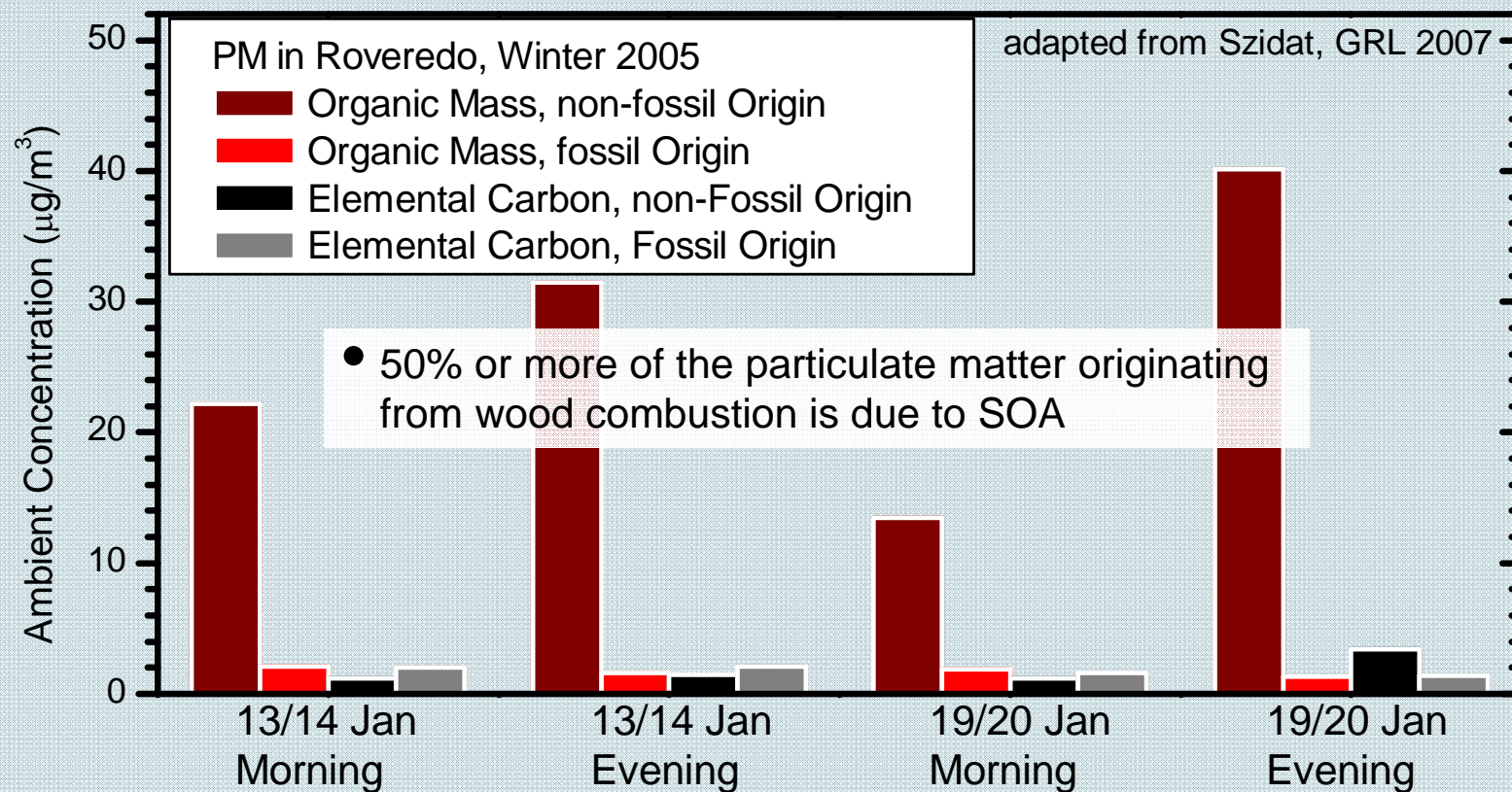
Primary/Secondary Emissions



Hydrocarbons & Combustion Quality



Ambient Side: Mostly Organic Mass



(Preliminary) Summary

- Primary PM gives an incomplete picture of the contribution of wood burning to ambient aerosol
- In the atmosphere, Secondary Organic Aerosol (SOA) mass exceeds primary PM; Organic Gaseous Carbon is the source of SOA.
- Organic material significantly contributes to toxicity
- Future legislation should contemplate the hydrocarbon emissions and, ideally, regulate them based on their SOA Production Potential.

