Supporting Online Material

New measurements challenge current SOA models: Rethinking the atmospheric lifecycle of SOA

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S1.0. Kinetic mass transfer

The kinetic mass transfer model described by Koo et al. (2003) is used to compare model predictions of SOA particle evaporation to laboratory and field measurements described by Vaden et al. (2011). The mass flux of species $i$ (representing a given volatility bin) to particles of size $k$ ($J_{i,k}$) is calculated using the equation (Seinfeld and Pandis, 1998).

$$J_{i,k} = 2\pi N_k d_k D_i f(Kn_k, \alpha)(c_i - c_{i,k}^{eq}) \eta_k$$ (1)

where $N_k$ and $d_k$ are the number and diameter of particles of size $k$, respectively; $D_i$, $c_i$, and $c_{i,k}^{eq}$ are the diffusivity, bulk gas-phase concentration of species $i$ away from the particle surface, and equilibrium concentration of species $i$ at the particle surface, respectively; $f(Kn, \alpha)$ is the correction for non-continuum effects and imperfect accommodation; $Kn_k$ is the Knudsen number; $\alpha$ is the accommodation coefficient; and $\eta_k$ is the Kelvin effect correction.

The equilibrium concentrations at particle surfaces, $c_{i,k}^{eq}$, are calculated assuming absorptive partitioning in pseudo-ideal solution:

$$c_{i,k}^{eq} = x_{i,k} c_i^*$$ (2)

where $x_{i,k}$ is the mole fraction of species $i$ in particles of size $k$, and $c_i^*$ is the effective saturation concentration of species $i$ (equal to given volatility species). For all species, a molecular weight of 150 g mol$^{-1}$, density of 1500 kg m$^{-3}$, diffusion coefficient of $5 \times 10^{-6}$ m$^2$ s$^{-1}$, and surface tension 0.05 N m$^{-1}$ are assumed following Riipinen et al. (2010). The Livermore Solver for Ordinary Differential Equations (LSODES) in FORTRAN is used.
to solve the mass transfer equations and output instantaneous particle diameters for comparison to experimental data.

For evaporation rates shown in Figure 2a, calculations are done using a 7-species basis set fit from Pathak et al. (2007) for ozonolysis of α-pinene under low NOx conditions in the dark. The initial aerosol mass fractions of each lumped species \( i \) (corresponding to a volatility bin) are estimated from the 7-species VBS yields (Pathak et al., 2007). Calculations are done assuming \( \Delta \text{ROG}=200 \text{ ppb} \). Particle evaporation rates are calculated as sum of evaporation rates of all species \( i \) as:

\[
\frac{dm_k}{dt} = \sum_{i=1}^{n} J_{i,k} \quad (3)
\]

where \( \frac{dm_k}{dt} \) is the instantaneous rate of change of mass of particles of size \( k \). For any given calculation, all particles are assumed to be of the same size. For evaporation calculations in Figure 2a, we assume that concentrations of organics in the gas-phase, \( c_i \) in equation 1, remains zero over the entire modeling period, consistent with experimental conditions of Vaden et al. (2011). With this assumption, particles do not interact with each other, and particle evaporation rate does not depend on the total number of particles \( N_k \). Also, the kinetic mass transfer equations need only be solved for the particle phase. Calculations in Figure 2a are shown for two values of mass accommodation coefficient: \( \alpha=1 \) and 0.001. A smaller value of \( \alpha \) reduces the kinetic evaporation rate of SOA particles. For clarity, other laboratory experiments from Vaden et al. \(^2\) that are similar to the field data are not shown in Figure 2.
For the growth calculations shown in Figure 2b, we assume a constant concentration gradient \((c_i - c_i^{eq})\) of \(1 \mu g m^{-3}\) is always present between gas and aerosol phase. For non-volatile SOA, \(c_i^{eq}\) is zero, and constant concentration gradient transforms to single species bulk gas-phase concentration \((c_i)\) of \(1 \mu g m^{-3}\). This value of \(c_i\) corresponds to semi-volatile organic species within the range of VBS. Calculations in Figure 2b are shown for three different values of mass accommodation coefficient: \(\alpha=1, 0.01\) and 0.001. Similar to evaporation rates, a smaller value of \(\alpha\) reduces growth rate of SOA.

Kinetic mass transfer equations use volatility distribution of lumped components comprising the SOA matrix, and mass accommodation coefficient \(\alpha_i\) as fitting parameters. The mass accommodation coefficient \(\alpha_i\) measures the rate at which molecules cross the interface between gas and condensed phase (Molina et al., 1996). Since very little is known about physical and chemical processes occurring on the surface and bulk of SOA particles, the mass accommodation coefficient \(\alpha_i\) is treated as a semi-empirical modeling parameter to account for resistance to mass transfer between gas and particle phases. But, as described by Molina et al. (1996), there are other potentially rate limiting processes and properties such as diffusion within the condensed phase, solubility, and chemical reactions on the surface and within particles, that affect the transfer of organics between gas and particles. In order to accurately explain the kinetics of gas-particle mass transfer, detailed information such as phase of particles, solubility of species in the particle, and chemical reaction mechanisms and rates in the condensed phase need to be known. Experiments of Vaden et al. (2011) suggest that SOA particles are highly viscous
quasi-solids, which are not at equilibrium with surrounding gas phase. Hydrophobic organics are trapped within SOA phase, pointing towards severe mechanistic uncertainties governing organic aerosols in the atmosphere. The take-home point is that using a single fitting parameter such as interfacial mass-accommodation coefficient to account for all these dynamic effects may not be sufficient. In addition, this would require use of unrealistically low and highly time-and-process varying values of mass accommodation coefficient $\alpha_m$. In this work, we have presented a simple example incorporating irreversible gas-particle partitioning using the framework of VBS. Since Vaden et al. (2011) showed that evaporation of laboratory and ambient SOA could almost be ignored, we stopped SOA evaporation, after it is formed. As discussed in the main text, several physical and chemical processes governing SOA lifecycle need to be further explored.

S2.0 References


