Gas and Particle Phase Acids in a Ponderosa Pine Forest

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We use data from a high-resolution time-of-flight chemical ionization mass spectrometer (HRToF-CIMS, Yatavelli et al 2012) to derive chemical formulas for aerosol particles and gas-phase acids measured continuously for a 10-day period during August 2011 in a Ponderosa Pine forest in South-Western Colorado, USA. This study was part of the "Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen - Rocky Mountain Biogenic Aerosol Study" (BEACHON-RoMBAS) project focused on the study of secondary organic aerosol (SOA) precursors, and their transformations and impacts in the atmosphere.

The newly developed MOVI technique (Yatavelli *et al*, 2010) was used to simultaneously study gas phase and aerosol particles. The use of acetate as reagent ion (Veres et al, 2008) in combination with the HRToF-CIMS allowed us to selectively and simultaneously measure the entire population of inorganic and organic acids at the same time. Data were acquired at 2Hz, MOVI cycles were repeated every 90 min. Data analysis was performed using the analysis package "Tofware", embedded within the commercial data analysis program "Igor Pro" (Wavemetrics, Inc.).

We will describe the specific methods developed to assign chemical formulas to all ion peaks measured in each mass spectrum, resulting in more than 1800 different unique formulas. The formulas, together with their ion peak areas, were used to perform elemental analysis and derive chemical properties such as elemental ratios (e.g. O:C, H:C, N:C) and average carbon oxidation state (OS_c), both for the bulk composition as well as a function of carbon number.

Figure 1 shows a diagram of approximate oxidation state as a function of carbon number for the aerosol during a 24-hr period of the campaign ("Kroll diagram", Kroll et al, 2011).

These data help to understand the volatile organic compound (VOC) emissions from a Ponderosa Pine forest, their gas-phase chemical transformations as well as the formation of secondary organic aerosol (SOA).
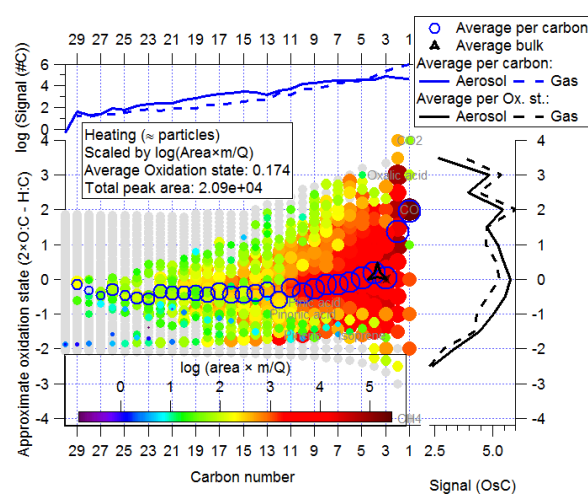

Figure 1: "Kroll diagram" for 24-hour average of "heating" ($\approx$ aerosol) on August 20th, 2011. Colored circles: individual data; blue circles: average data per carbon number, sized by log(ion peak area×m/Q), black triangle: bulk average OS_c, blue line: avg. log(ion peak area×m/Q) vs. carbon number: solid: aerosol, dashed: gas phase, black line: avg. log(ion peak area×m/Q) vs. oxidation state: solid: aerosol, dashed: gas phase; grey circles: expected possible data range

The data show wide ranges of carbon numbers and oxidations states, suggesting a variety of VOC emissions and chemical processing. In general, gas-phase signals show higher signal at lower carbon numbers and higher bulk oxidation states than aerosol signals.

We also compare our results for acids to total organic aerosol mass (OA), measured by the AMS, and find that a significant fraction of OA consists of acids.

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