

Time-resolved secondary organic aerosol formation potential of wood burning emissions

Alejandro Keller* and Heinz Bartscher

IAST, University of Applied Sci. and arts Northwestern Switzerland
Windisch, Switzerland

*alejandro.keller@fnhnw.ch

Joel Corbin †, Amewu Mensah and Berko Sierau

Institute for Atmospheric and Climate Science, ETH Zurich
Zurich, Switzerland

†now at: Paul Sherrer Institute (PSI), Villigen, Switzerland

Summary

- Using the Micro Smog Chamber, it is possible to produce secondary organic aerosol (SOA) with a chemical signature similar to atmospheric observations within few seconds.
- We have measured the SOA production potential of combustion appliances from small (7kW) batch-operated logwood stoves to medium size (up to 450kW) automatic installations.
- The least-volatile organic-gaseous-carbon-fraction from wood burning contributes the most to SOA formation.
- The low volatility of SOA precursors presents an opportunity for the development of abatement systems (e.g. NOSMOG) that target primary- as well as secondary emissions.
- Our results show that aging should be included as part of emission-control measurements and type-approval testing.
- Current standards are not representative of the real-world emissions of small combustion appliances. In particular during pyrolysis or high lambda operation, SOA can multiply the total emissions several-fold.

Why we want to age wood burning emissions (and how)

Aging forms secondary organic aerosol (SOA) through photo-oxidation in the atmosphere. This increases the amount of OC related to wood burning.

Important because: Filter samples taken by means of the reference method do not fit with atmospheric observations:

- At the test bench: OC/EC < 1
- In the atmosphere: OC/EC ~ 5 (Switzerland)
- Estimations: 50% of ambient OC comes from SOA (Lanz, ACP 7, p. 1503, 2007).

By irradiating the sample with high intensity UVC and UVA light we create a high concentration of oxidative species (O_3 , OH, NO_3), achieving the equivalent of days of atmospheric aging within 10 seconds.

OC = (particle-bounded) Organic Carbon

EC = Elemental Carbon (i.e. soot)

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)

References (Micro Smog Chamber)

- Keller & Bartscher, "A continuous photo-oxidation flow reactor for a defined measurement of the SOA formation potential of wood burning emissions," *Aerosol Sci.* **49** pp. 9-20, 2012.
- Bruns *et al.*, "Inter-comparison of laboratory smog chamber and flow reactor systems on organic aerosol yield and composition," *Atmos. Meas. Tech.*, **8**, 2315-2332, 2015.
- Corbin *et al.*, "Organic emissions from a wood stove and a pellet stove before and after simulated atmospheric aging," *Aerosol Sci. Tech.*, **49**(11), 1037-1050, 2015.

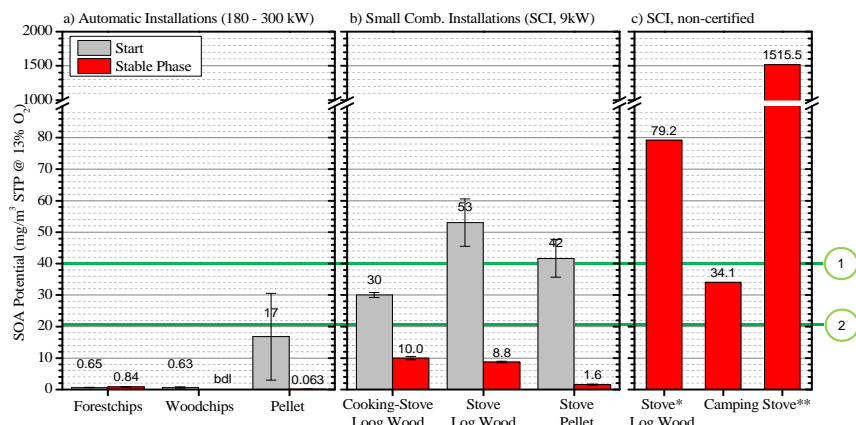


Figure 1. Average SOA production potential from 3 automatic medium size boilers (a), compared against the potential from 3 modern small combustion installations (b) and 3 log-wood stoves that do not fulfill the LRV standards (c). The data on panels a) and b) was measured by means of the micro smog-chamber, whereas c) presents traditional smog-chamber experiments from the literature (*Heringa *et al.*, ACP 11, 5945, 2011, and **Grieshop *et al.*, ACP 9, 1263, 2009). The green lines show the new German emission limit for batch operated (1) and automatic installations (2). Our tests show that the SOA production potential can have a negligible contribution to the total particulate matter emissions (a) or be in the same order of magnitude than current emission limits (b). Finally, non-certified or badly operated appliances can have several orders higher SOA-potential even during steady state combustion (c). bdl = below detection limit.

