

Mass Spectrometry of Wood-Combustion Soot

Organic Composition and Black-Carbon Surface Groups

ETH zürich

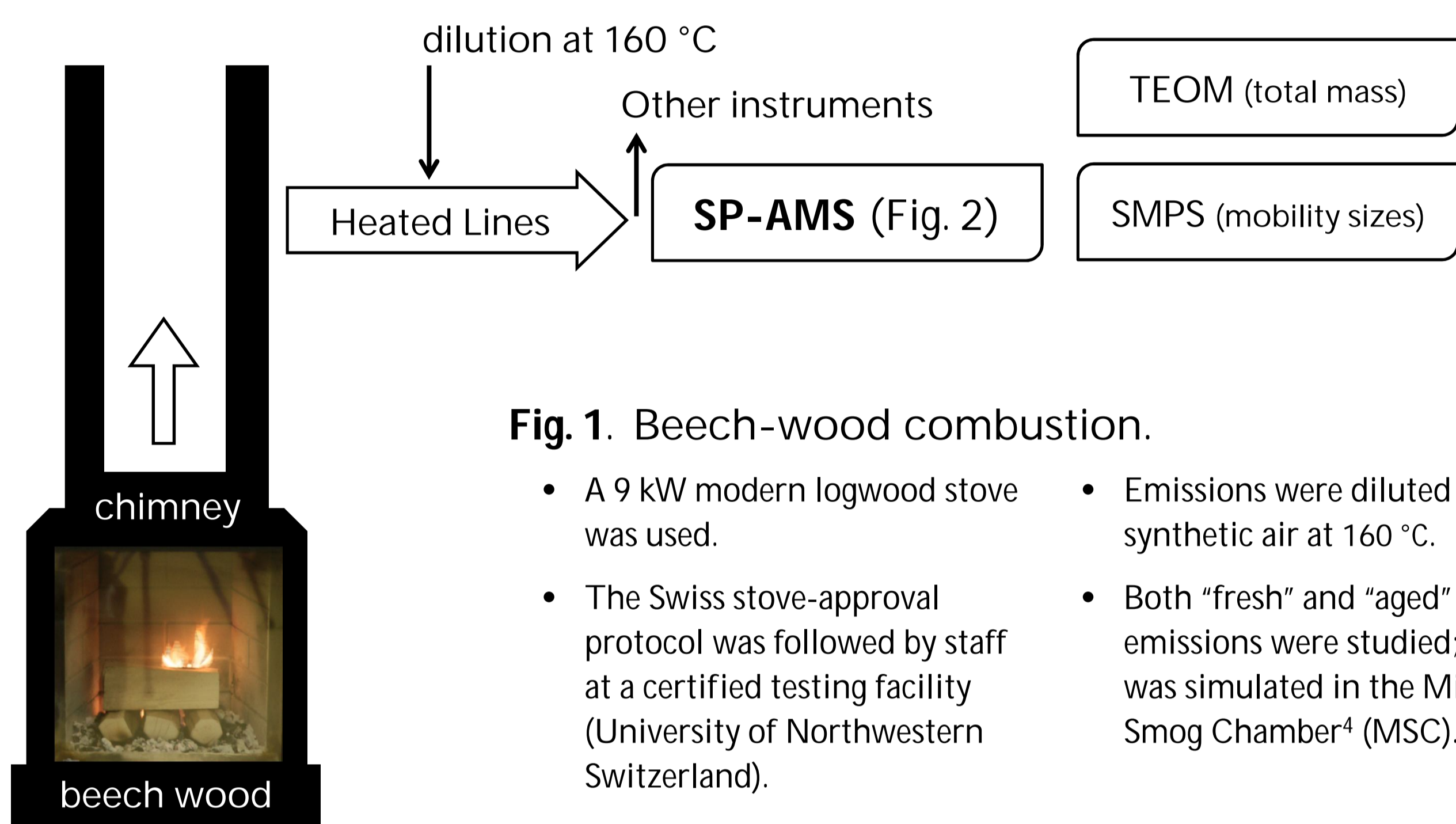
Joel C. Corbin¹ A. Keller² U. Lohmann¹ B. Sierau¹ and A. A. Mensah¹

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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 instrument¹ 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



