

Novel Smog Chamber Studies of Primary and Secondary Wood Burning Products at Low Temperature

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Background

Domestic wood burning is a significant source of atmospheric aerosols,¹ particularly in winter, as it is a common heating method in regions with moderate and cold climate. For example, data compiled from several field campaigns in central Europe, ranging from rural to urban sites, show that primary wood burning aerosols contribute 17-49% to the total sub-micron organic aerosol mass in the winter at these sites.¹ Although wood burning is known to contribute to the total aerosol burden in the atmosphere, there are still uncertainties in the magnitude and characteristics of wood burning emissions. For example, the chemical composition and optical properties of wood burning aerosols are not well characterized. This may be because previous laboratory studies were conducted at higher-than-ambient winter temperatures. This may affect both burner operation and gas/particle partitioning of semi-volatile organic aerosol, both of which may affect aerosol composition and loading. Also, gas phase emissions can undergo oxidation to form compounds with sufficiently low volatility to condense and form secondary aerosols. Relatively little is known about secondary wood burning aerosols, although significant formation has been demonstrated in previous laboratory studies.²⁻⁴ The effects of variables such as ambient temperature and burn parameters, particularly on secondary aerosol formation, are unknown. There is clearly a need for further study of primary and secondary wood combustion aerosols to advance our knowledge of atmospheric aerosols and their impacts.

Methods

We report results from smog chamber experiments characterizing primary and secondary wood burning products produced with varying fuel content performed at temperatures representative of central European winter for the first time. Emissions were produced with either ~2 kg (referred to as average loading) or ~7-8 kg (referred to as high loading) initial beech wood mass in a log burner (Attika Avant, 2009). Primary emissions from the flaming phase were diluted to atmospherically-relevant concentrations and injected into the chamber, where OH photochemistry initiated the formation and aging of secondary products. Experiments were performed at 263K and at 50-90% relative humidity. The non-refractory aerosol composition and concentrations were determined using an aerosol mass spectrometer (AMS). Black carbon was analyzed using Aethalometers with and without a thermal desorber in the sampling line. Measurements of gas phase species were made with a suite of instruments, including a proton transfer reaction time of flight mass spectrometer (PTR-MS). Total hydrocarbon concentrations and OH exposure allow for consistent comparisons between experiments.

Results and Conclusions

Primary organic aerosol concentrations in the chamber ranged between 20-125 $\mu\text{g}/\text{m}^3$ and photochemical aging of these emissions resulted in significant secondary aerosol formation for both loading conditions. (Figure 1)