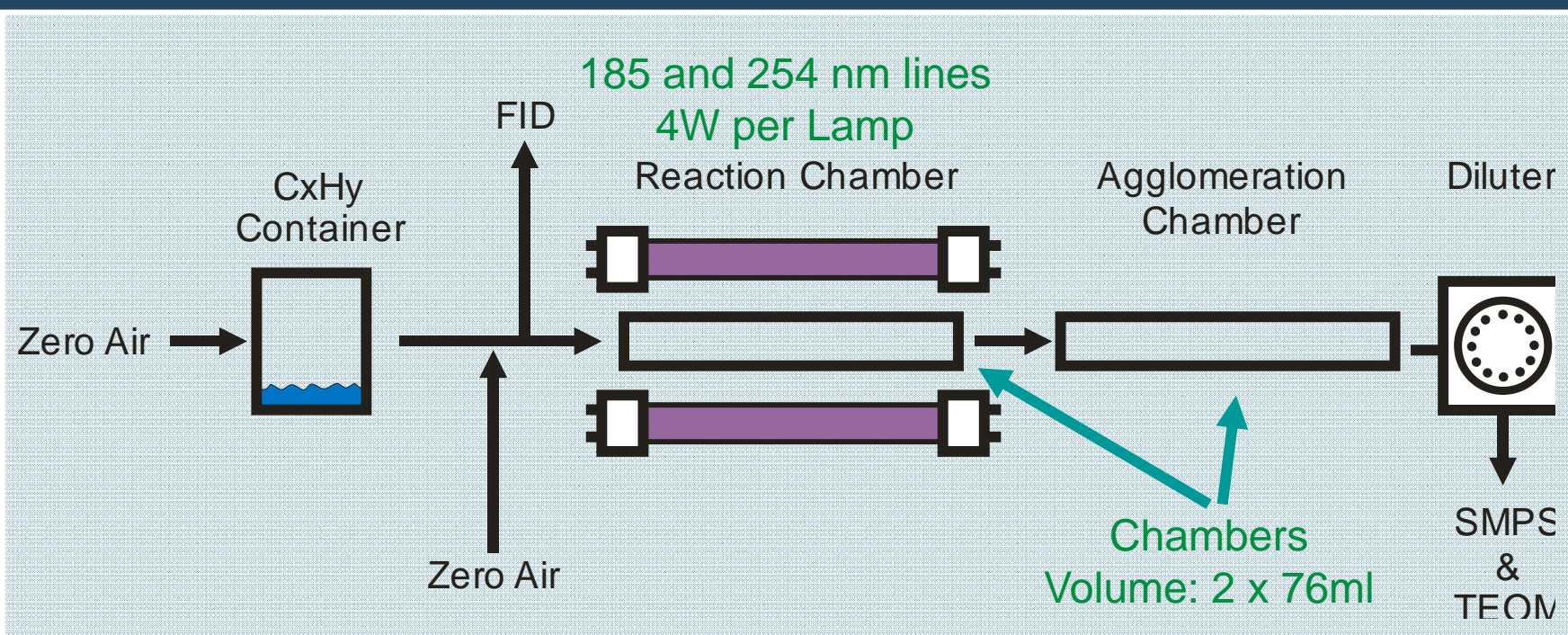
Measuring Organic Gaseous Carbon

| | Advantages | Disadvantages |
|---------------------------------|--|--|
| Condensables using Impingers | <ul style="list-style-type: none"> ▪ (somewhat) Portable ▪ Possible to make a very detailed chemical analysis | <ul style="list-style-type: none"> ▪ Of-line method ▪ Limited time resolution ▪ No information on SOA production potential |
| Flame Ionisation Detector (FID) | <ul style="list-style-type: none"> ▪ Available as a commercial device ▪ (somewhat) Portable ▪ Real time data ▪ Non-methane version differentiates between methane and other hydrocarbons | <ul style="list-style-type: none"> ▪ Requires FID-fuel and calibration gases ▪ No information on SOA production potential (?) |
| Smog-Chamber | <ul style="list-style-type: none"> ▪ Similar to the atmosphere ▪ Transforms hydrocarbons into SOA | <ul style="list-style-type: none"> ▪ Non-Portable* ▪ Long reaction time ▪ Expensive to run ▪ Limited time resolution |

