Atmospheric transformation of volatile organic compounds released from small-scale wood combustion

A. Hartikainen[1], P. Tiitta[1], P. Yli-Pirilä[1], A. Leskinen[2], M. Kortelainen[1], J. Jokiniemi[1], and O. Sippula[1]
[1]Department of Environmental and Biological Sciences, University of Eastern Finland, P.O. Box 1627, Kuopio, FI-70211, Finland
[2] Department of Applied Physics, University of Eastern Finland, Kuopio, FI-70211, Finland
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Presenting author email: anni.hartikainen@uef.fi

Combustion processes create substantial amounts of particulate and gaseous pollutants. The emissions of small-scale wood combustion are particularly high, due to varying conditions and incomplete combustion. Many of the volatile organic compounds (VOC) emitted in small-scale combustion, such as several aromatic compounds, are known precursors of secondary organic aerosol (SOA). Despite their low concentrations, VOCs have a significant role in the atmospheric chemistry. In atmosphere VOCs go through rapid changes, due to photolysis and oxidation, and also participate in ozone formation. During photochemical aging hydroxyl (OH) radicals are the main oxidant. In contrast, ozone and nitrate radicals dominate the reactions when there is no sunlight available (dark aging). In dark conditions compounds such as nitrous acid (HONO) can accumulate, and form an additional source of OH-radicals when photolysis starts (Monks, 2005).

In this study the VOCs emitted from a modern stove during the combustion of spruce logs were studied. Two modes of ignition, slow and fast, were used to assess the importance of combustion conditions in VOC formation. Flue gas was diluted and led to a smoke chamber (Leskinen *et al*, 2015), where it was consecutively exposed to ambient levels of ozone and UV-light to study dark aging and photochemical aging. In two experiments only UV-light was used, with no added ozone. In addition, the effect of HONO was studied by injecting it to chamber after dark aging in one experiment.

The OH exposures, determined by using butanol-d9 as a marker compound (Barmet *et al*, 2012), ranged from 3.5 to 6.6 $\times 10^{10}$ molecules$\times$cm^{-3}s, which is equal to approximately 0.4 to 0.77 days in the atmosphere. VOC concentrations were monitored using Proton-Transfer Reaction Time of Flight Mass Spectrometry (PTR-ToF-MS), which enables continuous measurement of VOCs with high resolution. Gas and particulate concentrations were also monitored with several other instruments, such as Aerosol Mass Spectrometer (SP-HR-ToF-AMS, Aerodyne Research, Inc.) and Fourier Transform Infrared Spectroscopy (FTIR) gas analyser.

More than 200 single ion peaks (concentration over 0.1 ppb in the chamber) were identified from the mass spectra. A molecular formula could be proposed to two thirds of the peaks. Initial composition was dominated by oxygenated VOCs, with unsaturated hydrocarbons as another important group. Slow ignition produced higher concentrations of VOCs. Samples contained compounds with adverse health effects, such as acetaldehyde and formaldehyde, as well as known SOA precursors.

Examples of the distinct aging patterns of VOCs are presented in Figure 1. Dark aging decreased the concentration of VOCs with double bonds, while the concentrations of nitrogen containing organic compounds increased in both gaseous and particulate phase. In contrast to dark aging, more VOCs decreased during photochemical aging. Simultaneously, with AMS, a considerable increase in organic aerosol mass was observed: 63 – 68 % and 77 – 115 % during dark and photochemical aging, respectively. The results highlight that VOC and organic aerosol emissions from a wood log-fired stoves transform fast in the atmosphere, and that changes take place in both night-, and daytime-like conditions.

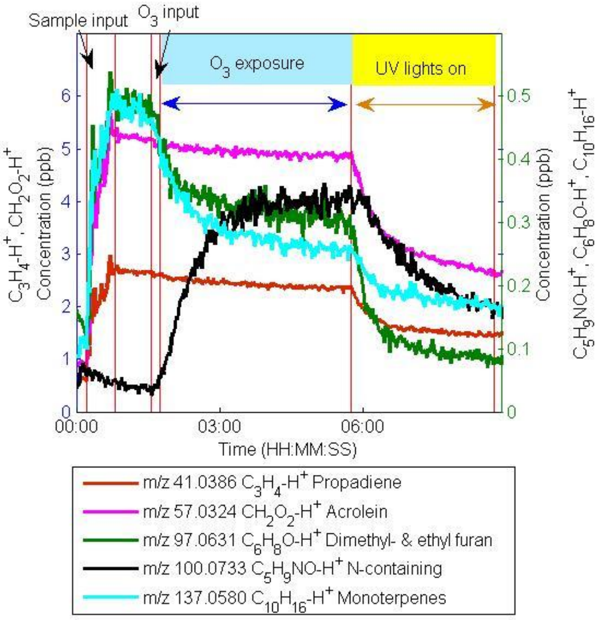

Figure 1. Concentrations of selected VOCs in the smoke chamber during aging (fast ignition, VOC/NO_x-ratio = 3)

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Barmet P. et al. (2012) *Atmos. Meas. Tech.* **5**, 647-656.
Leskinen, A., et. al. (2015) *Atmos. Meas. Tech.* **8**, 2267-2278.
Monks P. S. (2005) *Chem. Soc. Rev.* **34**, 376–395.