



## How oxidative aging and particulate water content change the volatility and chemical composition of $\alpha$ -pinene secondary organic aerosol particles

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The volatility of oxidation products of volatile organic compounds (VOCs) in the atmosphere is a key factor to determine if they partition into the particle phase contributing to secondary organic aerosol (SOA) mass. Once in the particle phase, the fate of semi-volatile compounds can be influenced by the presence of particulate water, which may initiate aqueous phase reactions. Additionally, water can act as a plasticiser in the (semi-)solid SOA particles reducing mass transport limitations in the particle bulk.

To study the links between initial particle composition, water content and volatility, we investigated SOA from photooxidation of  $\alpha$ -pinene at different oxidation levels (characterised by average oxygen to carbon ratio, O:C = 0.5, 0.7, and 0.95) with a filter inlet for gases and aerosols on a chemical ionisation mass spectrometer (FIGAERO-CIMS), which yields both composition and thermal desorption information for the collected particles. Particles were characterised directly after production, and again after several hours of evaporation in clean air in a residence time chamber (RTC) at two different relative humidity settings (RH < 2%, and 80%). Additionally, we monitored the changes in particle size during isothermal evaporation in the RTC, which yield a direct measure of particle volatility.

With increasing initial oxidative age, we observed reduced particle evaporation and shifts to higher desorption temperatures in FIGAERO-CIMS thermograms. Particle evaporation was increased in the presence of water vapour and presumably particulate water. In addition, SOA particles of the highest oxidation level exhibited strong signs of aqueous phase chemistry.

For a more detailed analysis of these particle phase processes, we applied Positive Matrix Factorization (PMF) to the thermogram mass spectra data. The identified factors represent volatility classes which can be compared qualitatively to volatility basis set (VBS) distributions derived from e.g. modelling the evaporation curves. Four to seven PMF factors were needed to reproduce the measured thermograms. Larger contributions of the low volatility classes were observed with increasing average O:C ratios. As expected from the thermograms, the residual particles after evaporation in the RTC contained a higher contribution of low volatility classes, but contrary to the expectation the average O:C ratio of the particles did not change with evaporation.

These results have important implications on our understanding of the fate of particles as they are transported and undergo further oxidation in the atmosphere. Higher oxidation levels and dry conditions make particles more resilient against evaporation. Under wet conditions, aqueous phase reactions seem to become more important at higher oxidation levels.