

Organic aerosols from residential wood burning emissions analysed by Ultra-high resolution mass spectrometry

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Biomass burning (BB) is considered as one of the largest primary sources of organic aerosols in the atmosphere. The chemical composition of BB aerosol is diverse and depends e.g., on the chemical composition of the burning material. Emissions from residential fireplace combustion of wood have been shown to be major contributors to air pollution during winter months. The fraction of BB particle mass is not easily identified with conventional analytical techniques due to the highly complex compound mixtures in organic aerosols.

Here we present results of ultra-high resolution mass spectrometry (UHR-MS), which has unique capabilities to characterize complex samples (Nizkorodov, 2011), (Rincón, 2012). UHR-MS allows identifying unambiguously the elemental composition of thousands of compounds in a single analysis and gaining information about the structure and formation mechanisms of organic compounds in aerosols.

The BB sample was collected from a typical open fire stove used in Portugal for residential heating. The burning test was made using a predominant tree species in Portugal *Pinus pinaster* (Maritime pine) and it was carried out at the combustion facility of the University of Aveiro. The complete description of the facility and other parameters continuously monitored during the experiment are published elsewhere (Goncalves, 2011). Particulate matter with aerodynamic diameters below 2.5 μ m was collected onto quartz fibre filters.

The water-soluble organic fraction of the filter extracts was separated from inorganic ions by a solid phase extraction step and re-dissolved in acetonitrile-water prior to analysis. UHR-MS analyses were performed using an LTQ Orbitrap Velos, with an accuracy below 2ppm, using an electrospray ionisation source. Mass spectra were measured by direct infusion, in negative and positive polarities and recorded within the range of 50-500m/z. Molecular formulas were assigned to the exact masses of more than 3000 compounds in a single sample using the XcaliburTM software and additional software written in-house.

Figure 1 shows a van Krevelen plot of H/C versus O/C of the compounds containing carbon, hydrogen and oxygen, detected in negative and positive polarity. Compounds with high H/C ratio (H/C>2) and a double bond equivalent (DBE) of zero are measured mostly in positive mode. They correspond to saturated oxygenated species, which contain at least 6 carbon and 3 oxygen

atoms in each formula. Possible compounds could be long chain polyalcohols. The lower left corner of the diagram contains the most unsaturated compounds (DBE>8) with low O/C and H/C ratios likely oxidized polyaromatic hydrocarbons. Compounds with O/C \geq 1 were detected mainly in negative polarity and include dicarboxylic, hydroxy and ketocarboxylic acids with less than 7 carbon atoms. Other signatures of the samples consist of a variety of carboxylic acids, phenolic compounds and carbonyl compounds.

Mass spectral pattern of these samples are also compared to ambient samples to identify the BB signatures in the ambient samples. More highly oxidized compounds, including organo sulfates and organo nitrates are more abundant in ambient samples compared to BB samples. In contrast a higher number of components from BB samples exhibit an olefinic and aromatic nature than in ambient samples. These findings are consistent with the lack of aging in the BB samples.

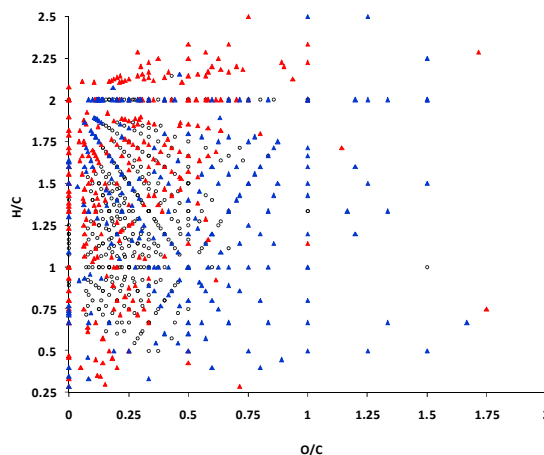


Figure 1. Van Krevelen diagram of C_xH_yO_z containing organics measured in negative (\blacktriangle), positive (\blacktriangle) MS mode and compounds measured in both polarities (\circ).

Nizkorodov, S.A., Laskin, J., and Laskin, A. (2011). *Phys. Chem. Chem. Phys.*, **13**, 3612-3629.

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