Mass Spectrometry of Wood-Combustion Soot

Organic Composition and Black-Carbon Surface Groups

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Context

- The black-carbon-containing soot particles formed via combustion have major effects on clouds and climate due to their light-absorbing properties.
- Soot-aerosol exposure is associated with adverse health effects including cardiovascular disease and cancer.
- The climate- and health-relevant composition of soot varies greatly with (i) combustion conditions and (ii) atmospheric oxidation and coating (aging).
- The SP-AMS is a new commercial instrument[1] designed for the online characterization of soot composition and coatings. Here, SP-AMS data analysis and interpretation techniques were developed and applied to wood-combustion soot.[2,3]

Experiment

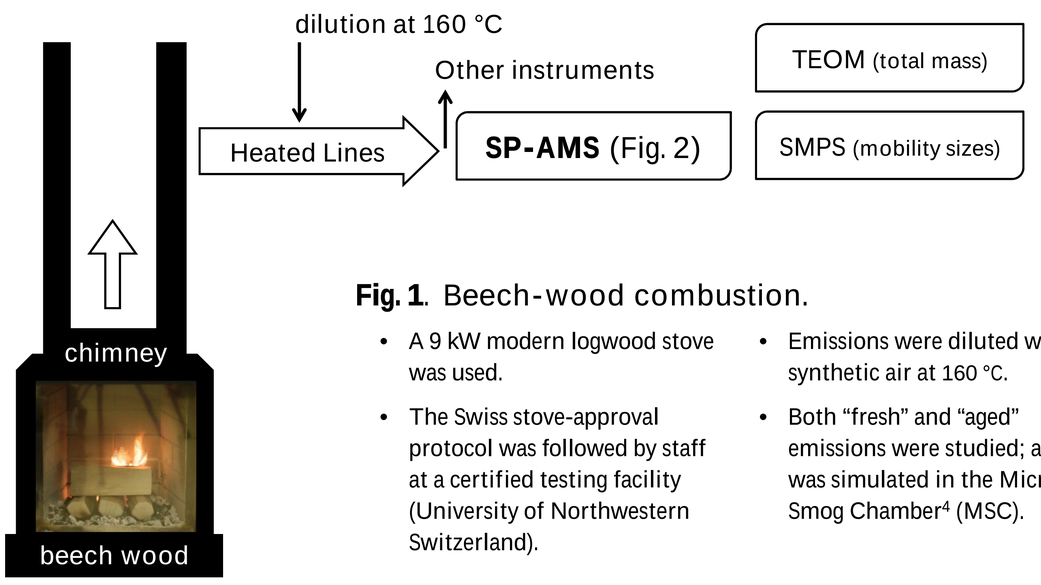


Fig. 1. Beech-wood combustion.

- A 9 kW modern logwood stove was used.
- The Swiss stove-approval protocol was followed by staff at a certified testing facility (University of Northwestern Switzerland).
- Emissions were diluted with synthetic air at 160 °C.
- Both "fresh" and "aged" emissions were studied; aging was simulated in the Micro Smog Chamber[4] (MSC).

Mass Spectrometer

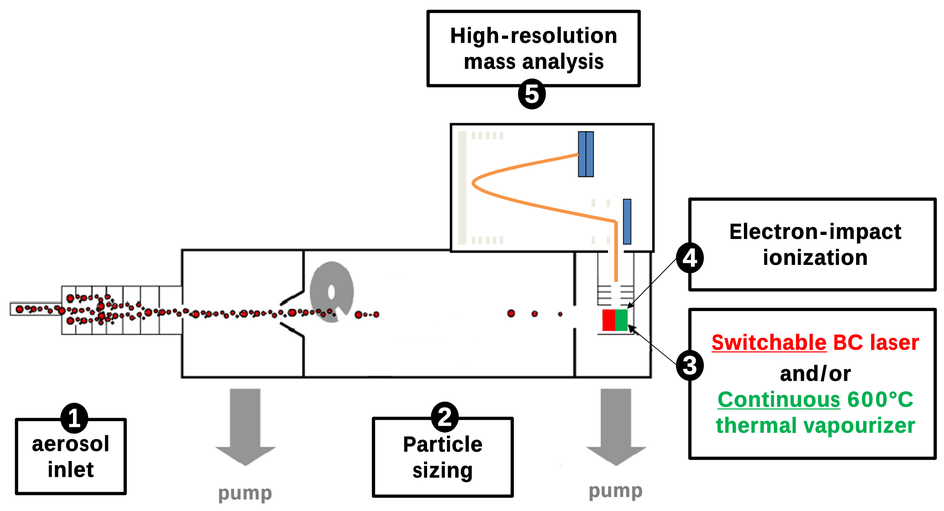


Fig. 2. The Soot-Particle Aerosol Mass Spectrometer (SP-AMS).

