Biomass burning emission characterization before and after chemical aging in an atmospheric reaction chamber

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Introduction

- Biomass burning is an important contributor to atmospheric aerosol due to both primary emissions and formation of secondary organic aerosol (SOA)
- High variability in plume composition and aging conditions
- Effects of atmospheric aging are not yet well understood (Hodshire et al, 2019)

Experimental method

- Fire in residential heating stove
- Beech wood and wheat straw as fuel
- Aging of diluted flue gas in atmospheric simulation chamber
- Aging with OH and NO_3 radicals
  - Comparison of daytime and nighttime chemistry
  - Batch mode experiments with aging duration of 4.5 hours
- Variation of relative humidity and NO_x concentration for aging experiments

Campaign set-up

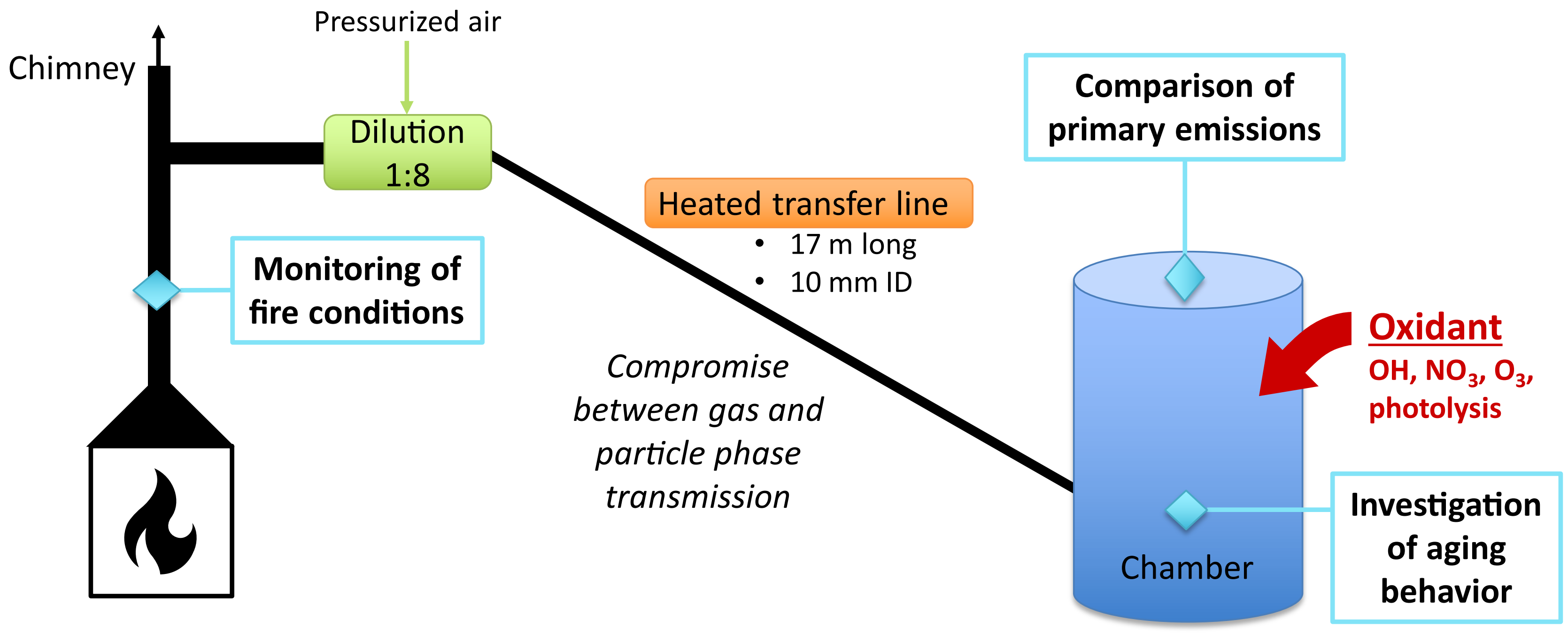


Fig. 1: Scheme showing the full experimental set-up. From left to right: Leibniz Biomass Burning Facility (LBBF), transfer line, atmospheric chemistry department chamber (ACD-C)

Primary emissions

Composition of particulate matter

- Aerosol Mass Spectrometry (AMS) to measure bulk concentration in the particulate matter with an aerodynamic diameter of 1.0 µm or less (PM_1)

