

# Molecular Characterization of Biogenic SOA using online Extractive Electrospray Ionization Mass Spectrometry: On the fate of condensed phase ELVOC

F. D. Lopez-Hilfiker<sup>1</sup>, V. Pospisilova<sup>1</sup>, U. Molteni<sup>1</sup>, M. Xiao<sup>1</sup>, J. Dommen<sup>1</sup>, A. Prevot<sup>1</sup>, U. Baltensperger<sup>1</sup>, J. G. Slowik<sup>1</sup>

<sup>1</sup>Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI, 5232, Switzerland

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Presenting author email: [felipe.lopez@psi.ch](mailto:felipe.lopez@psi.ch)

Recent measurements of the oxidation products from biogenic precursors by chemical ionization mass spectrometry (CIMS) have revealed a large source of extremely low volatility organic molecules (ELVOC) formed at high yield (Ehn et al. 2014). These molecules can contribute to new particle formation and subsequent particle growth despite their low gas phase abundance. Semi-continuous measurements of aerosol composition and volatility measured by FIGAERO-CIMS from both chambers as well as temperate and boreal forests show that >50% of the total organic aerosol from biogenic sources has low or extremely low volatility. This finding is largely consistent with a significant source of secondary organic aerosol (SOA) formed from the condensation of initially low volatility organic vapors; however, the tendency of these molecules to undergo ionization-induced fragmentation and/or thermal decomposition has to date prevented their direct measurement.

As such, the fate of highly oxidized organics formed in the gas phase in the condensed phase remains an open question. If highly oxidized organic molecules undergo net fragmentation during particle phase processing the overall efficiency which low volatility gas phase organics form aerosol is significantly diminished. Alternatively, if intra-particle reactions lead to the efficient formation of dimers and higher order accretion products then the effective yield and persistence of ELVOC based SOA formation is greatly enhanced.

Here, we present the first direct online measurements of individual organic aerosol components at atmospherically relevant particle mass loadings without thermal decomposition or ionization-induced fragmentation, using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) recently developed at PSI. We focus on the measurement of highly oxidized, low volatility organic molecules and oligomers, which are formed rapidly and in high yield from a variety of biogenic precursors (monoterpenes, sesquiterpenes, isoprene). We investigate the fate of highly oxidized gas phase organics in the particle phase and assess the degree that fragmentation and/or accretion reactions occur during particle ageing. To investigate these particle-phase formation and ageing mechanisms the EESI-TOF was deployed at the PSI atmospheric simulation chamber where biogenic precursor compounds were oxidized under a variety of conditions. We operate the chamber in both batch mode and continuous flow modes. Gas phase composition is measured online by CIMS (Jokinen et al. 2012) and particle phase composition is monitored by the EESI-TOF and SMPS. Figure 1a presents an example of one

such experiment during the oxidation of  $\alpha$ -pinene by ozone, during which  $15 \mu\text{g m}^{-3}$  of SOA was formed. The figure shows an example of the level of molecular detail and high time resolution provided by the EESI-TOF, illustrated by the particle phase evolution of a series of individual molecular species. Figure 1b shows a mass defect plot, which shows the distribution of monomers and some dimers, colored by number of carbon atoms and sized by the log of the signal during the early part of the experiment.

Our measurements utilizing the EESI-TOF and a variety of biogenic precursor molecules provide a new level of molecular insight that allows the direct assessment of particle phase oligomerization, fragmentation and intra-particle ageing reactions. We discuss these individual and combined effects on SOA formation, lifetime and response to atmospheric changes as well as the implications of these findings for measurements of gas-particle partitioning and validation of SOA formation models.

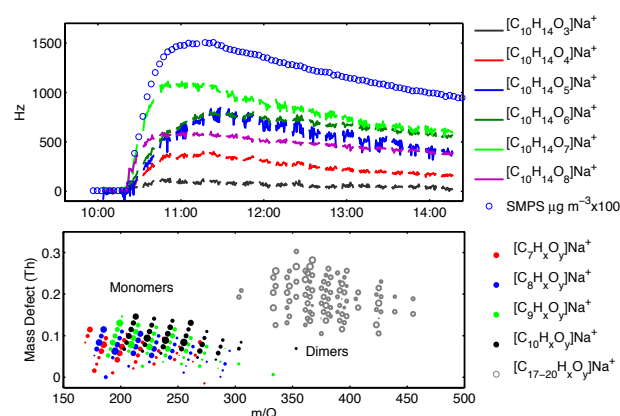


Figure 1. Top. Timeseries of an example chamber experiment during which a suite of highly oxidized organic molecules were detected online in the particle phase by EESI-TOF mass spectrometry. Bottom. Mass defect plot showing the different classes of compounds detected in real time during the experiment.

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Ehn, M. et al. 2014. *A large source of low-volatility secondary organic aerosol*. *Nature* 506(7489): 476–479.

Jokinen, T et al. 2012. *Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF Atmospheric Chemistry and Physics* 12(9): 4117–4125.