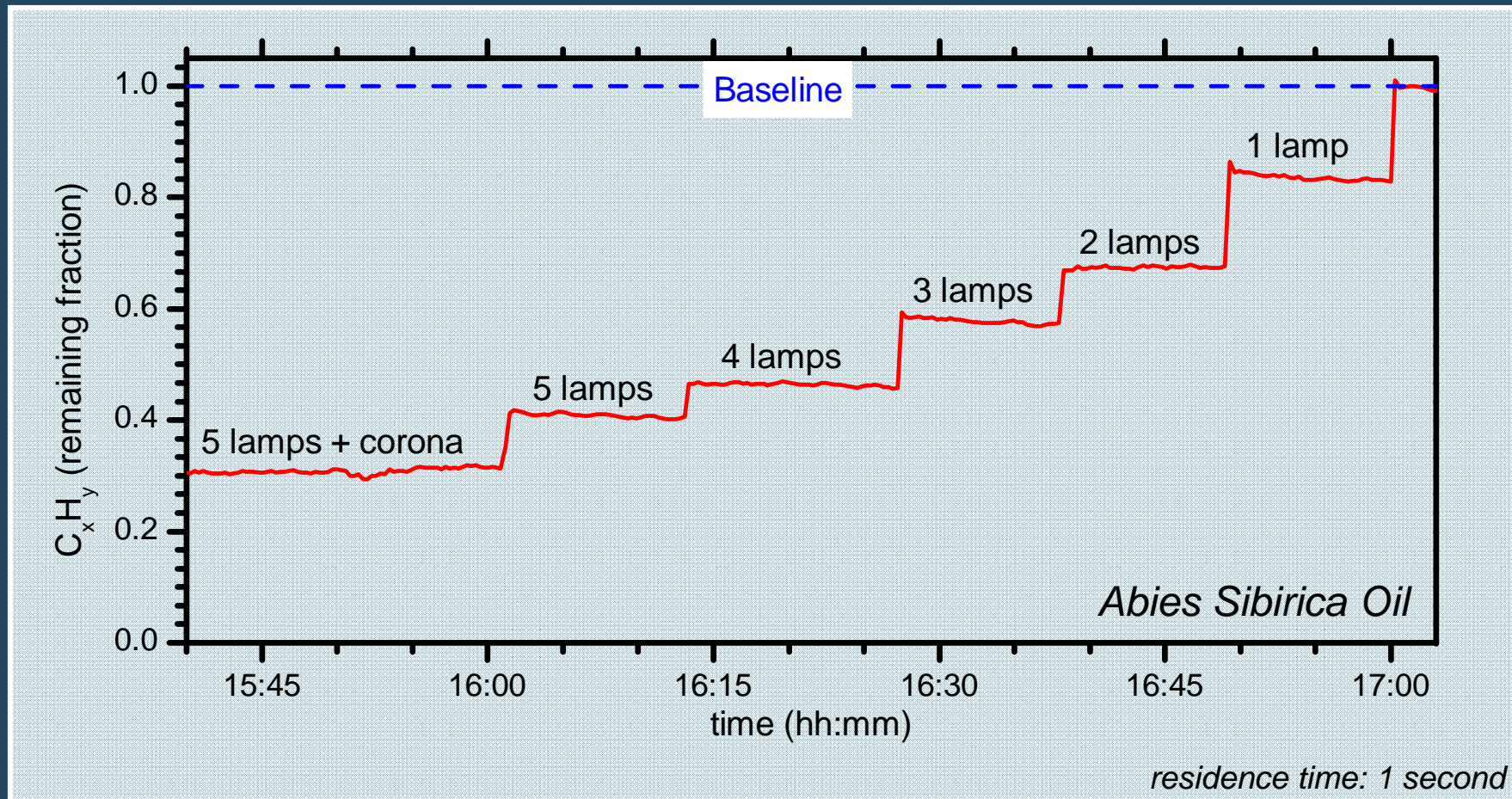
*Portable smog-chambers with reaction time of minutes:
 Kang, *Atmos. Chem. Phys.* 2007 & Lambe, *Atmos. Meas. Tech.* 2011

Experimental Setup (1)