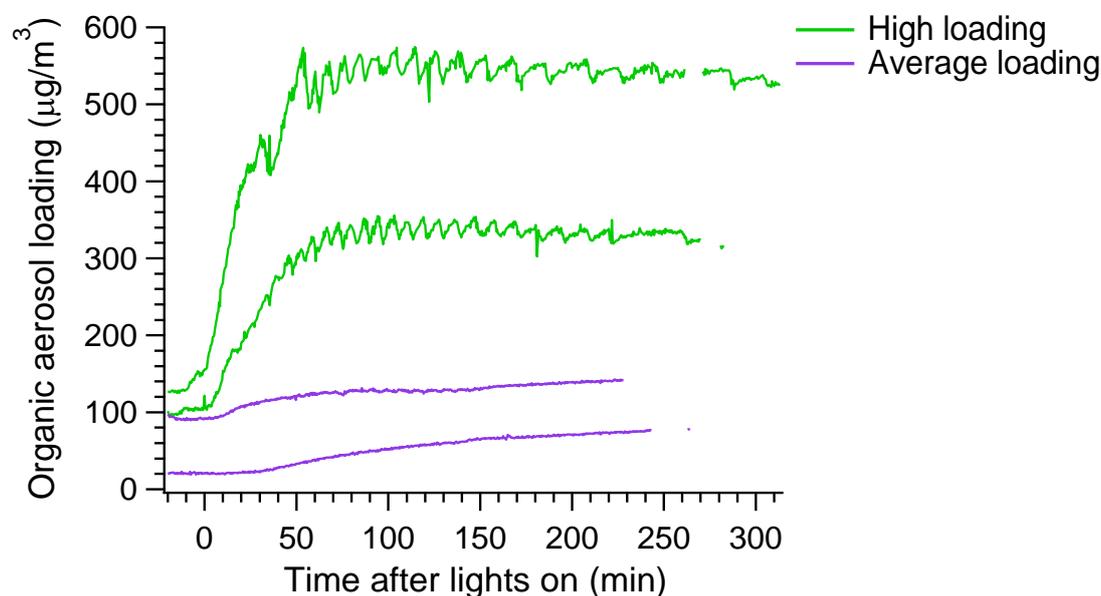


Figure 1. Organic aerosol mass loadings in the chamber as a function of time after UV lights were turned on. High loading corresponds to 7.1-7.8 kg starting wood content in the burner and averaging loading corresponds to 1.9-2.1 kg starting wood content.

However, the chemical composition of the emissions varied depending on initial fuel content in the burner. High resolution mass spectral data from high fuel loading primary organic aerosol was found to contain significantly more polycyclic aromatic hydrocarbons (PAHs) compared to average loadings. The high loading gas phase volatile organic compounds mass spectra also show an increase in PAHs and other aromatic compound concentrations compared to average loading experiments.

Both fuel loadings produced considerable amounts of SOA, however, the chemical composition of the secondary products varied depending on fuel loading. Aging of emissions from both loadings resulted in an increase in m/z 44, which is a marker for oxidized organics, in AMS mass spectra. AMS mass spectra of high loading organic aerosol after aging also show a large decrease in PAH concentration and an increase in aromatic signature peaks (e.g., m/z 51, 65, 77, 91, 105), which is not observed in AMS mass spectra of average loading organic aerosol.

Gas phase volatile organic compound data indicate a decrease in functionalized aromatic compounds, such as cresols and phenol, as well as PAHs with aging. These compounds are likely undergoing oxidation to form lower volatility products which can increasingly partition to the particles. These compounds may fragment in the AMS to produce the signature aromatic peaks observed. Also, increased ring-opening products are known to be formed from naphthalene oxidation under high NO_x conditions,⁷ similar to those observed during the high loading experiments. The increase in characteristic aromatic peaks in the high loading experiments may also be due to the formation of oxygenated PAH compounds which then undergo fragmentation in the AMS. Analysis of offline filter samples will provide additional information on the aerosol composition and possible presence of oxygenated or nitrogenated PAH

As PAHs and their oxidation products are known to have deleterious effects on health, this is a significant finding to aid in the mitigation of negative wood burning impacts by improving burner operation protocols.

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Wir schaffen Wissen – heute für morgen

