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Influence of Seed Aerosol Surface Area and Oxidation Rate on Vapor-Wall Deposition and SOA Mass Yields: A case study with α-pinene Ozonolysis

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Abstract

Laboratory chambers, invaluable in atmospheric chemistry and aerosol formation studies, are subject to particle and vapor wall deposition, processes that need to be accounted for in order to accurately determine secondary organic aerosol (SOA) mass yields. Although particle wall deposition is reasonably well understood and usually accounted for, vapor wall deposition is less so. The effects of vapor wall deposition on SOA mass yields in chamber experiments can be constrained experimentally by increasing the seed aerosol surface area to promote the preferential condensation of SOA-forming vapors onto seed aerosol. Here, we study the influence of seed aerosol surface area and oxidation rate on SOA formation in α-pinene ozonolysis. The observations are analyzed using a coupled vapor-particle dynamics model to interpret the roles of gas-particle partitioning (quasi-equilibrium vs. kinetically-limited SOA growth) and α-pinene oxidation rate in influencing vapor wall deposition. We find that the SOA growth rate and mass yields are independent of seed surface area within the range of seed surface area concentrations used in this study. This behavior arises when the condensation of SOA-forming vapors is dominated by quasi-equilibrium growth. Faster α-pinene oxidation rates and higher SOA mass yields are observed at increasing O_3 concentrations for the same initial α-pinene concentration. When the α-pinene oxidation rate increases relative to vapor wall deposition, rapidly produced SOA-forming oxidation products condense more readily onto seed aerosol particles, resulting in higher SOA mass yields. Our results indicate that the extent to which vapor wall deposition affects SOA mass yields depends on the

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particular VOC system, and can be mitigated through the use of excess oxidant concentrations.

1. Introduction

Secondary organic aerosol (SOA), formed from the oxidation of volatile and intermediate volatility organic compounds (VOCs and IVOCs), contributes a significant fraction of the global organic aerosol burden (Kanakidou et al., 2005; Hallquist et al., 2009; Tsigaridis et al., 2014). SOA formation studies, which are typically conducted in laboratory chambers in the presence of seed aerosol particles, provide fundamental data that can be used to predict the rate of atmospheric SOA formation. An essential parameter of interest in laboratory chamber studies is the SOA mass yield (Y), which is defined as the ratio of mass concentration of SOA formed to mass concentration of parent hydrocarbon reacted ((ΔHC), $Y = \Delta M_o/\Delta HC$ (Odum et al., 1996; Odum et al., 1997a; Odum et al., 1997b)). The measured SOA mass yields can subsequently be applied in atmospheric models to predict regional and global organic aerosol burdens. In order to obtain accurate SOA mass yields from the evolving aerosol size distribution in chamber experiments, the loss of both particles and vapors to the chamber walls needs to be accurately accounted for (Crump and Seinfeld, 1981; McMurry and Grosjean, 1985; McMurry and Rader, 1985; Cocker et al., 2001a; Weitkamp et al., 2007; Pierce et al., 2008; Hildebrandt et al., 2009; Loza et al., 2010; Matsunaga and Ziemann, 2010; Loza et al., 2012; Kokkola et al., 2014; McVay et al., 2014; Yeh and Ziemann, 2014; Zhang et al., 2014; Yeh and Ziemann, 2015; Zhang et al., 2015a; La et al., 2016).

The mechanisms by which particles in chambers deposit on chamber walls are reasonably well understood. Particles are transported to the boundary layer on the chamber walls via diffusion, gravitational settling, and electrostatic forces (Crump and Seinfeld, 1981; McMurry and Grosjean, 1985; McMurry and Rader, 1985; Pierce et al., 2008). The rate at which particles are transported to the edge of the boundary layer is dictated primarily by mixing conditions in the chamber. An effective approach for characterizing particle wall loss involves measuring the size-dependent wall loss rates of polydisperse inert seed aerosol (e.g. ammonium sulfate particles) injected into the chamber during seed-only experiments (Keywood et al., 2004; Pierce et al., 2008). The

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observed particle number concentration decay in each size bin is then fitted to a first-order exponential decay from which the first-order wall loss coefficients are determined as a function of particle size. These wall loss coefficients are subsequently used to correct for size-dependent particle wall loss in actual SOA formation experiments.