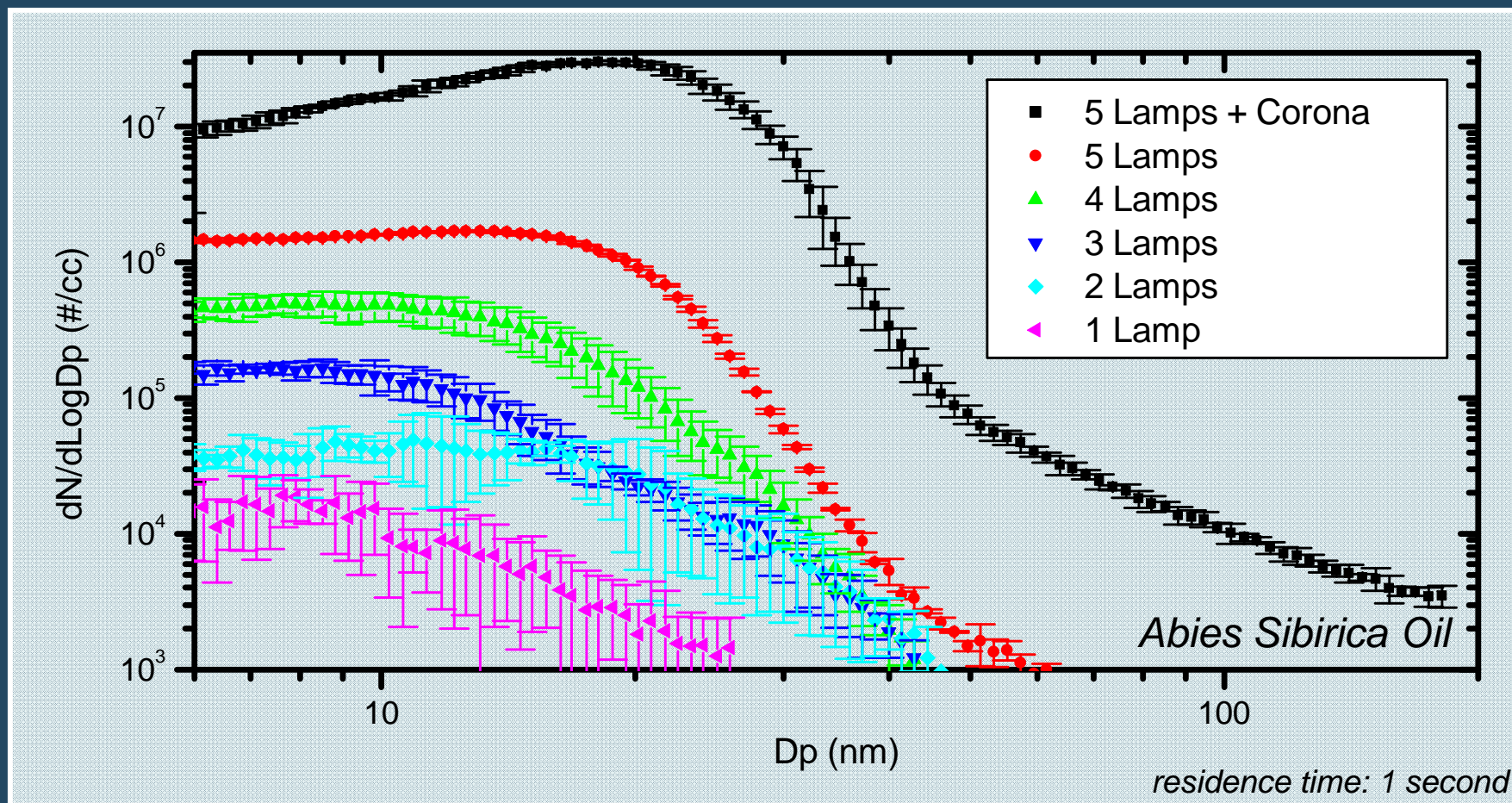
- Idea: Simulate photochemistry at a much faster rate (seconds instead of hours)



