

Volatility distribution and viscosity effects in evaporation of a-pinene SOA

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Dynamics of gas-particle partitioning change the composition and size of the atmospheric aerosol particles. To capture these changes for secondary organic aerosol (SOA) in global models, parameterizations for the saturation concentration (C^*) distribution of oxidized organics have been developed based on SOA growth experiments. However, a-pinene SOA – used as a proxy for atmospheric SOA – evaporates slower than expected based on these volatility distributions and this can be an indication of particle phase mass transport limitations due to semi-solid particle phase (Vaden *et al.*, 2011). Also, extremely low volatile organic compounds, not present in the previous C^* parameterizations, have been detected (Ehn *et al.*, 2014) and the effect of vapor wall losses on SOA experiments has been discussed (Kokkola *et al.*, 2014). In this study we investigate the role of different processes in the slow evaporation of a-pinene SOA.

We generated a-pinene SOA by ozone oxidation in a continuous flow tube reactor, selected a monodisperse (diameter 80 nm) particle sample with a nano-DMA and lead the selected particles to a clean 100 litre polished stainless steel chamber. The nano-DMA was operated in an open loop configuration in order to dilute the gas phase. Particles were sampled after the nano-DMA, bypassing the evaporation chamber, for the short residence time data (~7-15 s). Data at intermediate residence times (~30 minutes) was obtained by sampling at the end of the evaporation chamber while the chamber was being filled. The chamber was closed after filling and reopened for sampling after 2 hours which provided data at long residence times (~2-4 hours). Particle size was monitored with a Scanning Mobility Particle Sizer and composition with a High Resolution Aerosol Mass Spectrometer. The measurements were performed with evaporation taking place either in dry conditions, at RH 75 % or at RH 40 %.

The evaporation measurements were interpreted using a modified version of the kinetic multi-layer model KM-GAP (Shiraiwa *et al.*, 2012) and a liquid particle evaporation model. Organics were represented with volatility basis set (VBS) using 8 C^* bins between 10^{-3} - 10^4 $\mu\text{g}/\text{m}^3$. At RH 75 % the particles are presumably liquid, and, thus, we fit the liquid particle evaporation model to the data from these wet experiments using the genetic algorithm to find the initial particle composition. Several different 8-bin VBSs were found for the initial composition which all captured the observed evaporation well; in all cases > 20 % of initial mass was in $C^* \leq 10^{-2}$ bins, a major fraction of mass was in 10^{-1} - 10^0 $\mu\text{g}/\text{m}^3$ bins and also some $C^* \geq 10^1$ $\mu\text{g}/\text{m}^3$ compounds were present.

The conditions in the flow tube were similar in all experiments and, thus, at the start of the evaporation (at the nano-DMA) particle composition was presumably similar in all experiments. We used the initial composition obtained from the wet experiment for simulating the evaporation in the dry conditions with the kinetic multi-layer model with varying particle viscosity. To capture the observed evaporation, a strong composition dependence for the viscosity of the dry particles was needed with values increasing from $\sim 10^5$ Pa s over four orders of magnitude along the evaporation. However, evaporation at RH 40 % was similar to RH 75 % indicating that in atmospheric conditions particle phase mass transport limitations are not significant.

Particles' O:C ratio was constant along the evaporation, suggesting that the low-volatile compounds in particles were not highly oxidized but instead products from oligomerization – possibly taking place in the particle phase. Thus the effect of oligomer decomposition on the evaporation rate can not be disregarded.

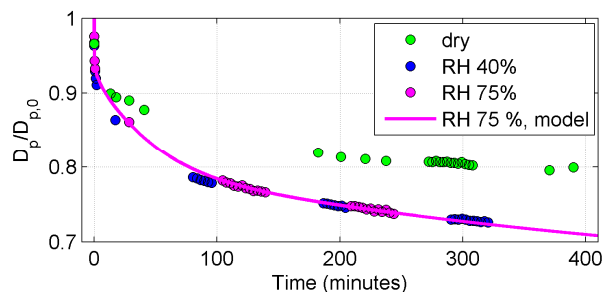


Figure 1. Measured particle diameter normalized with the initial diameter as a function of the evaporation time in the dry conditions, at RH 40 % and at RH 75 %. Also the best fit simulation for RH 75 % is shown.

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