Gas-particle partitioning of atmospheric aerosols: Interplay of physical state, non-ideal mixing and morphology

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Atmospheric aerosols, comprising organic compounds and inorganic salts, play a key role in air quality and climate. Mounting evidence exists that these particles frequently exhibit phase separation into predominantly organic and aqueous electrolyte-rich phases (*You et al.*, 2012). As well, the presence of amorphous semi-solid or glassy particle phases has been established (*Virtanen et al.*, 2010; *Koop et al.*, 2011). Using the canonical system of ammonium sulfate mixed with organics from the ozone oxidation of α-pinene, we illustrate theoretically the interplay of physical state, non-ideality, and particle morphology affecting aerosol mass concentration and the characteristic timescale of gas-particle mass transfer.

The state-of-the-art thermodynamic model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients; *Zuend et al.*, 2008; 2011) is used to investigate the effect of phase separation on secondary organic aerosol formation. We demonstrate that phase separation can significantly affect hygroscopic growth and gas-particle partitioning (particle mass and chemical composition).

It is generally assumed that VOC oxidation products rapidly adopt gas-aerosol equilibrium. Here we estimate the equilibration timescale of SOA gas-particle partitioning using a state-of-the-art kinetic flux model (kinetic multi-layer model of gas-particle interaction in aerosol and clouds; *Shiraiwa et al.*, 2012). Equilibration timescale is found to be of order seconds to minutes for partitioning of relatively high volatility organic compounds into liquid particles, thereby adhering to equilibrium gas-particle partitioning. However, equilibration timescale increases to hours or days for organic aerosol associated with semi-solid particles, low volatility, large particle size, and low mass loadings (Fig. 1). Instantaneous equilibrium partitioning may lead to substantial overestimation of particle mass concentration and underestimation of gas-phase concentration (*Shiraiwa & Seinfeld*, 2012).

Moreover, we demonstrate that semi-solid or glassy phases may kinetically inhibit the hygroscopic growth especially under low relative humidity and temperature. Thus, the interplay of physical state, non-ideal mixing and morphology have significant implications for the interpretation of laboratory data and the development of improved atmospheric air quality and climate models.

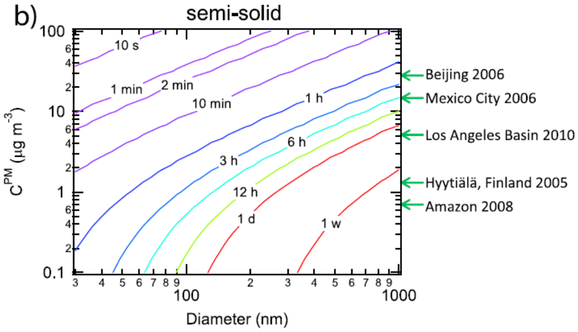

Figure 1. Equilibration timescale of SOA partitioning SVOC ($C^* = 10$ µg m^{-3}) in (b) semi-solid (bulk diffusivity $D_b = 10^{-15}$ cm^{-2} s^{-1}) matrix as functions of particle diameter (nm) and mass concentration of pre-existing particles. Ambient organic mass concentrations are indicated (*Shiraiwa & Seinfeld*, 2012).

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