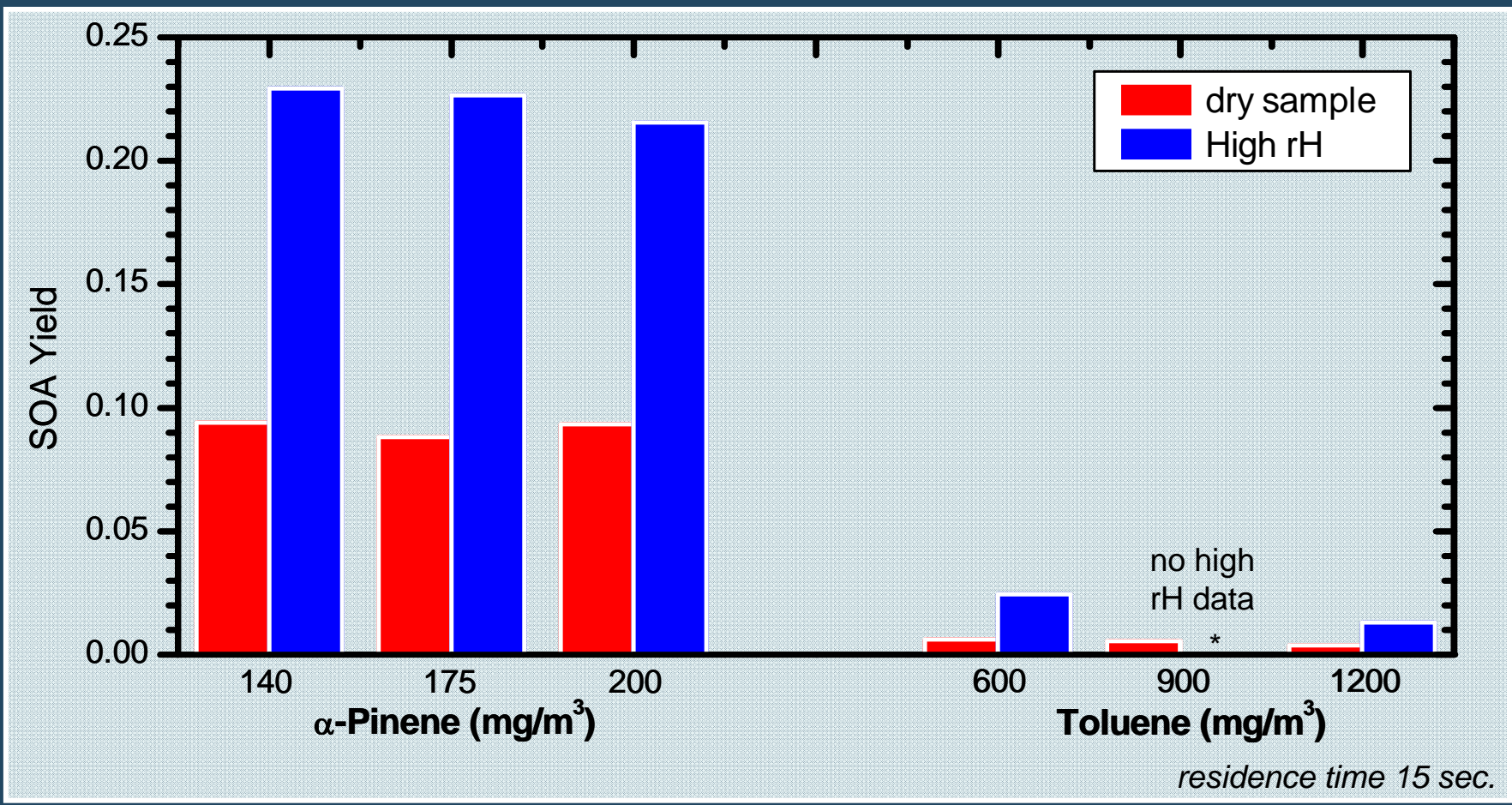
Reduction in OGC Mass by UV (and O₃)



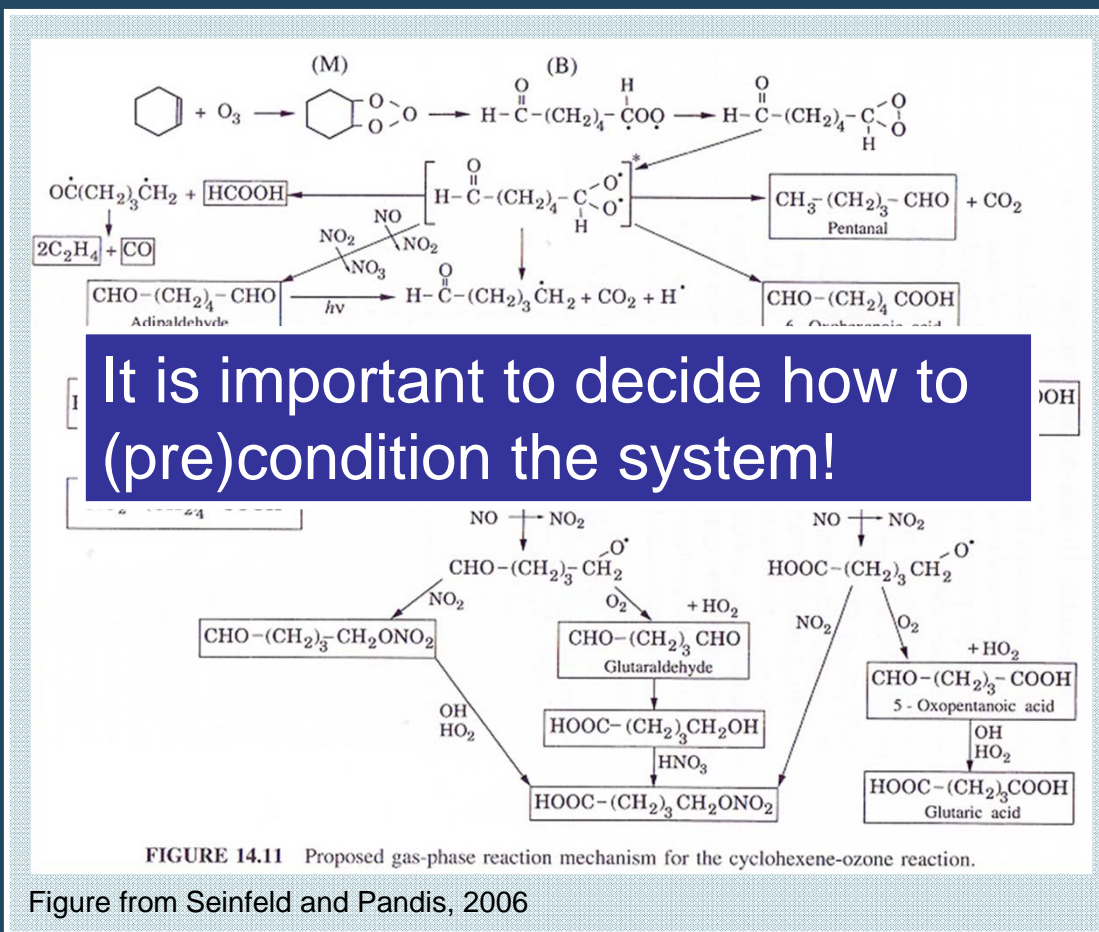
SOA Size Distribution, micro smog-chamber