Mass Spectrometer

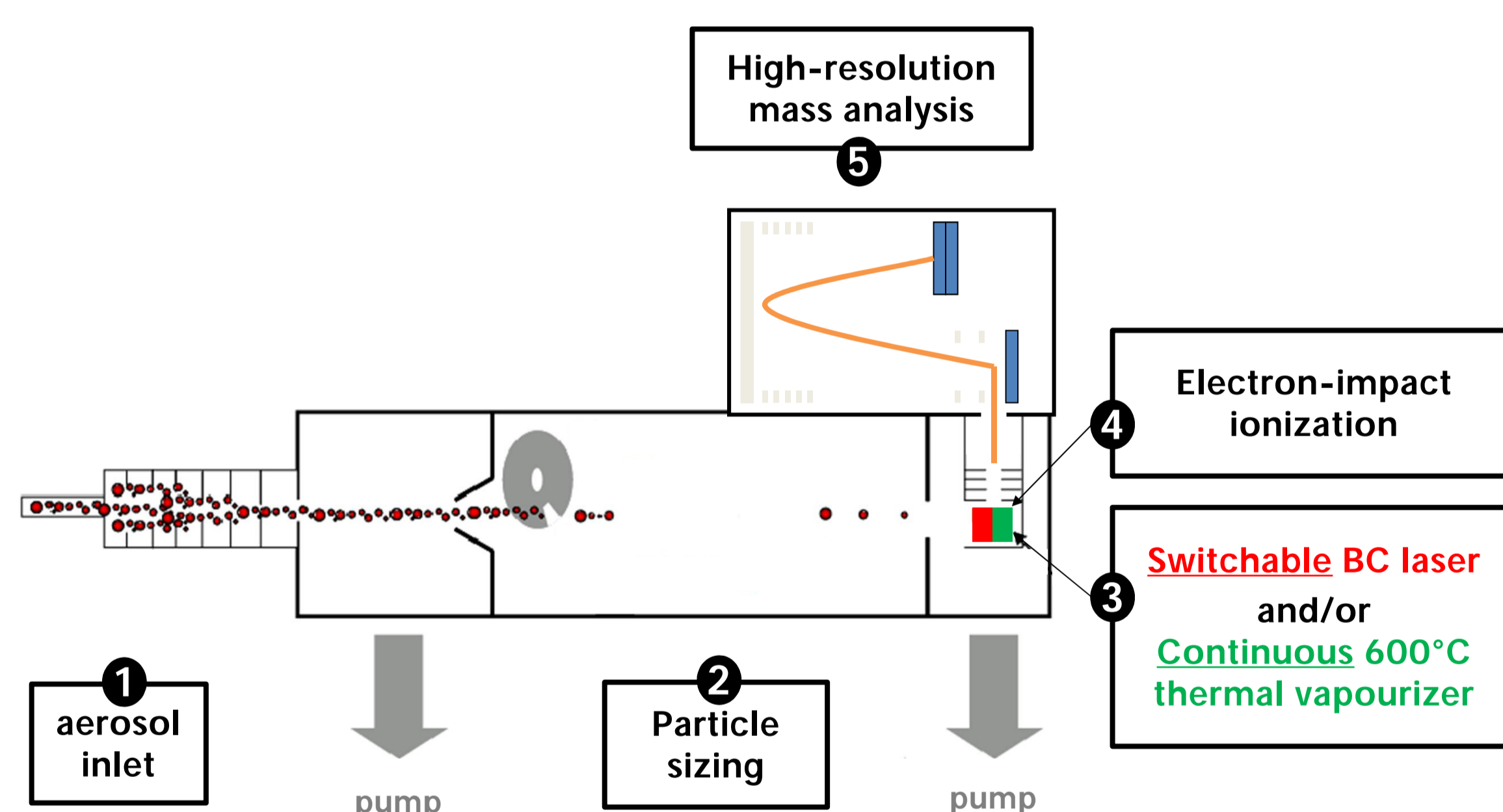


Fig. 2. The Soot-Particle Aerosol Mass Spectrometer (SP-AMS).

