

Chemical and Structural Characterization of Organic Aerosol Emitted from Laboratory Burning of Boreal and Arctic Peat by 21T FT-ICR MS.

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Large-scale peatland fires are known high emitters of organic-carbon-rich particulate matter (PM), and are expected to further increase in frequency and size in the northern hemisphere due to climate change. 21T Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is a powerful tool for the chemical characterization of organic aerosols emitted by peatland fires, due to their extreme molecular complexity that includes heavily- and low-oxygenated molecules, as well as combinations with multiple heteroelements like N, S and P.

Peat samples from four locations (2x Boreal/Arctic), were dried and burned in lab experiments simulating real-world peatland wildfires. The resulting PM was collected on filters and extracted by MeOH/DCM for extensive characterization of the organic aerosol by 21T FT-ICR-MS. Electrospray ionization (ESI+/-) was applied to address polar organic species, in combination with atmospheric pressure photoionization (APPI) to address non-/low polar constituents. Structural information was obtained by infrared multiphoton dissociation (IRMPD) of isolated mass ranges.

Chemical characterization of Boreal and Arctic peat burning emissions by ESI revealed an extremely complex mixture of organic aerosol compounds, including high numbers of oxidized N and S species. The combustion type was predominately smoldering with some variance between the samples, highlighting the influence of the local vegetation and microbial activity on the peat composition and its combustion. Arctic peat generated a partially similar, but less oxidized and more nitrogen- and sulfur-containing organic aerosol, clearly different compared to the Boreal peat. The high abundance of sulfur-containing compounds is a result of the particularly high amounts of organic sulfur species in *Sphagnum* moss derived peat. Northern peatland wildfires therefore need to be considered as a primary source of organic sulfur compounds to the atmosphere.

Two main structural motifs were characterized in all peat samples: single-core condensed aromatic ring systems with minor alkylation (combustion-derived) and multicore ring systems with medium/low aromaticity and high degree of alkylation (lignin-decomposition derived).