SOA Yield for Model Hydrocarbons



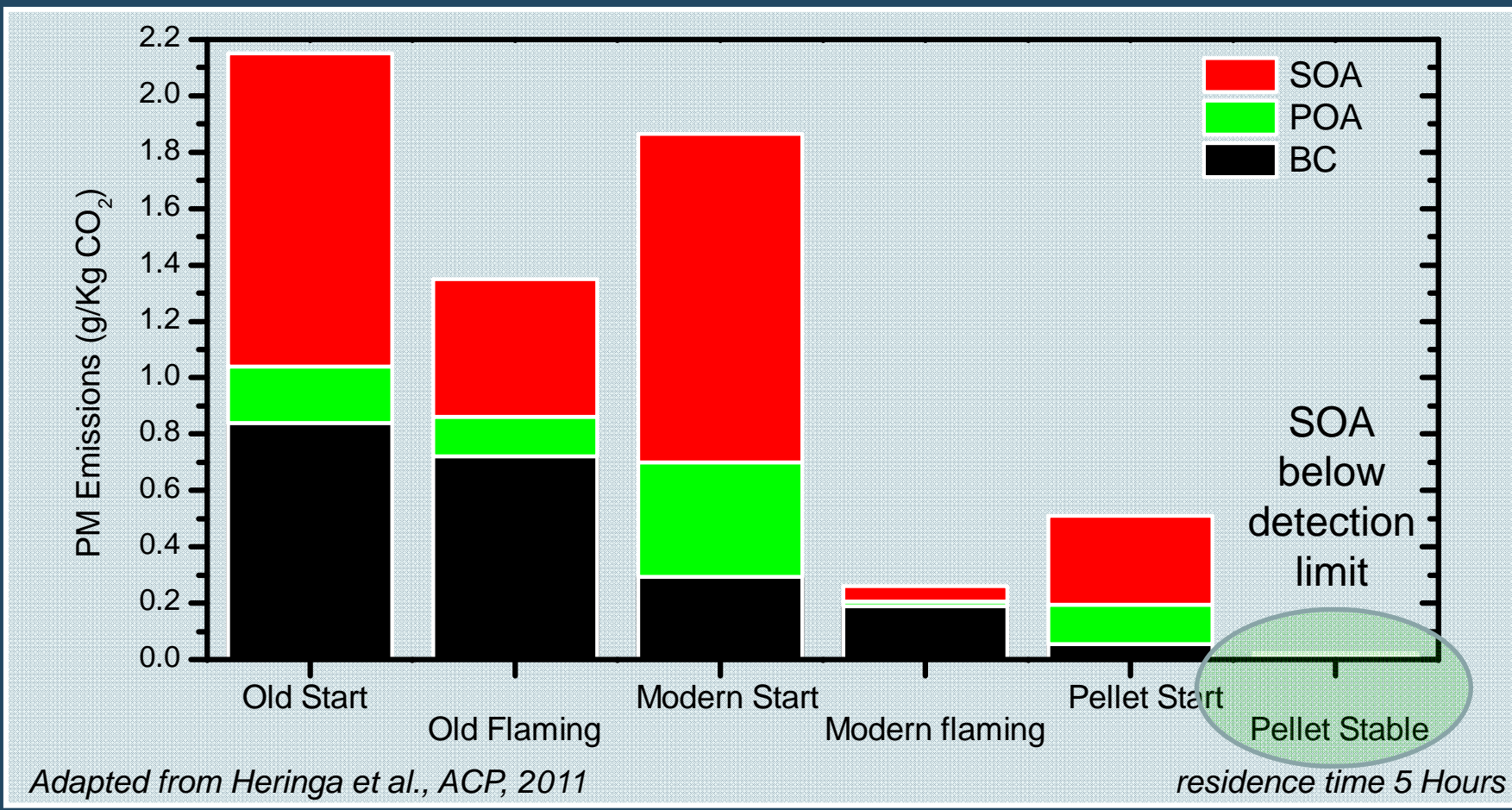
Example of SOA formation process



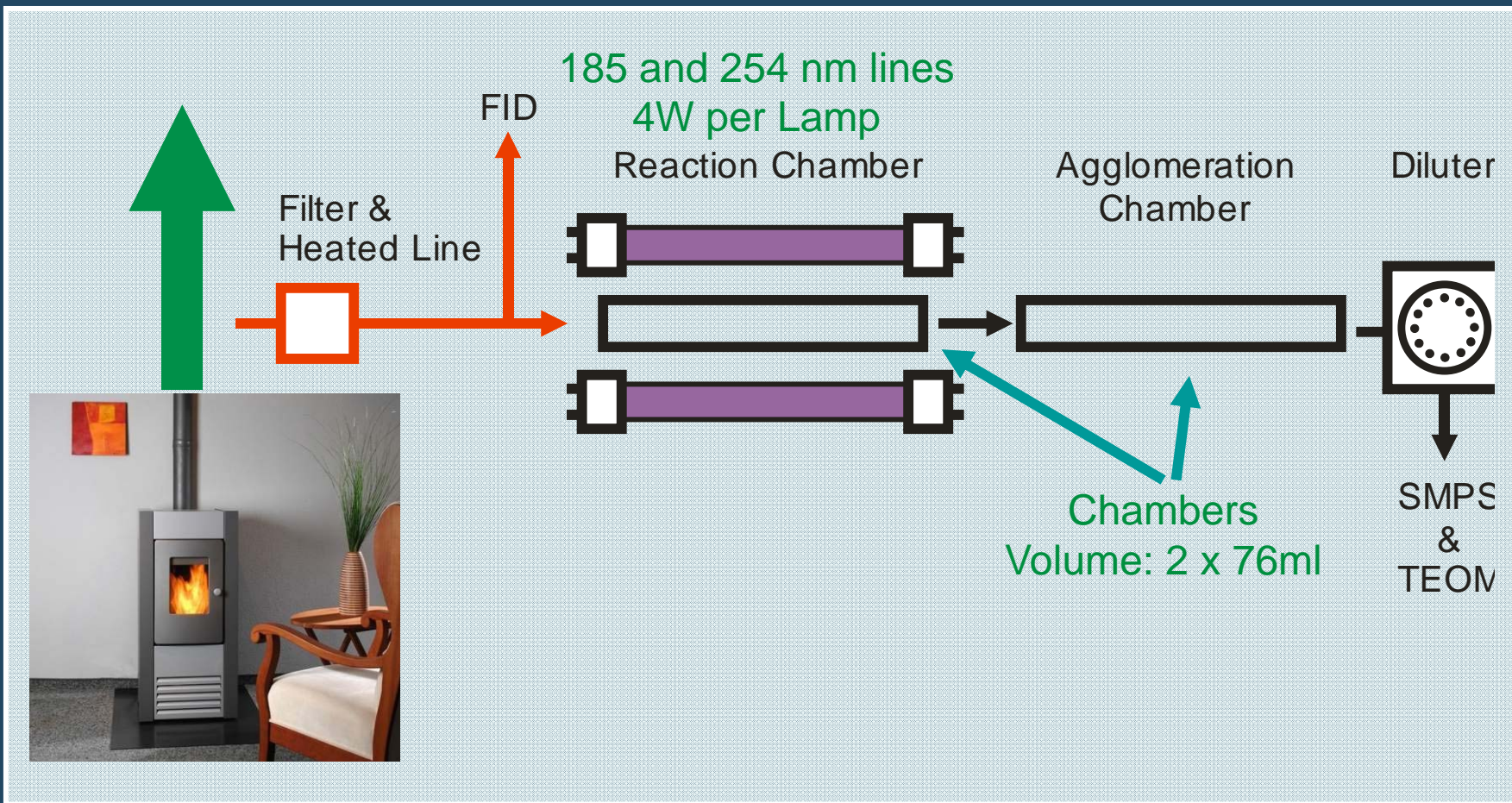
Important factors:

- rH, Temperature
- Oxidative species (O₃, OH), and other species like NO_x
- Precursor concentration
- Seed aerosol concentration
- ...

