α-pinene secondary organic aerosol yields increase under higher relative humidity and low NOx conditions

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In this study, we investigate through systematic smog chamber experiments secondary organic aerosol (SOA) formation from the oxidation of α-pinene, a major biogenic precursor. The aim is to examine the impact of NOx/VOC ratios and particulate water content on SOA chemical composition and yields. This is performed by varying NOx/α-pinene ratios (0.04–3.8), aerosol seed composition (acidic to neutralized sulfate-containing) and relative humidity (RH) from 25% to 65%. We present wall-loss-corrected yields as a function of the absorptive mass concentration. A combination of a scanning mobility particle sizer and an Aerodyne high resolution time-of-flight aerosol mass spectrometer was used to determine SOA mass concentration and chemical composition.

Figure 1 shows a comparison of SOA yields as a function of RH obtained at low and high NOx conditions. We observe a substantial increase of SOA yields with RH, up to six times (1.5–6.4) compared to low RH. The yields at low NOx/VOC ratios (0.04–0.07) were in general higher compared to yields at high NOx/VOC ratios (1–3.8).

SOA yields are generally described by the absorptive equilibrium partitioning of condensable species to a well-mixed liquid phase, which depends upon the chemical species' saturation vapor pressures and their liquid-phase activities. Donahue and co-workers proposed the use of a "volatility basis set" (VBS) for a better representation of the wide range of SOA in the atmosphere (Donahue et al., 2011).

In this study, we present a novel approach of data evaluation using volatility bin distributions derived from the smog chamber data as basis for thermodynamic phase partitioning calculations. α-pinene photooxidation products described in the literature were assigned to volatility bins according to their vapor pressures. Phase partitioning between the gas and condensed phase(s) was calculated taking liquid-liquid phase partitioning into account (Zuend et al., 2010). Activity coefficients were calculated with AIOMFAC (Zuend et al., 2011) and vapor pressures using EVAPORATION (Compernolle et al., 2011). We found that equilibrium partitioning between gas phase and liquid phases can explain the increased SOA yields at high RH by adding more fragmented and oxidized organic compounds to the model mixtures in addition to α-pinene products

described in the literature. This increase is driven by both a mass effect because of the additional water in the particles and solution non-ideality described by the activity coefficients.
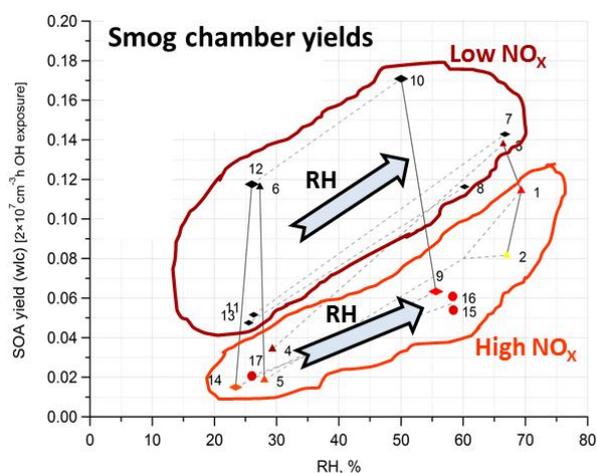

Figure 1. SOA yields as a function of RH for low NOx (1–2 ppbv) and high NOx (20–75 ppbv) conditions. Corresponding experiments with RH change are connected by dashed lines, corresponding experiments with NOx level change by solid lines.

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