Vapor-wall deposition mechanisms in chambers are not as well understood or accounted for as those for particles. The degree to which SOA-forming vapors deposit onto chamber walls is governed by the rate at which these gas-phase organic molecules are transported to the walls, the strength of adherence of the organic molecule to the wall, and the extent of reversible vapor-wall partitioning (Loza et al., 2010; Matsunaga and Ziemann, 2010; Zhang et al., 2015a). For example, Loza et al. (2010) showed that the loss of 2,3-epoxy-1,4-butanediol, an isoprene oxidation product analogue, to walls in the Caltech chamber was essentially irreversible on short time scales but became reversible on longer time scales. In contrast, glyoxal, a common isoprene oxidation product, exhibited reversible vapor-wall partitioning over all time scales. Recent studies show that SOA mass yields measured in chamber experiments can be significantly underestimated due to wall deposition of SOA-forming vapors that would otherwise contribute to SOA growth (McVay et al., 2014; Zhang et al., 2014; La et al., 2016). Zhang et al. (2014) found that chamber-derived SOA mass yields from toluene photooxidation may be underestimated by as much as a factor of four as a result of vapor wall loss. Consequently, the use of underestimated chamber-derived SOA mass yields in atmospheric models will lead to the underprediction of ambient SOA mass concentrations (Cappa et al., 2016).

For the toluene photooxidation system, Zhang et al. (2014) showed that the measured SOA mass yields increased with increasing seed aerosol surface area, demonstrating that increasing the seed-to-chamber surface area ratio promoted the condensation of SOA-forming vapors onto seed aerosol particles. However, increasing the seed aerosol surface area to promote condensation of SOA-forming vapors onto seed aerosol particles may not be effective in all VOC oxidation systems. A modeling study by McVay et al. (2014) showed that the SOA mass yield depends on seed aerosol surface area only in cases where the condensation of SOA-forming vapors onto seed aerosol

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particles is kinetically limited (i.e., the timescale for gas-particle equilibrium is competitive with or greater than the timescale for reaction and vapor-wall deposition). In addition to the seed aerosol surface area, VOC oxidation rate may also play an important role in the effect of vapor wall loss on SOA formation. Ng et al. (2007) showed that the SOA mass yields from *m*-xylene photooxidation are dependent on the oxidation rate, with higher OH concentrations (hence faster oxidation rates) resulting in higher SOA mass yields. It was suggested that the "oxidation rate effect" could arise as a result of competition between growing particles and chamber walls for condensable VOC oxidation products (Ng et al., 2007). However, McVay et al. (2016) reported similar SOA growth at low and high OH concentrations in α-pinene photooxidation. Taken together, these studies show the importance of understanding how gas-particle partitioning and VOC oxidation rate impact vapor-wall deposition and SOA mass yields in laboratory chamber experiments.

In this study, we examine the influence of seed aerosol surface area and oxidation rate on SOA formation in α-pinene ozonolysis chamber experiments. α-pinene is the most abundant monoterpene, with global emissions estimated to be ~66 Tg yr^{-1} (Guenther et al., 2012). Ozonolysis is the major atmospheric oxidation pathway of α-pinene, and is estimated to account for reaction of ~46 % of emitted α-pinene (Griffin et al., 1999; Capouet et al., 2008). α-pinene ozonolysis, a major source of atmospheric SOA on both regional and global scales (Kanakidou et al., 2005; Hallquist et al., 2009; Carlton et al., 2010; Pye et al., 2010), has been the subject of numerous studies (Hoffmann et al., 1997; Griffin et al., 1999; Cocker et al., 2001b; Gao et al., 2004; Presto et al., 2005; Presto and Donahue, 2006; Pathak et al., 2007a; Pathak et al., 2007b; Song et al., 2007; Shilling et al., 2008; Henry et al., 2012; Ehn et al., 2014; Kristensen et al., 2014; Zhang et al., 2015b). Here, we measure the α-pinene SOA mass yield as a function of seed aerosol surface area concentration (0 to 3000 μm^2 cm^{-3}) and O_3 mixing ratio (100 vs. 500 ppb). These results are analyzed using a coupled vapor-particle dynamics model to evaluate the roles of gas-particle partitioning and VOC oxidation rate in influencing vapor-wall deposition effects on the measured SOA mass yields.