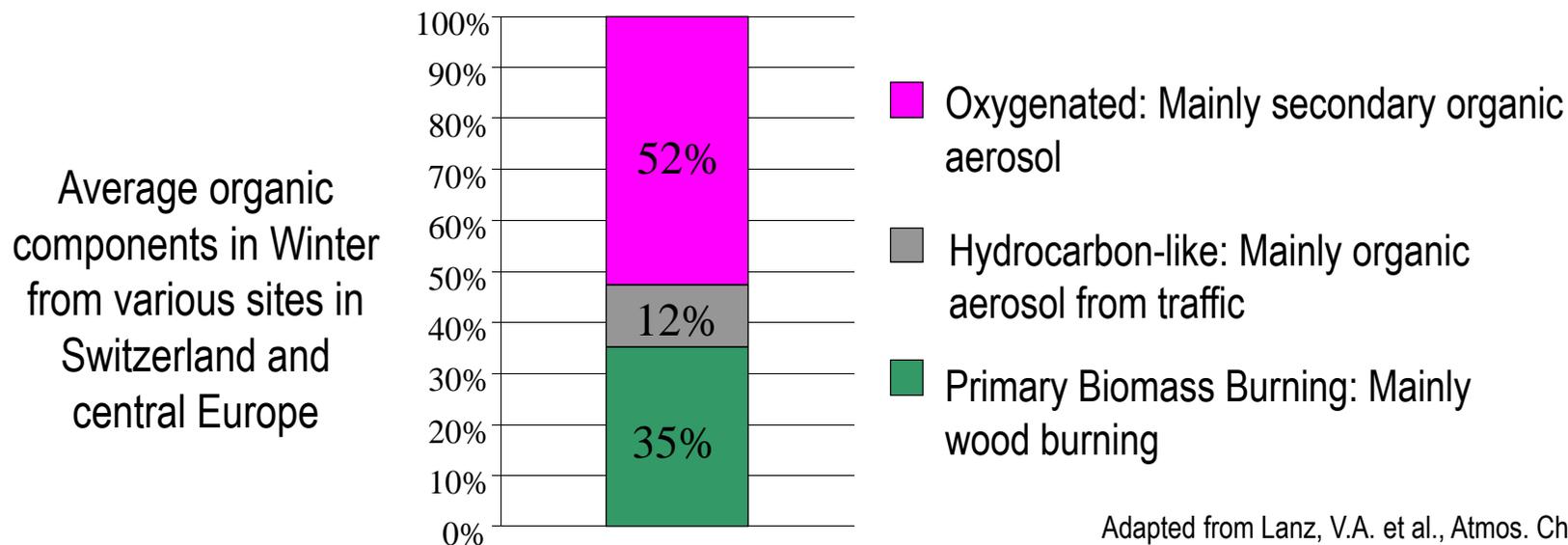
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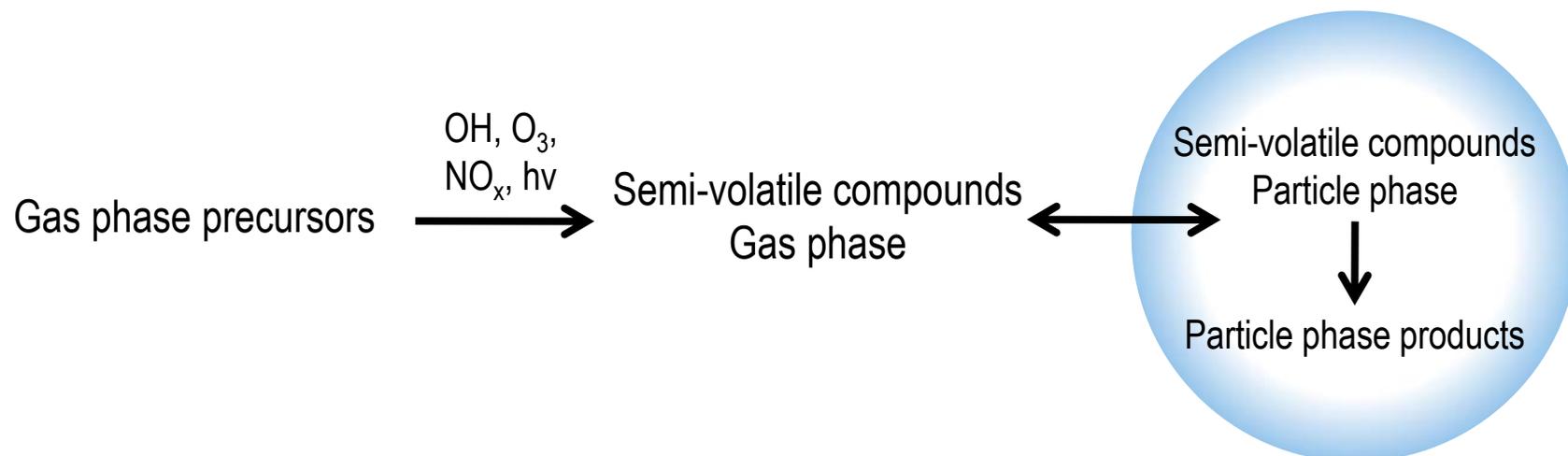
17th ETH Conference on Combustion Generated Nanoparticles

- Biomass burning contribution to atmospheric aerosol loading is significant, particularly in winter.