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

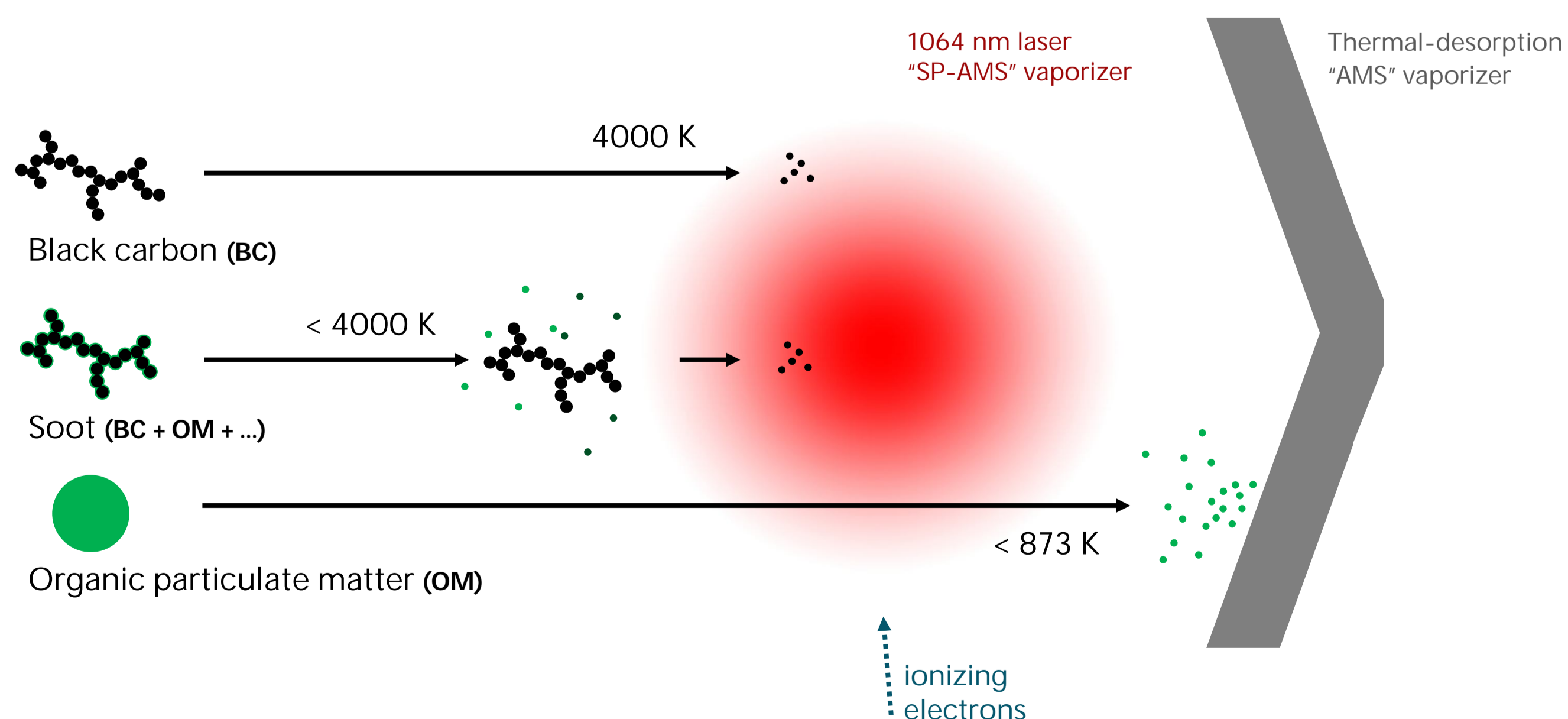


Fig. 3. SP-AMS particle vaporization.