2. Experimental

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2.1. Dark α-pinene ozonolysis experiments

Experiments were conducted in the Georgia Tech Environmental Chamber (GTEC) facility. Details of the dual chamber facility are provided elsewhere (Boyd et al., 2015). Only one FEP Teflon chamber (volume 13 m^3) was used for the entirety of this study. Before each experiment, the chamber is flushed with dried, purified air for at least 36 h until the aerosol number concentration is < 30 cm^{-3}. All experiments were conducted under dry conditions (< 5 % RH) at room temperature (25 °C). NO_x mixing ratios in these experiments are < 1 ppb. Experimental conditions are summarized in Table 1.

22 ppm of cyclohexane (Sigma Aldrich, ≥ 99.9 %) was first injected into the chamber to act as an OH scavenger (~440 times the initial α-pinene concentration). After the cyclohexane concentration had stabilized in the chamber for 30 min, a known concentration (~50 ppb in all experiments) of α-pinene (Sigma Aldrich, > 99 %) was injected into the chamber, followed by inorganic seed aerosol via atomization of an aqueous ammonium sulfate (AS) solution (in seeded experiments). To vary the seed aerosol surface area, different concentrations of AS solutions were used to generate seed aerosol particles in the seeded experiments. In the "low AS" experiments, a 0.015 M AS solution was used to generate seed particles, and the resulting initial total AS seed surface area concentration was ~1000 μm^2 cm^{-3}. In the "high AS" experiments, a 0.05 M AS solution was used to generate seed aerosol particles, and the resulting initial total AS seed surface area concentration was ~3000 μm^2 cm^{-3}. In selected experiments, no seed aerosol particles were introduced into the chamber and SOA was formed via nucleation. After the seed aerosol concentration in the chamber stabilized, O_3 (100 or 500 ppb), which was generated by passing purified air into a photochemical cell (Jelight 610), was introduced into the chamber. The start of O_3 injection into the chamber marked the beginning of the reaction (i.e., reaction time = 0 min). The initial α-pinene:O_3 molar ratio was fixed at approximately 1:2 and 1:10 in the 100 and 500 ppb O_3 experiments, respectively. O_3 was injected into the chamber for 13.5 and 54.25 min in the 100 and 500 ppb O_3 experiments, respectively, to achieve the desired O_3 concentrations. The O_3 injection times were established in separate experiments in which only O_3 was injected into the chamber.

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The α-pinene and O_3 concentrations were measured by a Gas Chromatograph-Flame Ionization Detector (GC-FID, Agilent 7890A) and O_3 monitor (Teledyne T400), respectively. GC-FID measurements were taken 12 min apart. A High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) was used to measure the aerosol elemental composition (DeCarlo et al., 2006; Canagaratna et al., 2015). Details on the operation of the HR-ToF-AMS and its data analysis are described elsewhere (Canagaratna et al., 2015). Aerosol size distributions, number and volume concentrations were measured by a Scanning Mobility Particle Sizer (SMPS, TSI), which consists of a Differential Mobility Analyzer (DMA, TSI 3081) and a Condensation Particle Counter (CPC, TSI 3775). For nucleation and low AS experiments, the measured aerosol size range was set to 14 to 686 nm diameter. For high AS experiments, the measured aerosol size range was set to 17 to 983 nm. Prior checks were made to confirm that no particles larger than 686 nm were detected in the nucleation and low AS experiments. The SOA mass concentrations reported in this study were measured using the SMPS. The SOA density was calculated from the ratio of the aerosol size distributions measured by the HR-ToF-AMS and the SMPS during nucleation experiments (DeCarlo et al., 2004; Bahreini et al., 2005).