1. Sample aerosols are introduced and focussed into a narrow beam by an aerodynamic lens.
2. A particle-beam chopper allows periodic background measurements. The chopper also allows aerodynamic particle sizing in a separate Particle Time-of-Flight (PToF) mode.
3. Particles are vaporized by one of two vaporizers, see Fig. 3.
4. Vaporized particulate matter is ionized by 70 eV electrons.
5. Ion abundances and elemental composition are measured by mass spectrometry.

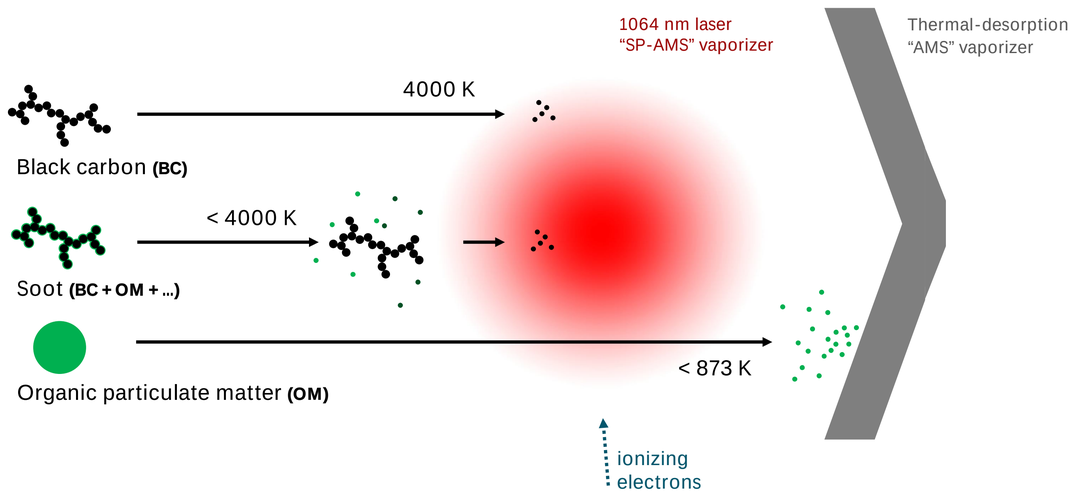


Fig. 3. SP-AMS particle vaporization.

- A continuous-wave 1064 nm laser "SP-AMS" vaporizer is absorbed by BC, vaporizing entire soot particles. ("Soot" defines the entire particle and here includes impurities of OM and ash.)
- A 600 °C thermal-desorption "AMS" vaporizer vaporizes non-refractory particulate matter.
- The AMS vaporizer was operated continuously.
- The SP-AMS laser vaporizer was periodically switched on and off, allowing the separate characterization of BC and OM.

Results

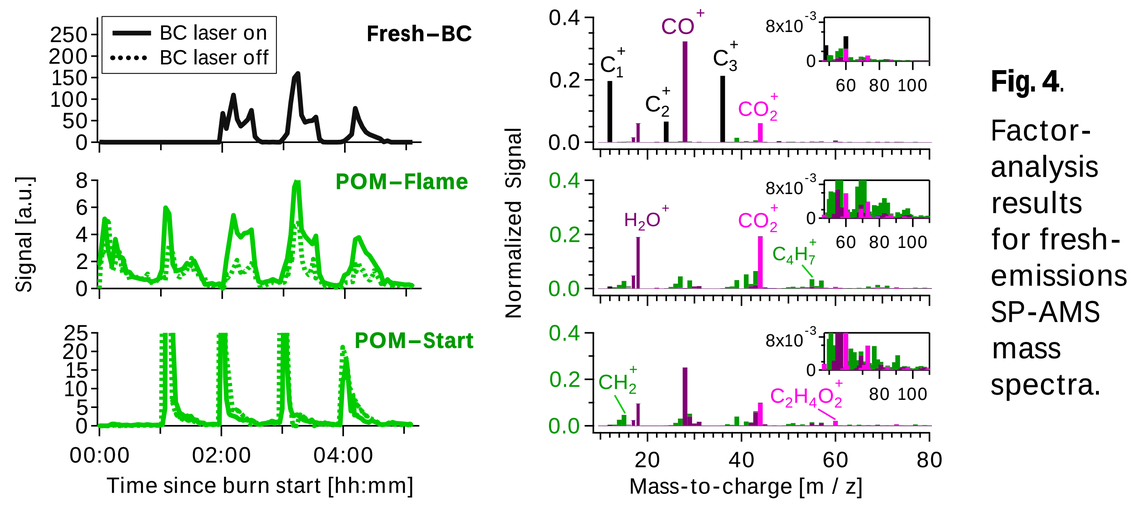


Fig. 4. Factor-analysis results for fresh-emissions SP-AMS mass spectra.