- 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

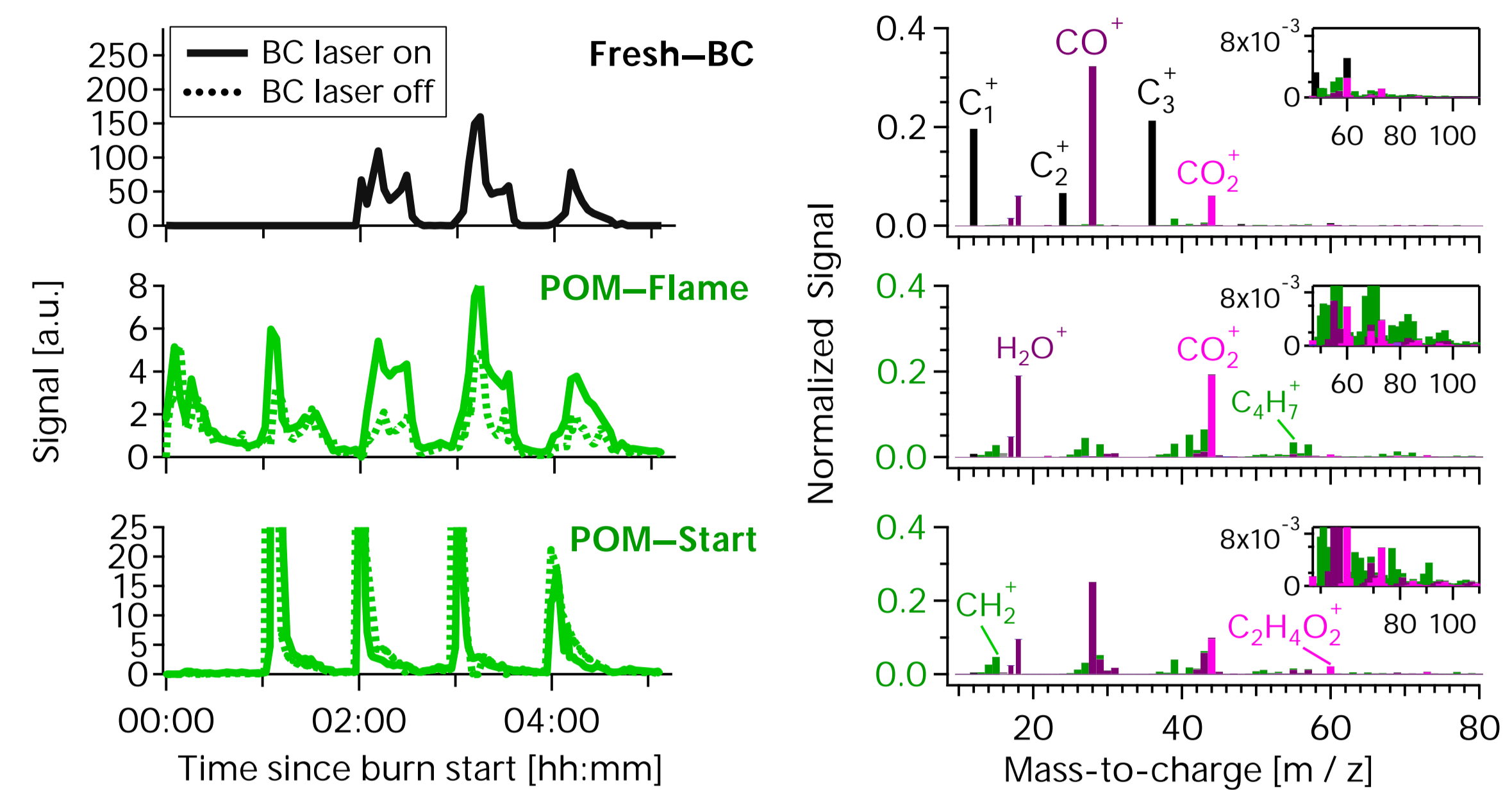


Fig. 4. Factor-analysis results for fresh-emissions SP-AMS mass spectra.

- Positive Matrix Factorization (PMF) was performed to reduce ~400 quantified ions to 3 representative mass spectra and time series⁵ 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 groups⁶. 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.