2.2. Particle wall deposition correction

Particle wall deposition needs to be accounted for to determine the SOA mass concentration in the chamber. Two limiting assumptions have traditionally been made regarding interactions between particles deposited on the chamber walls and suspended vapors when accounting for particle wall loss in the computation of SOA mass yields (Weitkamp et al., 2007; Hildebrandt et al., 2009; Loza et al., 2012; Zhang et al., 2014). The first case assumes that particles deposited on the walls cease to interact with suspended vapors, and therefore the SOA mass present on these deposited particles does not change after deposition (Loza et al., 2012; Zhang et al., 2014). Adding the SOA mass present on these deposited particles to that present on the suspended particles provides a lower bound of the total SOA mass concentration. In the second case, it is assumed that particles deposited on the walls continue to interact with suspended vapors as if these particles had remained suspended, and therefore the SOA mass present on these

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deposited particles increases at the same rate as those suspended (Hildebrandt et al., 2009; Weitkamp et al., 2007). Thus, this case provides an upper bound of the total SOA mass concentration due to the additional uptake of suspended vapors to wall-deposited particles. However, it must be kept in mind that the calculated SOA mass concentration can be underestimated even in the upper bound case since the calculation accounts neither for differences in the vapor-particle and vapor-wall interaction and transport timescales nor for the significantly larger amount of absorbing mass of the chamber walls (relative to the deposited particles) for suspended vapors (McVay et al., 2014; Zhang et al., 2014; McVay et al., 2016).

In this study, we calculate SOA mass yields using the lower bound of the total SOA mass concentration obtained from SMPS measurements, which has been described in detail previously (Loza et al., 2012), and will be reviewed briefly here. For each particle size bin i at each time increment Δt, the particle number distribution deposited on the wall ($n_{w,i,j}$) is:

$$n_{w,i,j} = n_{s,i,j} \times (1 - \exp(-\beta_i \Delta t)) \tag{1}$$

where $n_{s,i,j}$ is the suspended particle number distribution in particle size bin i at time step j, Δt is the difference between time step j and time step $j + 1$, and β_i is the size-dependent first-order exponential wall loss rate obtained from seed-only experiments. The particle wall loss corrected number distribution ($n_{total,i,j}$) is obtained from the sum of the particle number distribution of deposited particles ($n_{w,i,j}$) and suspended particles ($n_{s,i,j}$):

$$n_{total,i,j} = n_{s,i,j} + n_{w,i,j} \tag{2}$$

Assuming spherical particles, the particle wall loss corrected volume concentration ($V_{total,j}$) is:

$$V_{total,j} = \sum_{i=1}^{m} \frac{n_{total,i,j}}{D_{p,i} \ln 10} \times (D_{p,i+} - D_{p,i-}) \times \frac{\pi}{6} D_{p,i}^3 \tag{3}$$

where m is the number of particle size bins, $D_{p,i+}$ and $D_{p,i-}$ are the upper and lower limits for size bin i, respectively, and $D_{p,i}$ is the median particle diameter for size bin i. The term

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$D_{p,i}$ln10 is needed to convert from a lognormal distribution. Figures S1-S4 and Table S1 show results from the particle wall loss correction. To calculate the SOA mass concentration ($\Delta M_{o,j}$), the SOA density (ρ_{org}) is multiplied by the difference of the particle wall loss corrected volume concentration ($V_{total,j}$) and the initial seed volume concentration (V_{seed}):

$$\Delta M_{o,j} = \rho_{org} \times (V_{total,j} - V_{seed}) \quad (4)$$

The measured densities of the α-pinene SOA are 1.39 and 1.37 g cm^{-3} for the 100 and 500 ppb O_3 experiments, respectively, and are within the range (i.e., 1.19 to 1.52 g cm^{-3}) reported in previous α-pinene ozonolysis studies (Bahreini et al., 2005; Kostenidou et al., 2007; Song et al., 2007; Shilling et al., 2009).