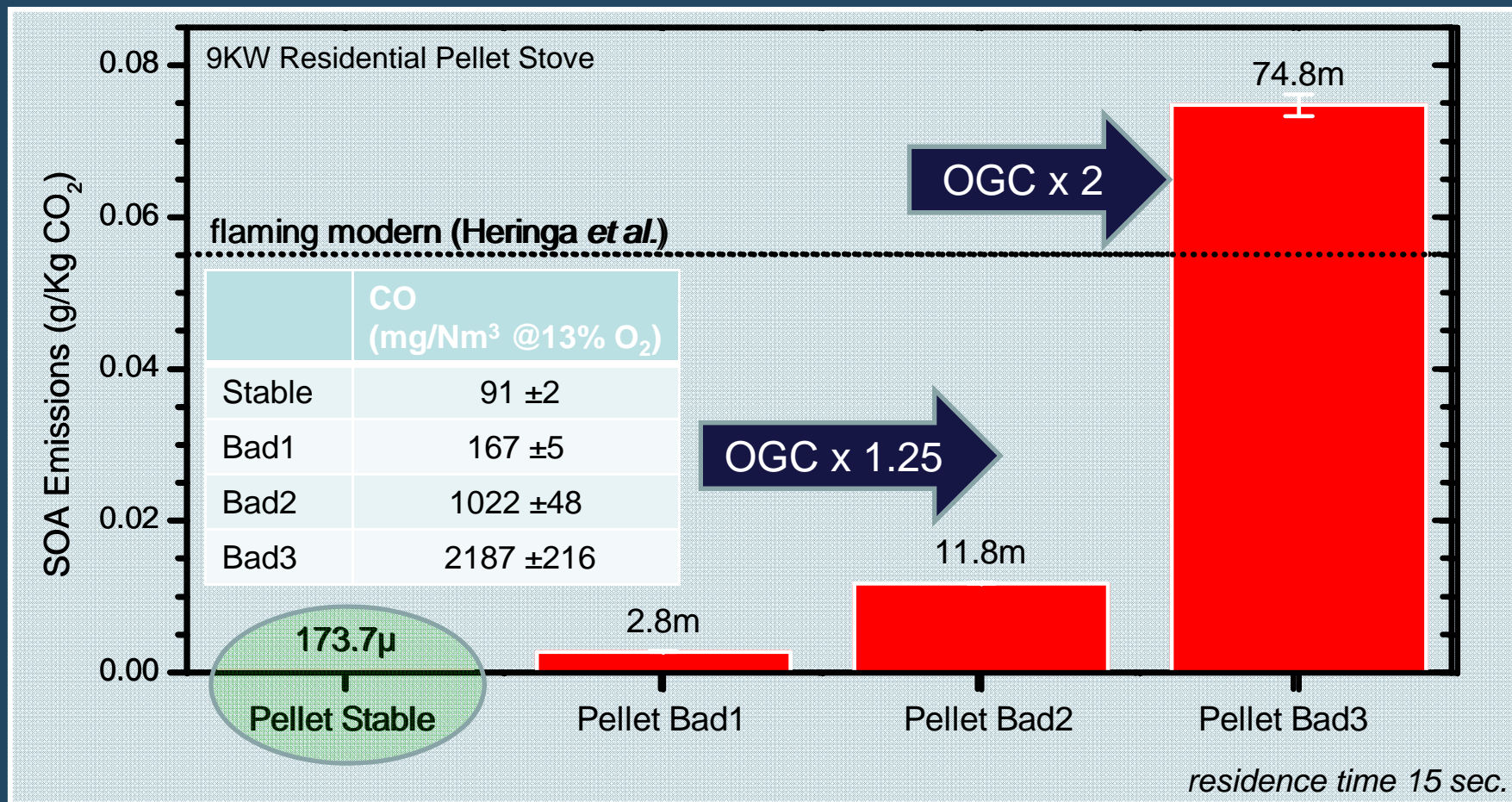
Wood-Burning Emissions (Smog Chamber)



Experimental Setup (2)



SOA Emissions (mini Smog-Chamber)



Conclusions

- SOA is an important source of ambient PM. As such, it must be considered when doing emissions characterization and included in emission-limit legislation.
- 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.
- SOA formation is a complex process that depends on many factors. The question of choosing the *correct* preconditioning parameters is not trivial.

Thanks to

- J. Wüest and E. Wildhaber from FHNW
- A. Prevôt, M. Herunga from PSI

This work was supported by the Swiss Federal Office for the Environment (FOEN) and the CCES from the ETH Zurich