Online Measurements of Organic Acids in the Gas and Particle phase

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We present measurements of a large suite of gas and particle phase carboxylic acid containing compounds made with a Filter Inlet for Gas and AEROsol (FIGAERO) coupled to a high resolution time of flight chemical ionization mass spectrometer (HR-ToF-CIMS) developed at the University of Washington. The instrument was deployed on the Jülich Plant Atmosphere Chamber to study α-pinene oxidation, and subsequently at the SMEAR II forest station in Hyytiälä, Finland and the SOAS ground site, in Brent Alabama. We focus here on results from JPAC and Hyytiälä, where we utilized the same ionization method most selective towards carboxylic acids (acetate negative ion proton transfer). In all locations, hundreds of organic acid compounds were observed in the gas and particles and many of the same composition acids detected in the gas-phase were detected in the particles upon temperature programmed thermal desorption. Particulate organics detected by FIGAERO are highly correlated with and explain at least 25 – 50% of the organic aerosol mass measured by an AMS. The fraction of a given compound measured in the particle phase follows expected trends with elemental composition such as O/C ratios, but many compounds would not be well described by an absorptive partitioning model assuming unity activity coefficients. The detailed structure in the thermograms reveals a significant contribution from large molecular weight organics and/or oligomers in all regions. Approximately 50% of the measured carboxylic acid functionalities in the particle phase are associated with compounds having effective vapour pressures 4 or more orders of magnitude lower than commonly measured monoterpene or isoprene oxidation products. We discuss the implications of these findings for measurements of gas-particle partitioning and validation of SOA formation models.