3. Vapor-particle dynamics model

A coupled vapor-particle dynamics model is used to evaluate the influence of seed aerosol surface area and oxidation rate on SOA formation in the α-pinene ozonolysis chamber experiments. This model is similar to that used in McVay et al. (2014), and will be briefly described here. Parameters from the experimental data (temperature, pressure, initial α-pinene concentration) are used as model inputs. The initial size distribution is set to that measured by the SMPS, with the exception of the two nucleation experiments. Because nucleation is not explicitly simulated, an approximation is used in which the smallest diameter bin is initialized with the total number of particles measured at the end of the experiment (see Table S1). In each simulation, the decay of α-pinene, the consumption of O_3, the SOA mass concentration, and the SOA mass yield are calculated throughout the duration of the experiment. We assume a linear injection rate of O_3 based on the time required to inject the desired O_3 concentration. For example, O_3 is injected at a rate of 500/54.25 ppb min^{-1} for the first 54.25 min during the 500 ppb O_3 experiments. O_3 simultaneously decays by reaction with α-pinene at a rate constant of 9.4×10^{-17} cm^3 molec.$^{-1}$ s^{-1} (Saunders et al., 2003). The O_3+α-pinene reaction is assumed to occur in a well-mixed chamber and produces 5 classes of first-generation products, which are grouped according to mass saturation concentrations, similar to the volatility basis set (Donahue et al., 2006): >10^3 (assumed to be completely volatile), 10^2, 10, 1 and 0.1 μg

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m^{-3}. Branching ratios between these products are optimized to fit the experimental data. These branching ratios cannot be compared directly to previously reported VBS parameters for α-pinene ozonolysis (e.g., Henry et al. (2012)) since VBS parameters are typically mass-based, while the branching ratios in the model are mole-based. Furthermore, the branching ratios here account for the influence of vapor wall deposition, while typical VBS parameters do not. We assume that these 5 classes of products have molecular weights 168, 184, 192, 200 and 216 g $mole^{-1}$ based on the group contribution method (Donahue et al., 2011). The first-generation products are assumed not to undergo further reaction with O_3 upon formation.

The aerosol dynamics in the chamber obey the aerosol general dynamic equation (Seinfeld and Pandis, 2006):

$$\left(\frac{\partial n(D_p,t)}{\partial t}\right) = \left(\frac{\partial n(D_p,t)}{\partial t}\right)_{\text{coag}} + \left(\frac{\partial n(D_p,t)}{\partial t}\right)_{\text{cond/evap}} + \left(\frac{\partial n(D_p,t)}{\partial t}\right)_{\text{wall loss}} \quad (5)$$

Coagulation is not considered, since an alternative version of the model including coagulation showed no change in the predicted α-pinene ozonolysis SOA mass concentrations in simulations with and without coagulation. The change in particle number distribution due to particle wall loss is:

$$\left(\frac{\partial n(D_p,t)}{\partial t}\right)_{\text{wall loss}} = -\beta_j(D_p)n(D_p,t) \quad (6)$$

where, as noted in section 2.2, $\beta_j(D_p)$ is the size-dependent first-order wall loss rate coefficient obtained from fitting seed-only experiments. The rate at which vapor condenses onto a spherical aerosol particle is:

$$J_i = 2\pi D_p D_i (G_i - G_i^{eq}) F_{FS} \quad (7)$$

where G_i is the concentration of gas-phase species i, G_i^{eq} is the saturation concentration of gas-phase species i, D_i is the gas-phase molecular diffusivity (assumed to be 3×10^{-6}