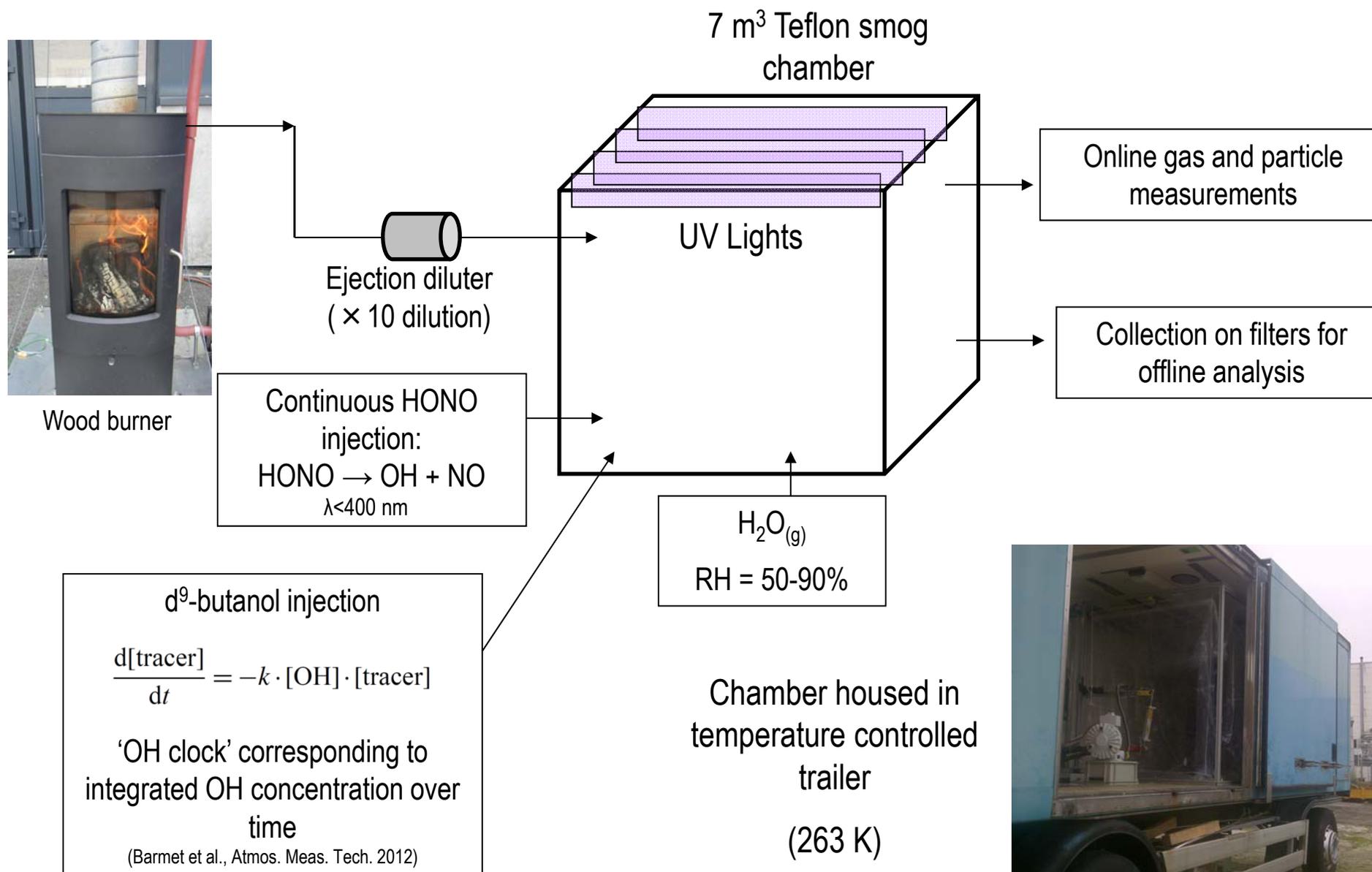
- Large uncertainties in the magnitude and characteristics of wood combustion emissions.
- Secondary aerosols, formed from oxidation of primary emissions, from wood combustion is significant, although poorly characterized.
- Polycyclic aromatic hydrocarbons (PAHs) are known primary emissions from domestic wood combustion.

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- Improve understanding of wood burning emissions characteristics by performing studies under different conditions.
- Improve understanding of conditions which result in formation of PAHs.
- Characterize secondary products under varying chamber conditions.