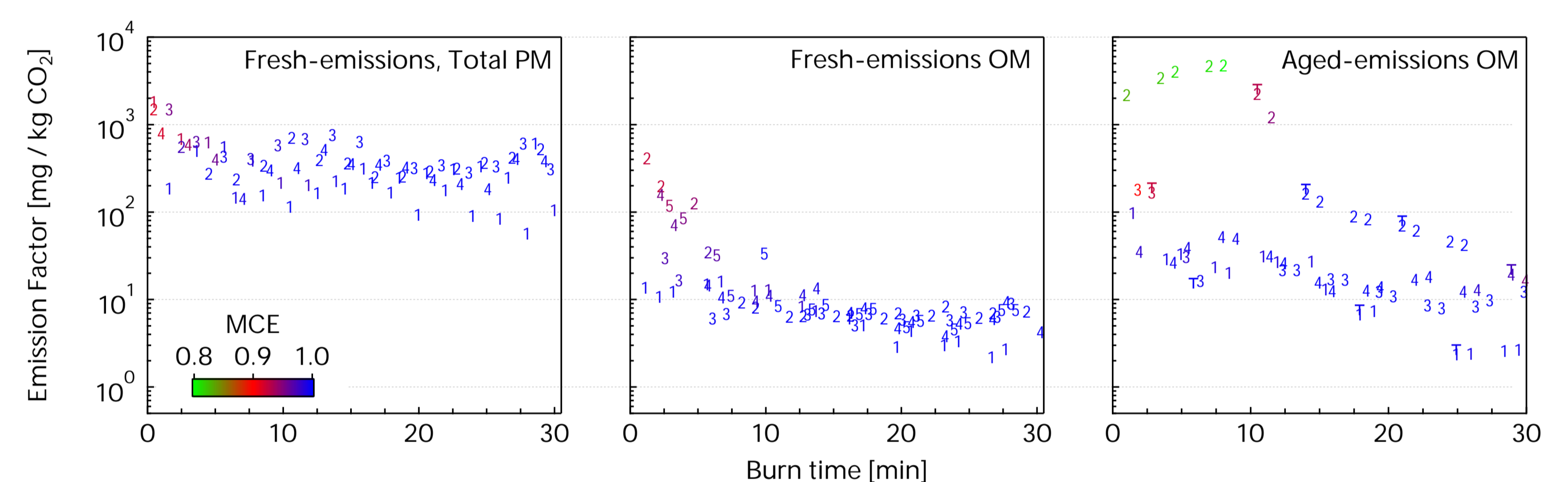
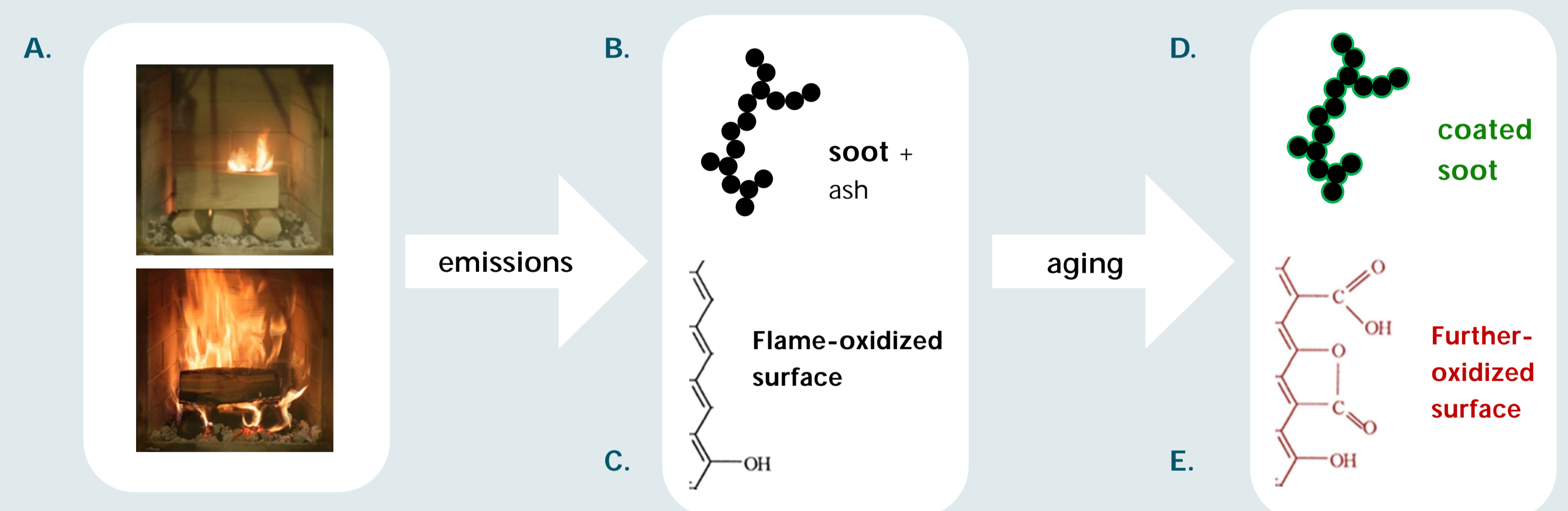


Fig. 5. Emission factors for the 1st, 2nd, 3rd ... burns of different experiments.

- 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



- 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.
- 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.
- 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.
- Simulated aging increased OM emission factors by a factor of 3 – 4.** Current stove-testing protocols do not measure this OM⁴. However, for this stove, BC emissions dominated.
- Surface-group oxidation increased upon simulated atmospheric aging² and remained approximately constant at all stages of combustion.** Increased surface oxidation is known to enhance particle toxicity⁸ and has not been previously measured in situ. Future work will compare these signals for other soot types.

References

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