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# Fine Particle Emissions from Solid Biofuel Combustion Studied With Single Particle Mass Spectrometry

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An increased use of biofuels in residential heating is desired to decrease net emissions of green house gases, such as CO<sub>2</sub> to the atmosphere. This includes conventional woody biofuels, as well as novel crop fuels such as corn. It is well established that the particle emissions during less optimised combustion in small scale wood combustion are most often dominated by products of incomplete combustion, i.e. organic and elemental carbon (OC/EC), McDonald et al. (2006). In contrast during optimised combustion in modern domestic pellet combustion systems, the aerosol can be dominated by ash compounds, especially KCl and K<sub>2</sub>SO<sub>4</sub> formed via heterogeneous reactions in the gas-phase.

However, little research has focused on the variations in physical and chemical particle properties over the combustion cycle. This is partly due to the lack of experimental methods with sufficient time resolution to follow the inherently transient nature of batch wise wood log combustion. Further, little information is available on emissions from novel fuels such as corn. For example, corn has higher ash content than conventional wood fuels.

In this work we used an Aerosol Time-of-Flight Mass Spectrometer (TSI Inc., Shoreview, MN, USA) to study chemical signatures of single particles from three wood log fuels (oak, pine and birch) and corn. The instrument was equipped with an aerodynamic focusing lens inlet. The wood fuels were combusted in a conventional wood stove, while the corn was combusted in a commercially available corn stove, which operates similarly to modern wood pellets stoves.

Each wood-combustion experiment involved start-up from a cold stove with a full load of fuel. Fuel was then added once and experiments were conducted until only glowing embers remained. Particles were sampled and diluted with particle free air using a three stage dilution system which allowed dilution ratios between 1:10 and 1:10000. In a few experiments a Differential Mobility Analyzer was used upstream of the ATOFMS to determine the particles effective density.

A Scanning Mobility Particle Sizer was used to determine the particle size distribution (20-800 nm). A gas analyzer (TSI CA-6215) was used to determine the flue gas composition (O<sub>2</sub>, NO<sub>x</sub>, CO).

Preliminary results show clear differences in the particle composition between:

1. The three different wood fuels
2. Wood and corn fuels
3. Different regions in the combustion cycle for the wood fuels

When the corn stove was operating optimally, markers for inorganic ash components were dominant. These included <sup>39</sup>K<sup>+</sup>, <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup> and <sup>213</sup>K<sub>3</sub>SO<sub>4</sub><sup>+</sup>. Note that the corn combustion process is semi-continuous as opposed to batch-wise log combustion, where distinct combustion phases can be identified.

During the start-up phase and during throttling of the supply air in wood combustion, strong organic markers were present. Several of these, for example *m/z* =45 (C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>), -59 (C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>) and -71 (C<sub>3</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>) have previously been detected from pure levoglucosan (Silva et al. 1999), a dominant organic component from low temperature wood combustion. In the efficient combustion phase, many markers for organic compounds diminished, while e.g. <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup> was strongly enhanced. A large number of high mass peaks in the positive spectrum (e.g. *m/z* +203, +209 and +235) were present during soft wood combustion (Pine). These are likely markers of polycyclic aromatic hydrocarbons (PAHs).

Overall the laser-desorption ionization approach used in the ATOFMS instrument enables us to detect signatures from both organic compounds and low volatility alkali salts, such as KCl and K<sub>2</sub>SO<sub>4</sub>. The combination of these two classes of signatures is promising for source receptor studies. The ATOFMS is also a promising tool to assess various fuels for their impact on emissions.

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