Varying starting wood content in the burner

1.9 – 2.1 kg



7.1 – 7.8 kg



Beech wood, moisture content ~8-13%

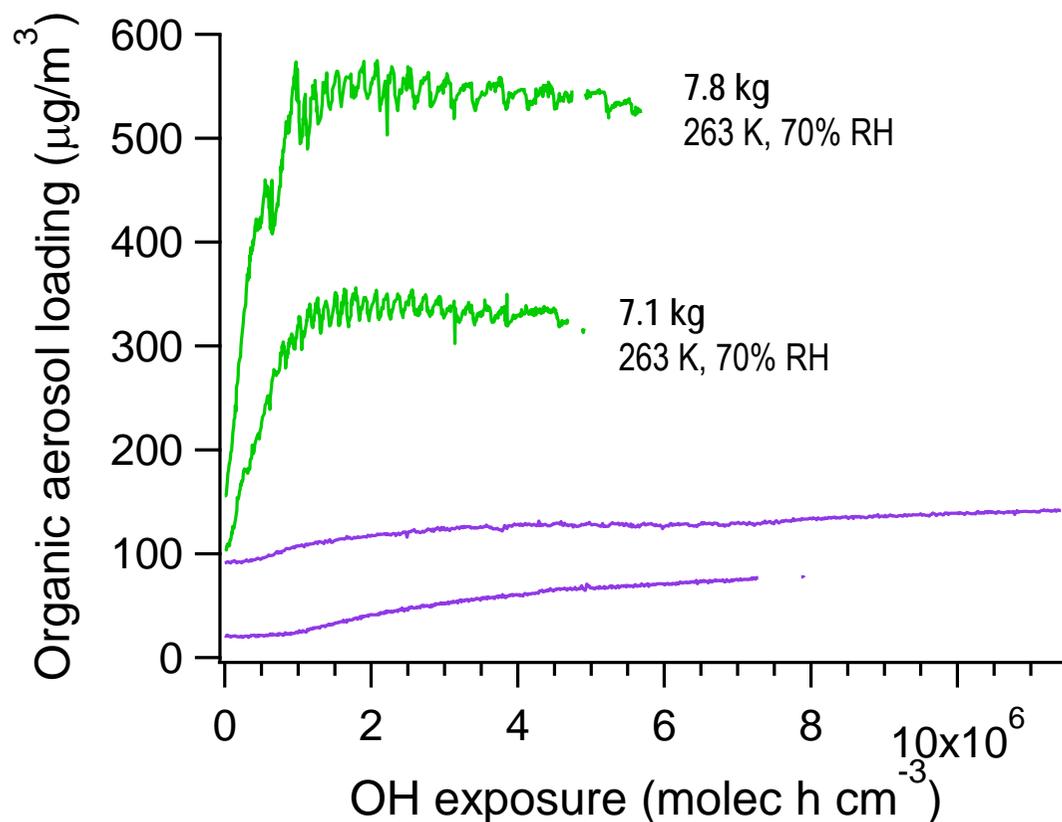
Instrumentation

Gas phase

- Proton transfer reaction mass spectrometer (PTR-MS)
- NO_x analyzer
- O₃ analyzer
- Total hydrocarbon analyzer
- CO₂, CO, CH₄

Particles

- High resolution aerosol mass spectrometer (AMS)
- Aethalometers (with and without thermal desorber)
- Scanning mobility particle sizer (SMPS)
- Condensation particle counter (CPC)
- Offline filter analysis

