1   **Supporting Online Material**

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

4   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).

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

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; α is the accommodation coefficient; and η_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:

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

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 5×10^{-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

40   to solve the mass transfer equations and output instantaneous particle diameters for

41   comparison to experimental data.

42   For evaporation rates shown in Figure 2a, calculations are done using a-7-species

43   basis set fit from Pathak et al. (2007) for ozonolysis of α-pinene under low NOx

44   conditions in the dark. The initial aerosol mass fractions of each lumped species i

45   (corresponding to a volatility bin) are estimated from the 7-species VBS yields (Pathak et

46   al., 2007). Calculations are done assuming ΔROG=200 ppb. Particle evaporation rates are

47   calculated as sum of evaporation rates of all species i as:

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

49   where dm_k/dt is the instantaneous rate of change of mass of particles of size k. For any

50   given calculation, all particles are assumed to be of the same size. For evaporation

51   calculations in Figure 2a, we assume that concentrations of organics in the gas-phase, c_i

52   in equation 1, remains zero over the entire modeling period, consistent with experimental

53   conditions of Vaden et al. (2011). With this assumption, particles do not interact with

54   each other, and particle evaporation rate does not depend on the total number of particles

55   N_k. Also, the kinetic mass transfer equations need only be solved for the particle phase.

56   Calculations in Figure 2a are shown for two values of mass accommodation coefficient:

57   α=1 and 0.001. A smaller value of α reduces the kinetic evaporation rate of SOA

58   particles. For clarity, other laboratory experiments from Vaden et al. [2] that are similar to

59   the field data are not shown in Figure 2.

60   For the growth calculations shown in Figure 2b, we assume a constant

61   concentration gradient $(c_i - c_i^{eq})$ of 1 µg m^{-3} is always present between gas and aerosol

62   phase. For non-volatile SOA, c_i^{eq} is zero, and constant concentration gradient transforms

63   to single species bulk gas-phase concentration (c_i) of 1 µg m^{-3}. This value of c_i

64   corresponds to semi-volatile organic species within the range of VBS. Calculations in

65   Figure 2b are shown for three different values of mass accommodation coefficient: α=1,

66   0.01 and 0.001. Similar to evaporation rates, a smaller value of α reduces growth rate of

67   SOA.

68   Kinetic mass transfer equations use volatility distribution of lumped components

69   comprising the SOA matrix, and mass accommodation coefficient α_i as fitting

70   parameters. The mass accommodation coefficient α_i measures the rate at which molecules

71   cross the interface between gas and condensed phase (Molina et al., 1996). Since very

72   little is known about physical and chemical processes occurring on the surface and bulk

73   of SOA particles, the mass accommodation coefficient α_i is treated as a semi-empirical

74   modeling parameter to account for resistance to mass transfer between gas and particle

75   phases. But, as described by Molina et al. (1996), there are other potentially rate limiting

76   processes and properties such as diffusion within the condensed phase, solubility, and

77   chemical reactions on the surface and within particles, that affect the transfer of organics

78   between gas and particles. In order to accurately explain the kinetics of gas-particle mass

79   transfer, detailed information such as phase of particles, solubility of species in the

80   particle, and chemical reaction mechanisms and rates in the condensed phase need to be

81   known. Experiments of Vaden et al. (2011) suggest that SOA particles are highly viscous

82 quasi-solids, which are not at equilibrium with surrounding gas phase. Hydrophobic

83 organics are trapped within SOA phase, pointing towards severe mechanistic

84 uncertainties governing organic aerosols in the atmosphere. The take-home point is that

85 using a single fitting parameter such as interfacial mass-accommodation coefficient to

86 account for all these dynamic effects may not be sufficient. In addition, this would

87 require use of unrealistically low and highly time-and-process varying values of mass

88 accommodation coefficient α_m. In this work, we have presented a simple example

89 incorporating irreversible gas-particle partitioning using the framework of VBS. Since

90 Vaden et al. (2011) showed that evaporation of laboratory and ambient SOA could almost

91 be ignored, we stopped SOA evaporation, after it is formed. As discussed in the main

92 text, several physical and chemical processes governing SOA lifecycle need to be further

93 explored.

94 **S2.0 References**

95 Koo, B. Y., Ansari, A. S., and Pandis, S. N.: Integrated approaches to modeling the
96 organic and inorganic atmospheric aerosol components, Atmos. Environ., 37, 4757-4768,
97 10.1016/j.atmosenv.2003.08.016, 2003.
98 Molina, M. J., Molina, L. T., and Kolb, C. E.: Gas-phase and heterogeneous chemical
99 kinetics of the troposphere and stratosphere, Annu. Rev. Phys. Chem., 47, 327-367, 1996.
100 Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S.
101 N.: Ozonolysis of alpha-pinene: parameterization of secondary organic aerosol mass
102 fraction, Atmospheric Chemistry and Physics, 7, 3811-3821, 2007.
103 Riipinen, I., Pierce, J. R., Donahue, N. M., and Pandis, S. N.: Equilibration time scales of
104 organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics,
105 Atmospheric Environment, 44, 597-607, DOI 10.1016/j.atmosenv.2009.11.022, 2010.
106 Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: from Air
107 Pollution to Climate Change, Wiley, New York, 1326 pp., 1998.
108 Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation
109 kinetics and phase of laboratory and ambient secondary organic aerosol, Proc. Natl.
110 Acad. Sci. U. S. A., doi: 10.1073/pnas.1013391108, 2190-2195, 2011.
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