

Ageing of the chemical fingerprint at the molecular level of emissions generated by wood burning: a smog chamber study

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Biomass burning is a predominant source of primary organic aerosol (POA), which during the strong pollution events of winter contributes the highest to the total organic aerosol mass (Lanz et al. 2010). However, the contributions estimated to this day by source apportionment models fail to take into account the large secondary fraction potentially formed via the ageing of primary biomass burning emissions.

A large gap still exists in our comprehension of the complex chemical transformations of biomass burning aerosol in the atmosphere. This fact is partly due to the lack of appropriate technology able to provide information at the molecular level with a sufficient time resolution. While online instruments like the HR - ToF - AMS (High Resolution – Time of Flight – Aerosol Mass Spectrometer) or the Aethalometer provide access to the bulk chemical composition of the particulate phase, their chemical resolution do not permit the identification of the actual molecules that compose the organic fraction of the aerosol. The composition of the organic fraction at the molecular level was for a long time only provided by offline measurements with time resolutions incompatible with other methods designed to study emission ageing.

Such technology is now available. The TAG (Thermal Desorption Aerosol Gas Chromatograph) coupled with an HR-ToF-AMS offers detection limits compatible with smog chamber studies. The TAG-AMS (Williams et al. 2014) permits the on-line collection and analysis of the aerosol at the molecular level, with a time resolution of less than an hour. The TAG-AMS used here allows the quantification of the most polar compounds with the implementation of an online derivatization step. For the first time we deployed the TAG-AMS to investigate the ageing of biomass burning emissions within the context of smog chamber experiments.

The experiments took place at the PSI (Paul Scherrer Institute, Switzerland) cool chamber. In order to simulate wintertime conditions, the temperature within the chamber was set at 2 °C and relative humidity was kept at 50 %. After injection, the emissions were characterized for 30 minutes. Photo-oxidation was then initiated and lasted for 4 to 5 hours. The concentration of the OH radical formed by the photochemical decomposition of HONO was inferred from the monitoring of nine-time deuterated butanol (d9-butanol) with a PTR-ToF-MS (Proton Transfer Reaction – Time of Flight – Mass Spectrometer).

Three different types of stoves were tested:

- Stove A: logwood stove, fabricated before 2002.

- Stove B: logwood stove, fabricated after 2010.

- Stove C: pellet stove, fabricated after 2010.

Five to seven samples were collected and analyzed by the TAG-AMS during each experiment. Along with the PTR-ToF-MS and TAG-AMS, a second HR-ToF-AMS and an Aethalometer AE33 were used for real time analysis of the bulk chemical composition of the particulate phase, including the non-refractory material and the black carbon.

A hundred of fine particulate organic compounds were identified and quantified. Here we compare the molecular level data measured by the TAG to the total organic aerosol as obtained by the AMS. We also present the evolution of specific markers of biomass burning during ageing, including but not limited to, levoglucosan and its isomers mannosan and galactosan, substituted guaiacol compounds (vanillin, acetovanillone, connyferyl aldehyde), and substituted syringol compounds (syringaldehyde, syringyl acetone, acetosyringone). We evaluate the potential degradation of certain of these compounds and the implications of such results for marker based source apportionment studies.

Lanz et al., Characterization of aerosol chemical composition with aerosol mass spectrometry in Central Europe: an overview, *Atmos. Chem. Phys.*, *10*, 104553-10471, 2010.

Williams et al., The first combined Thermal Desorption Aerosol Gas Chromatograph- Aerosol Mass Spectrometer (TAG-AMS), *Aerosol Sci. Technol.* *48*, 358-370, 2014.