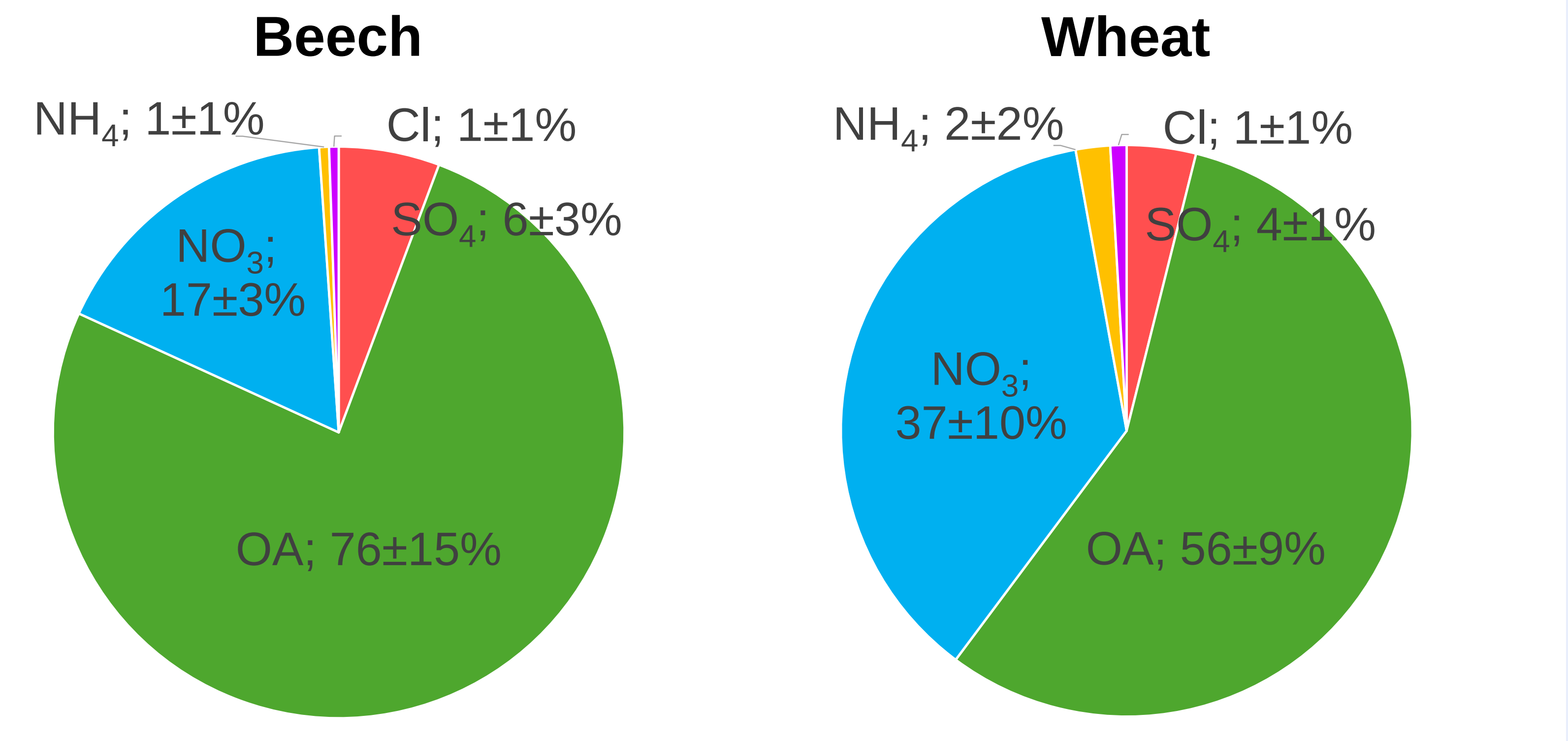
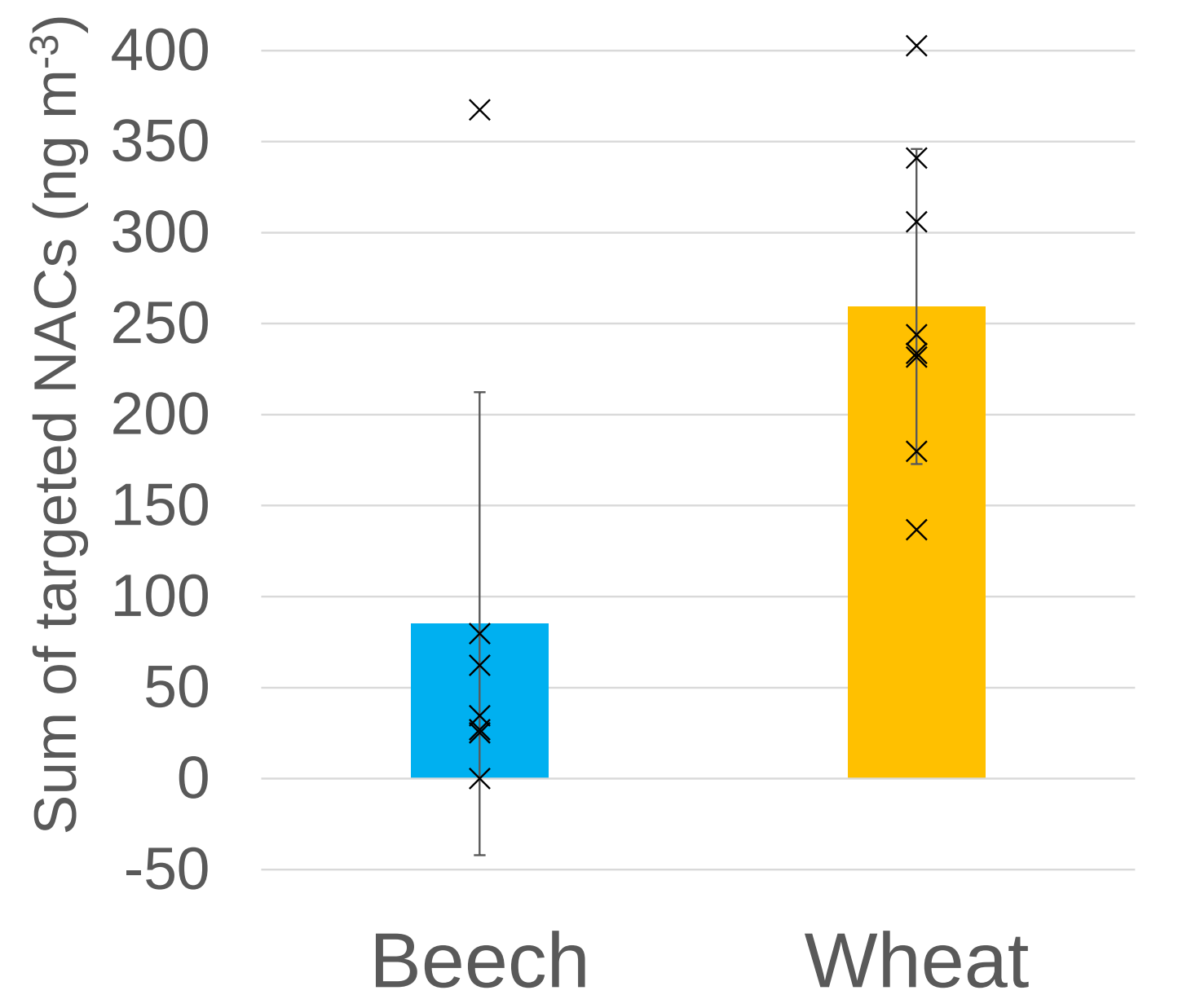