- Positive Matrix Factorization (PMF) was performed to reduce ~400 quantified ions to 3 representative mass spectra and time series[5] using a newly-developed AMS uncertainty model.
- A "Fresh–BC" factor explained refractory SP-AMS signals (laser on) as originating from BC plus oxygenated surface groups[6]. These oxygenated-surface signals increased after MSC aging.
- OM was explained by a "POM–Flame" factor, correlated with flaming combustion, and a more-abundant "POM–Start" factor, associated with the addition of new wood to the embers of a previous burn.
- The POM–Start mass spectrum was highly correlated with that of levoglucosan, implicating cellulose/hemicellulose pyrolysis as the major source of OM in the stove.

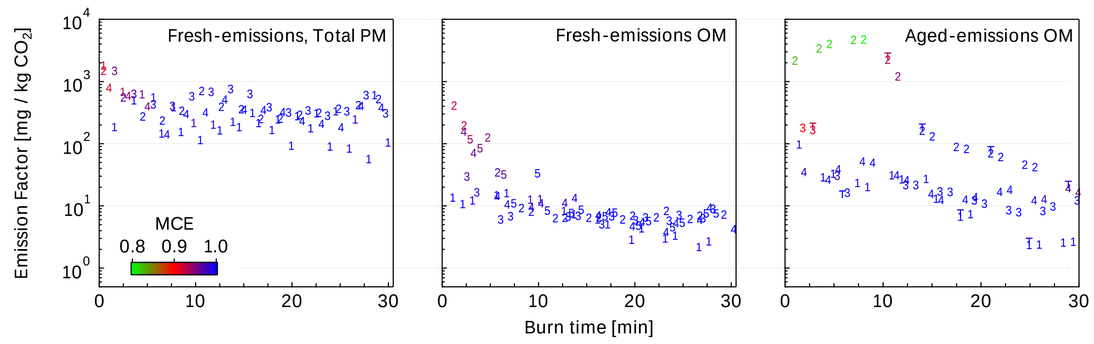
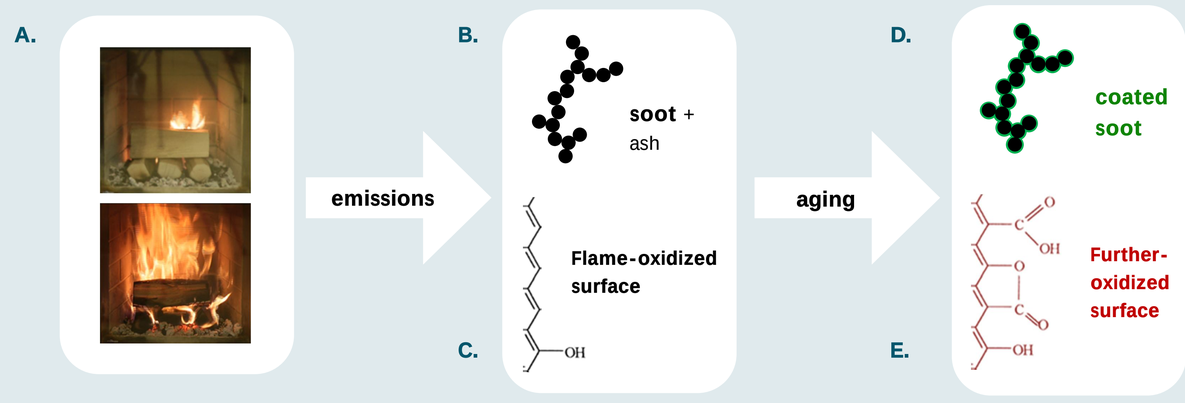


Fig. 5. Emission factors for the 1st, 2nd, 3rd ... burns of different experiments.

- Organic PM (OM) emissions were low relative to other species such as black carbon (BC) and ash.
- Simulated aging in the MSC allowed highly-time-resolved OM emission factors to be determined from the SP-AMS (laser off).
- OM emission factors were a factor of 3 – 4 higher after aging.
- OM emissions were highest during ignition (first 5 minutes) or after failed ignition (rightmost panel, burn #2).

Conclusions & Implications



A. Most organic PM (OM) was emitted when new wood was added to the stove. This OM originated from the pyrolysis of cellulose/hemicellulose and was of different composition to OM emitted during flaming combustion or when wood was burnt top-down, suggesting potential changes in its climate and health effects.

B. Significant amounts of potassium (K) were internally-mixed with the beech soot. As the SP-AMS is soot-selective, it may therefore be used to distinguish biomass-combustion soot from, e.g., traffic soot in future atmospheric studies.

C. Signals originating from refractory, oxygenated black-carbon surface groups were identified and were approximately constant at all stages of combustion. These surface groups play an important role in soot's health effects[7,8] and have not previously been measured online.

D. Simulated aging increased OM emission factors by a factor of 3 – 4. Current stove-testing protocols do not measure this OM[4]. However, for this stove, BC emissions dominated.

E. Surface-group oxidation increased upon simulated atmospheric aging[2] and remained approximately constant at all stages of combustion. Increased surface oxidation is known to enhance particle toxicity[8] and has not been previously measured in situ. Future work will compare these signals for other soot types.

References

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