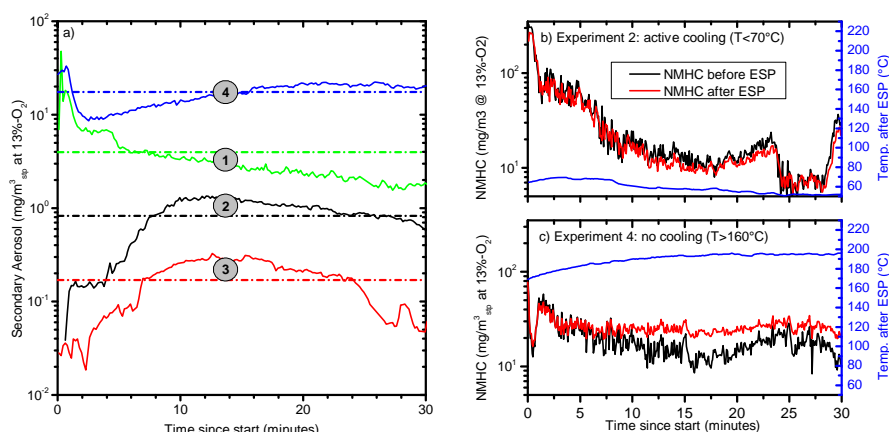


Figure 2. Secondary organic aerosol production potential during the warm-start of a 9 Kw logwood equipped with the NOSMOG system (a). The NOSMOG prototype (Hexmodul AG, Oekosolve AG and Salerno Engeler GmbH) cools down the flue-gas before removing the particulate matter by means of an Electrostatic Precipitator (ESP). Cooling affects partitioning and therefore the emission of SOA precursors. The curves represent: a warm start using only the electrostatic precipitator (ESP) but no cooling (1), two warm starts with a reduced temperature at the ESP (2 & 3), and a final warm start after turning off the cooling (4). The dashed lines show the average SOA production potential for the 30 minutes measurement. Panels b) and c) show the concentrations of non-methane hydrocarbons (NMHC), measured by means of a FID, before and after the ESP and the raw gas temperature for experiments 2 and 4 respectively. At low temperatures, the raw gas partition is shifted towards the particle phase and the ESP is capable of removing substances that would otherwise produce secondary organic aerosol (experiments 2 and 3). There is, however, no evident reduction of NMHC due to the use of NOSMOG (panel b), suggesting that only a small fraction of the NMHC is responsible for the SOA production. As the system is heated up again (experiment 4 in panels a and c), previously captured low-volatility species are resuspended, causing an increased production of SOA and a higher concentration of NMHC after the ESP.

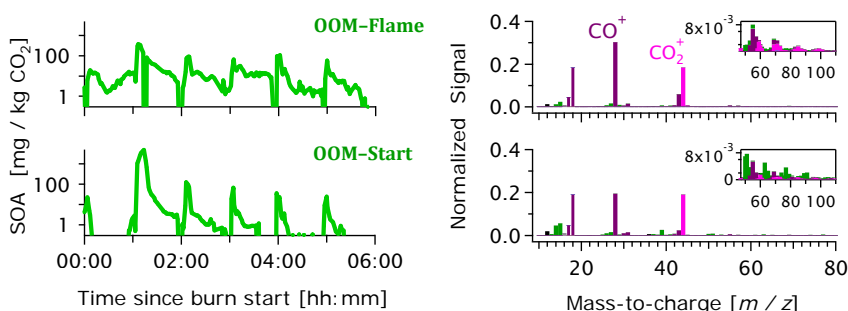


Figure 3. Positive Matrix Factorization (PMF) factors for SOA data (i.e. oxidized organic aerosol, OOM) during six consecutive combustion cycles (one cold start and five warm starts) of a logwood stove. The left column shows the Aerosol Mass Spectrometer (AMS) factor time series. The right column and insets show the corresponding AMS factor mass spectra. Two main factors were identified, corresponding to the (warm) start-phase of a cycle and the flaming (i.e. steady state) combustion. A similar analysis with primary, i.e. non-oxidized, organic aerosol shows that the mass spectra of the start-phase are highly correlated with pyrolysis products like levoglucosan (uncentered $r = 0.84$), whereas the flaming-phase correlates with lignin-combustion organic material (uncentered $r = 0.79$). In the case of aged emissions, the assignment to pyrolysis products or lignin-combustion is not straightforward due to the changes induced by photo-chemical aging. Nevertheless, the highest primary as well as secondary organic-aerosol emission takes place during the start-phase, when pyrolysis is the dominant process. See Corbin *et al.*, 2015.

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