Fig. 2: Relative contributions of organic aerosol (OA), nitrate (NO_3^-), ammonium (NH_4^+), chloride (Cl^-) and sulfate (SO_4^{2-}) to non-refractive PM_1 for beech wood and wheat straw primary emissions

- Fig. 2 shows higher importance of nitrate for wheat straw particle emissions
- Nitrogen content is lower in wood than in foliage (Coggon, et al. 2016)

Filter collection for analysis of organic species

- Measurement of nitroaromatic compounds (NACs) with ultra-high performance liquid chromatography electrospray ionization mass spectrometry (UHPLC-ESI-Orbitrap-MS)
  - High variance between experiments
- Higher concentrations of organic nitrates measured in wheat straw samples



Targeted NACs:
2,4-Dinitrophenol, 2,6-Dinitro-4-Methylphenol, 2-Methyl-4-Nitrophenol, 3-Methyl-4-Nitrophenol, 4-Nitrocatechol, 4-Nitroguaiacol, 4-Nitrophenol, 2-Nitrophenol, 5-Nitroguaiacol

- **Beech**: NACs present 15% (±15%) of all detected targeted compounds
- **Wheat**: NACs present 64% (±7%) of all detected targeted compounds

→ Significant difference in PM organics

Fig. 2: Targeted UHPLC-ESI-Orbitrap-MS measurements of nitroaromatic compounds (NACs)

Aging behavior

Enhancement in organic aerosol

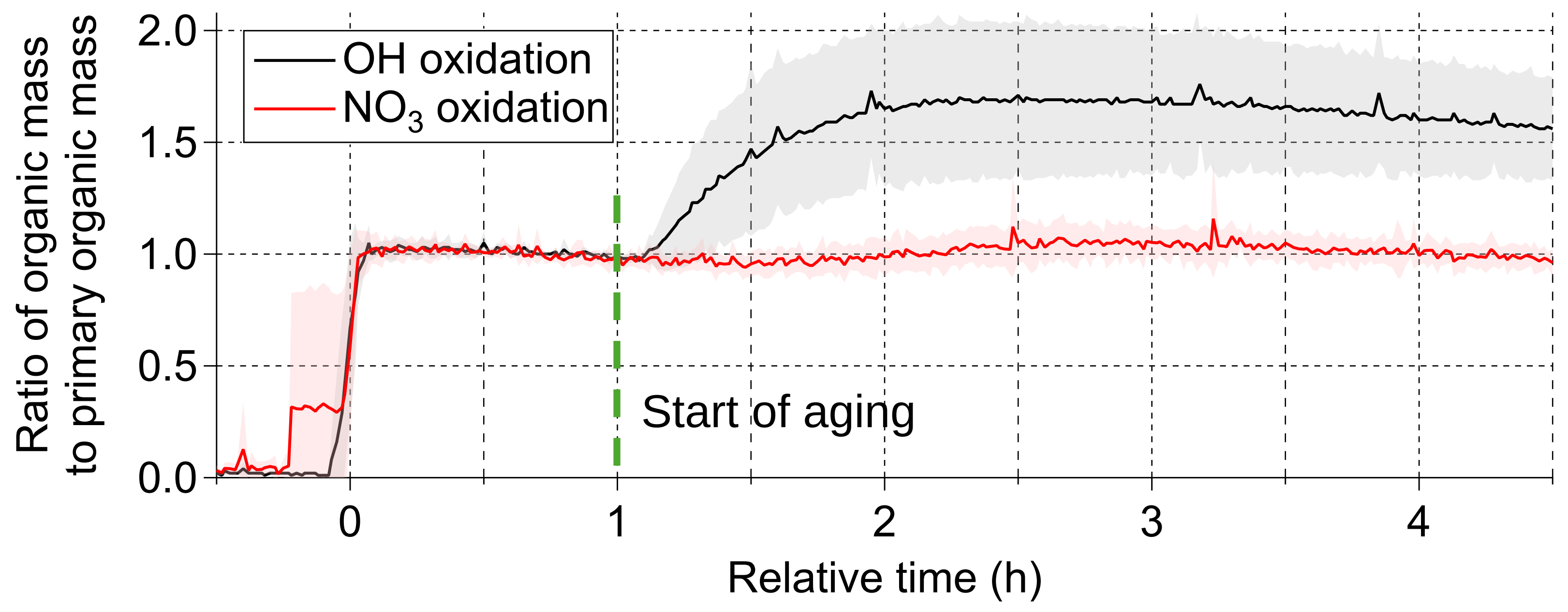
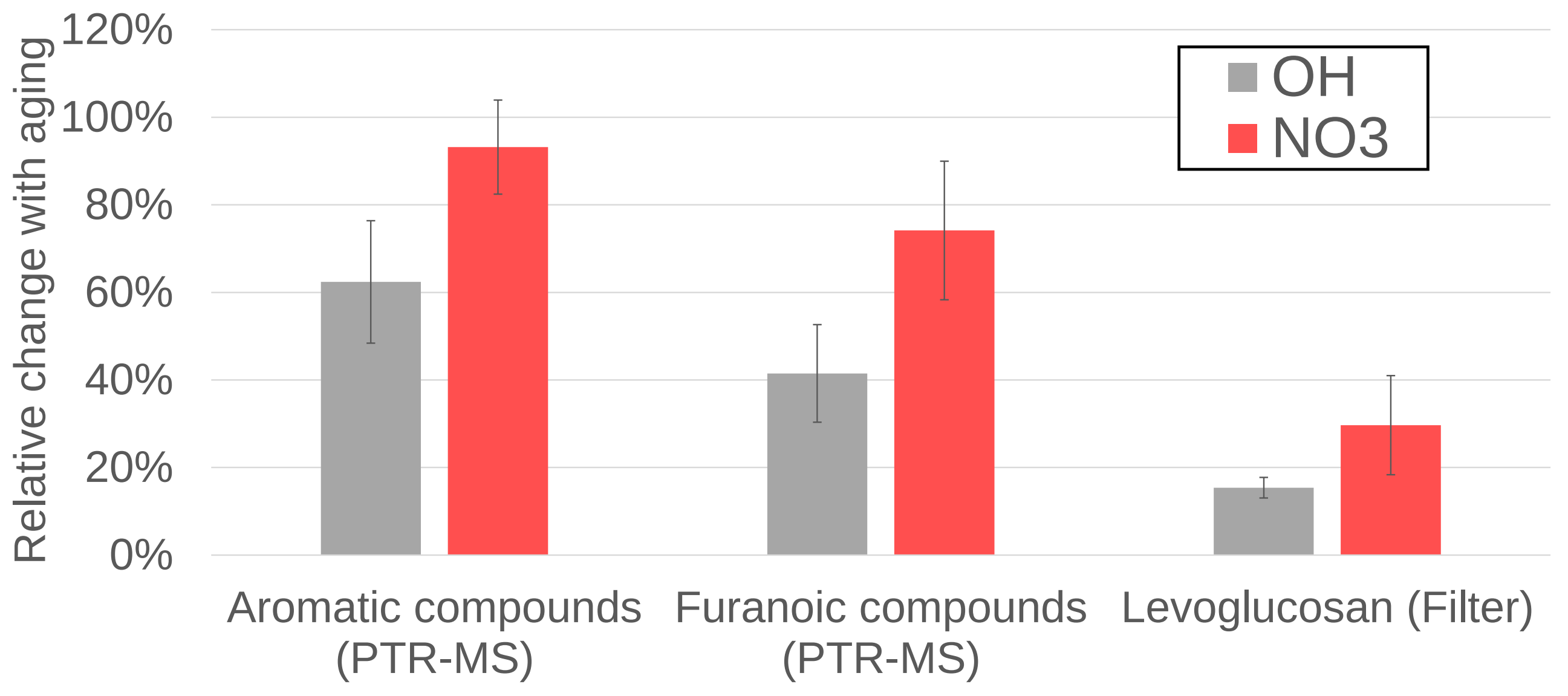


