Role of particle phase processes and condensation of LVOCs in the atmospheric nanoparticle growth – a modelling study

T. Yli-Juuti[1,2], I. Riipinen[3], U. Pöschl[2] and M. Shiraiwa[2]

[1]Department of Applied Physics, University of Eastern Finland, Kuopio, FI-70211, Finland
[2]Multiphase Chemistry Department, Max Planck Institute for Chemistry, DE-55128, Mainz, Germany
[3]Department of Applied Environmental Science and Bert Bolin Centre for Climate Research, Stockholm University, Stockholm, SE-10691, Sweden
Keywords: nanoparticle growth, condensation, organic aerosol, new particle formation.
Presenting author email: taina.yli-juuti@uef.fi

Atmospheric secondary aerosol particles can impact climate if these nanoparticles grow tens of nanometers in diameter and reach cloud condensation nuclei sizes. This growth is largely due to uptake of atmospheric organic and inorganic trace gases, out of which organics make a significant fraction. Oxidation of volatile organic compounds in the atmosphere produces large variety of compounds with different volatility. Only low-volatile organic compounds (LVOC) can contribute significantly to the nanoparticle mass. In addition to gas phase oxidation, LVOCs can be formed in particle phase processes. Therefore, uptake of organic compounds on nanoparticles can proceed two ways: by condensation of gas phase LVOCs or by uptake of gas phase semi-volatile organic compounds (SVOC) followed by production of LVOCs in the particle phase (Riipinen et al, 2013).

This study aims to identify the groups of organic compounds and the processes that are important for atmospheric nanoparticle growth. We focus on four processes: salt formation and oligomerization in particle phase, condensation of LVOCs and particle phase mass transport. First two processes transfer SVOCs into LVOCs and the last one is related to kinetic limitations arising from physical phase state of the particles. The four processes likely take place at the same time but have varying importance along the particle growth and possibly also affect each other (Riipinen et al, 2012).

We developed and utilized a new growth model, KM-GAP-T (KM-GAP with Thermodynamics). KM-GAP-T combines two previously developed models KM-GAP (Shiraiwa et al, 2012) and MABNAG (Yli-Juuti et al, 2013) and, therefore, includes 1) detailed representation of mass fluxes in/between gas phase, particle surface and particle bulk phase, 2) comprehensive thermodynamics of acid-base chemistry of organic-inorganic mixture based on E-AIM (Clegg and Seinfeld, 2006), 3) kinetics of particle phase oligomerization and 4) non-ideality of the mixture based on E-AIM.

We designed the nanoparticle growth simulations to represent boreal forest environment. The condensing organic trace gases were grouped and represented by four model compounds: a LVOC, two SVOCs (an aldehyde and a peroxide) that can form a dimer in the particle phase and an organic acid. Condensing compounds contained also sulphuric acid, ammonia and water. Many of the properties of atmospheric organic compounds are unknown or have large uncertainty, and thus a range of values was tested for such properties, e.g. reaction rate of SVOCs for forming a dimer (k_b) and saturation vapour pressures (p_{sat}).

Based on the model simulations condensation of LVOCs is important, especially at the smallest particle sizes (Fig. 1). Oligomerization may contribute to the growth if reaction rate of SVOCs is high, e.g. due to acidity of the particles, especially if the p_{sat} values of these compounds are at the lower end of the SVOC range. Organic salt formation is important at elevated base concentrations in case of relatively strong organic acids.
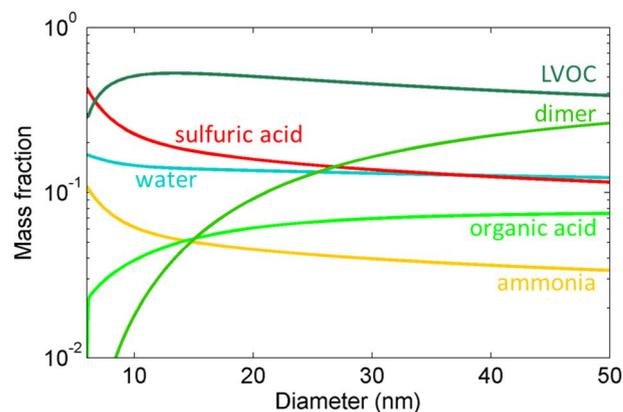

Figure 1. Mass fractions of each compound in particle phase in a simulation with $k_b = 10^{-20}$ cm^3 s^{-1} and p_{sat} of SVOCs $6 \cdot 10^{-4}$ Pa and $2 \cdot 10^{-4}$ Pa and estimated boreal forest gas phase conditions.

Clegg, S. L., & Seinfeld, J. H. (2006) *J. Phys. Chem. A* **110**, 5718-5734.

Shiraiwa, M., Pfrang, C., Koop, T., & Pöschl, U. (2012) *Atmos. Chem. Phys.* **12**, 2777-2794.

Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., & N. M. Donahue (2012) *Nature Geosci.* **5**, 453-458.

Yli-Juuti, T, Barsanti, K., Hildebrandt Ruiz, L., Kieloaho, A.-J., Makkonen, U., Petäjä, T., Ruuskanen, T., Kulmala, M., & Riipinen, I. (2013) *Atmos. Chem. Phys.* **13**, 12507-12524.