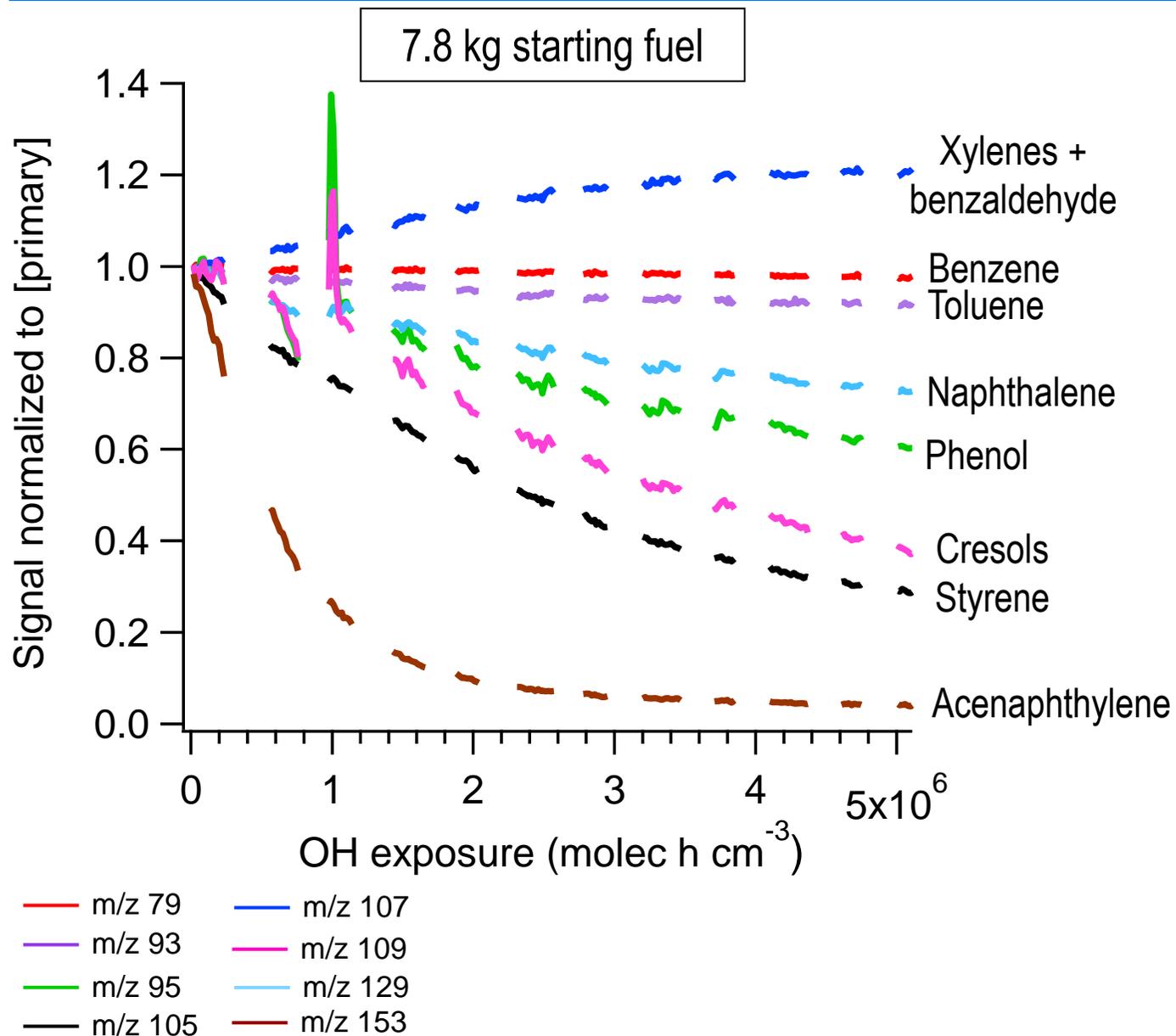


— High loading
— Average loading

- Primary organic aerosol (POA) loadings diluted to ambient levels.
- Significant secondary organic aerosol (SOA) formation observed for both high and average loading.

SOA values (Total organic aerosol – POA) after OH exposure of $4.6 \times 10^6 \text{ molec h cm}^{-3}$

Starting fuel loading (kg)	SOA/POA
1.9	0.4
2.1	2.2
7.1	2.1
7.8	2.6



- Decrease in phenols, naphthalene, acenaphthylene, cresols, styrene, with aging.
- No significant change in benzene or toluene.

- Significant secondary aerosol formation from aging of wood combustion emissions at ambient winter temperatures.
- Increased formation of PAHs with higher wood loading in burner compared to average loading.
- Secondary products formed during aging of emissions from high loading burns significantly different than average loading emissions.
- PAHs are known to have deleterious health effects and adjustment of burner operation can significantly decrease PAH formation.

OPTimization of the use of Wood
As a Renewable Energy Source
(OPTIWARES)



WOOd combustion and SHipping – primary
aerosol emissions and secondary aerosol
formation potential (WOOSHI)



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