Fig. 3: Timeseries of OA development during aging of wheat burning emissions in comparison to primary OA. Varying levels of relative humidity and NO_x. Line represents average of 4 experiments, shaded area standard deviation. Measurements were wall-loss corrected.

- **Photooxidative aging with OH:** Significant increase in OA mass during aging: Ratio of aged to primary OA of 1.59 ± 0.24 after 4 h
- **Aging with NO_3 radical:** No significant increase in OA mass during aging: Ratio of aged to primary OA of 0.99 ± 0.06 after 4 h
- Indication of important differences between day- and nighttime processing of biomass burning emissions.

Change in biomass burning tracers

- Investigation of low oxidized species characteristic to biomass burning
  - Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) for gas-phase compounds
  - Shown species have been reported as important SOA precursors (Stewart et al. 2021)



Photooxodative aging results in stronger decrease of chosen precursors

Fig. 4: Comparison of biomass burning tracer concentration before and after aging for wheat experiments. Bars represent averages, error bars standard deviations.

Conclusion

- Fire constitutes a complex source with high variability in individual emission events
- Primary emissions vary strongly between fuel sources
- Significant differences between night- and daytime oxidation
- Photooxidative aging results in increasing organic aerosol and O/C

References

Coggon, M. M., et al. (2016), Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers, Geophysical Research Letters 43.18: 9903-9912. **Hodshire, A. L.**, et al (2019), Aging effects on biomass burning aerosol mass and composition: A critical review of field and laboratory studies., Environmental science & technology 53.17: 10007-10022. **Stewart, G. J.** et al. (2021), Comprehensive organic emission profiles, secondary organic aerosol production potential, and OH reactivity of domestic fuel combustion in Delhi, India., Environmental Science: Atmospheres 1.2: 104-117.