Impact of seed composition and aerosol acidity on volatility of secondary organic aerosol compounds formed from α-pinene ozonolysis

Matthieu Riva¹, Otso Peräkylä¹, Liine Heikkinen¹, Mikael Ehn¹

¹Department of Physics, P.O. Box 64, 00014, University of Helsinki, Helsinki, Finland <u>Keywords</u>: Volatility, SOA, FIGAERO-CIMS.

Presenting author email: matthieu.riva@helsinki.fi

Atmospheric aerosols are critical in many environmental processes. It is now recognized that the largest mass fraction (20–90%) of atmospheric fine particles (PM_{2.5}) is generally organic, and is mostly dominated by secondary organic aerosol (SOA) formed from the oxidation of volatile organic compounds (VOCs) (Hallquist *et al.*, 2009). Monoterpenes, which are abundantly emitted into the Earth's atmosphere and derived from terrestrial vegetation, are well-established important SOA precursors.

The most abundant monoterpene in the troposphere is α pinene. The ozonolysis of α -pinene has become a model SOA system for many experimental works. Identification of multifunctional particle phase products has been reported, including carboxylic acids and highmolecular-weight compounds, although molecular structures and formation pathways of oligomers remain uncertain. Recently, highly oxidized compounds (HOMs) were identified in significant concentrations in the gas phase from the α -pinene ozonolysis (Ehn et *al.*, 2014). These HOMs could then condense irreversibly onto aerosol surfaces to produce SOA. Further heterogeneous oxidation processes have been revealed by the presence of dimers in particle phase (Kristensen et al., 2014; Zhang et al., 2015). For instance Kristensen et al. (2014) have identified that humidity can significantly increase the concentrations of dimers in the particle phase. Oligomers could, however, have a significant impact on the physical properties, such as volatility, of SOA, which remain hitherto poorly characterized (Lopez-Hilfiker et al., 2016).

The aim of the present work was to examine the impact of humidity, seed composition as well as the aerosol acidity on volatility of SOA formed from α -pinene ozonolysis. Experiments were conducted under wet (50-60% RH) or dry (<5 % RH) conditions at room temperature ($24 \pm 2^{\circ}$ C) and atmospheric pressure in a 2m³ Teflon chamber. Gas- and particle-phase multifunctional organic compounds were chemically characterized using Filter Inlet for Gases and AEROsols (FIGAERO) coupled to a high resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) with iodide as reagent ion chemistry. Hundreds of compounds were observed in both gas and particle phases. SOA was characterized by temperatureprogrammed thermal desorption of collected particles. Thermograms were obtained for individual compounds under a large variety of conditions (i.e. humidity, acidity, seed composition). These results reveal the heterogeneous processes occurring in the particle phase, which influence the concentration of oligomers. The presence of such HOMs in particle phase is correlated with a lower volatility of SOA.

This work was supported by the European Research Council (ERC) (Grant 638703-COALA).

- Ehn, M.; Thornton, J.A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I.-H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurtén, T.; Nielsen, L.B.; Jørgensen, S.; Kjaergaard, H.G.; Canagaratna, M.; Maso, M.D.; Berndt, T.; Petäjä, T.; Wahner, A.; Kerminen, V.-M.; Kulmala, M.; Worsnop, D.R.; Wildt, J.; Mentel, T.F. (2014). Nature 505, 476-479.
- Hallquist, M.; Wenger, J.C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N.M.; George, C.; Goldstein, A.H.; Hamilton, J.F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M.E.; Jimenez, J.L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T.F.; Monod, A.; Prévôt, A.S.H.; Seinfeld, J.H.; Surratt, J.D.; Szmigielski, R.; Wildt, J. (2009). *Atmos. Chem. Phys.* 9, 5155-5236.
- Kristensen, K.; Cui, T.; Zhang, H.; Gold, A.; Glasius, M.; Surratt, J.D. (2014). *Atmos. Chem. Phys.* 14, 4201-4218.
- Lopez-Hilfiker, F.D.; Mohr, C.; Ambro, E.L.; Lutz, A.; Riedel, T.P.; Gaston, C.J.; Iyer, S.; Zhang, Z.; Gold, A.; Surratt, J.D.; Lee, B.H.; Kurten, T.; Hu, W.W.; Jimenez, J.; Hallquist, M.; Thornton, J.A. (2016). *Environ. Sci. Technol.* Just Accepted.
- Zhang, X.; McVay, R.C.; Huang, D.D.; Dalleska, N.F.; Aumont, B.; Flagan, R.C.; Seinfeld, J.H. (2015). *Proc. Natl. Acad. Sci.* **112**, 14168-14173.