

## Insights into the storage aging effects on dimer esters and other oligomers in beta-pinene secondary organic aerosol samples

J. Resch<sup>1</sup>, K. Li<sup>1</sup>, M. Kalberer<sup>1\*</sup>

<sup>1</sup>Department of Environmental Sciences, University of Basel, Basel, Switzerland

Collection of secondary organic aerosol (SOA) onto filters is often used in combination with LC-MS for detailed chemical characterization. Studies have shown that a large fraction of laboratory-generated SOA can be attributed to high molecular weight oligomeric compounds. Often there is a significant delay between sample collection and analysis which may lead to changes in the chemical profile of the samples.

In this study beta-pinene SOA was generated by O<sub>3</sub> and OH oxidation and collected onto filters, which were either extracted in a mixture of water and acetonitrile or left on the filter, to investigate changes in the overall chemical composition profile over time up to one month. The samples were analyzed by UHPLC-ESI-MS in negative polarity mode. An untargeted approach led to several thousand detected compounds and principal component analysis indicated a significant difference between the samples stored on filters or as extracts. In order to understand these differences, further focus was put on previously identified carboxylic acids, dimer esters and other oligomers tentatively assigned to the ester class.

The signal intensity for oligomers in the chromatograms decreases over time in extracts, which can be explained by hydrolysis causing decomposition of esters and other components. On the other hand, the signal intensity on filters shows a strong increase for dimers and trimers, which suggests a further chemical aging of the SOA particles (or "film") deposited on the filters which allows further reactions of SOA monomer compounds to form dimers and trimers. The two different storage conditions represent two atmospheric processing conditions: (1) the aging of SOA under dry conditions favoring oligomerization over long time scales of days and (2) the effects occurring when SOA partitions into cloud droplets where water is promoting hydrolysis and decomposition of oligomers back to monomers.

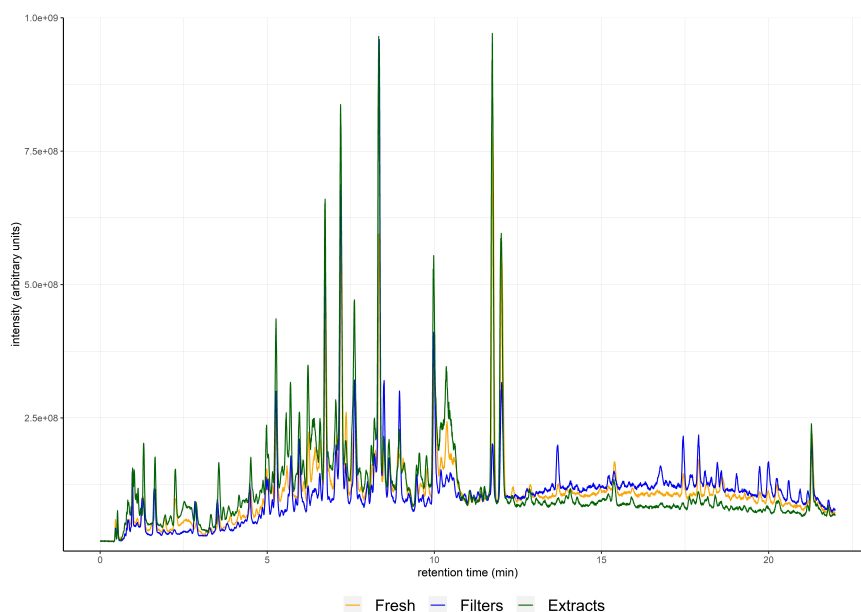


Figure 1: Total Ion Chromatogram representing fresh (orange), 4-week-old filter (blue) and extracts (green). Monomers elute at a retention time between 2-12 minutes and oligomers between 12-22 minutes.