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Online measurement of biogenic organic acids in the boreal forest using atmospheric pressure chemical ionization mass spectrometry (APCI-MS)

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Emission of biogenic volatile organic compounds (BVOCs) by vegetation in the boreal forest and their subsequent atmospheric oxidation leads to the formation of secondary organic aerosol (SOA) which has important impacts on climate and human health. Oxidation of BVOCs produces a variety of mostly unidentified species in oxygenated organic aerosol (OOA). Presently aerosol mass spectrometers (AMS) are able to determine quantitative information about the relative oxygen to carbon content of organic aerosols and thereby reveal the photochemical age and volatility of organic aerosol by distinguishing between low volatile oxygenated organic aerosol (LV-OOA), semivolatile oxygenated organic aerosol (SV-OOA) and hydrocarbon like organic aerosol (HOA)[1]. However, the AMS can usually not be used to measure and quantify single organic compounds such as individual biogenic organic marker compounds.

Here we show the results of online measurements of gas and particle phase biogenic acids during HUMPPA-COPEC 2010 at Hyytiälä, Finland. This was achieved by coupling a self built miniature Versatile Aerosol Concentration Enrichment System (mVACES) as described by Geller et al. [2] with an Atmospheric Pressure Chemical Ionization Ion Trap Mass Spectrometer (APCI IT MS; Hoffmann et al., [3]). The benefits of the on-line APCI-MS are soft ionization with little fragmentation compared to AMS, high measurement frequency and less sampling artifacts than in the common procedure of taking filter samples, extraction and detection with LC-MS. Furthermore, the ion trap of the instrument allows MS/MS experiments to be performed by isolation of single m/z ratios of selected molecular species. By subsequent addition of energy, the trapped ions form characteristic fragments which enable structural insight on the molecular level.

Comparison of APCI-MS data to AMS data, acquired with a C-ToF-AMS [4], revealed a good correlation coefficient for total organics and sulphate. Furthermore, data show that high molecular organic acids in biomass burning aerosol seem to make up a larger amount than in "normal" boreal forest aerosol indicating that the aerosol is highly oxidized. FT-IR data of filter measurements also show high O:C ratio during the biomass burning events. Interestingly, although the instrumental setup was not targeted on gas phase organic acids, the majority of the measured signal is attributed to gas phase species. The online mass spectra show clear patterns on the molecular level and reveal a significant influence of the oxidation state of the molecules on gas-to-particle partitioning. Especially the intermediate volatile organic compounds (IVOCs), e.g. pinonic acid, did show high concentrations and a clear diurnal cycle in gas phase.

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