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$m^2\ s^{-1}$ (McVay et al., 2014)), and F_{FS} is the Fuchs-Sutugin correction for non-continuum gas-phase diffusion:

$$F_{FS} = \frac{0.75\alpha_p(1+\mathrm{Kn})}{\mathrm{Kn}^2 + \mathrm{Kn} + 0.283\mathrm{Kn}\alpha_p + 0.75\alpha_p} \tag{8}$$

where α_p is the vapor-particle mass accommodation coefficient, and Kn is the Knudsen number, Kn = $2\lambda_{AB}/D_p$. The vapor-particle mass accommodation coefficient accounts for any resistance to vapor molecule uptake at the particle surface (e.g. surface accommodation and particle-phase diffusion limitations). λ_{AB} is the mean free path of the gas-phase species, which is:

$$\lambda_{AB} = 3D_i \times \sqrt{\frac{\pi M_i}{8RT}} \tag{9}$$

where R is the ideal gas constant, T is the temperature, and M_i is the molecular weight of diffusing gas-phase molecule i. For each particle size bin, Eqs. 7-9 are used to compute the flux of each gas-phase species to and from an aerosol particle, scaled by the particle number concentration in the size bin. The net rate of change for each gas-phase species due to evaporation or condensation is obtained from the total flux summed over all the particle size bins.

G_i^{eq} varies for each particle size bin because it depends on the mass concentration of species i and the total organic mass concentration in the size bin:

$$G_i^{eq} = \frac{A_i C_i^*}{\sum_k A_k + M_{init}} \tag{10}$$

where A_i is the concentration of species i in the particle phase, C_i^* is the saturation concentration of species i, $\sum_k A_k$ is the sum of all the species concentration in the particle phase, and M_{init} is the mass concentration of any absorbing organic material initially

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present in the seed aerosol. To avoid numerical errors in Eq. 10 at the first time step, M_{init} is set to 0.01 μg m^{-3}.

The oxidation products of α-pinene ozonolysis are assumed to be subject to vapor-wall deposition, which is simulated using a first-order wall-loss coefficient (McMurry and Grosjean, 1985):

$$k_{wall,on} = (\frac{A}{V})\frac{\frac{\alpha_{wall}\bar{c}}{4}}{1+\frac{\pi}{2}(\frac{\alpha_{wall}\bar{c}}{4\sqrt{k_e D_i}})} \tag{11}$$

where A/V is the surface area-to-volume ratio of the chamber (estimated to be 2.5 m^{-1}), α_{wall} is the vapor-wall mass accommodation coefficient, and k_e is the eddy diffusion coefficient that describes mixing conditions in the chamber. Based on the measured size-dependent particle wall loss rates (method is described in Zhang et al. (2014)), k_e is estimated to be 0.03 s^{-1} for the GTEC chamber. Vapor-wall deposition is assumed to be reversible, and the rate constant of vapor desorption from the chamber walls is:

$$k_{wall,off} = \frac{k_{wall,on}}{K_W C_W} = k_{wall,on}(\frac{C_i^* M_w \gamma_w}{C_W M_p \gamma_p}) \tag{12}$$

where C_w is the equivalent organic mass concentration in the wall (designated to treat gas-wall partitioning in terms of gas-particle partitioning theory and not necessarily representative of a physical layer of organic concentration on the wall (Matsunaga and Ziemann, 2010)), K_w is the gas-wall partitioning coefficient, M_w is the effective molecular weight of the wall material, γ_w is the activity coefficient of the species in the wall layer, M_p is the average molecular weight of organic species in the particle, and γ_p is the activity coefficient of the species in the particle. For simplicity, we assume that $M_w = M_p$ and $\gamma_w = \gamma_p$. C_w is set to 10 mg m^{-3} based on previous inferences by Matsunaga and Ziemann (2010). Sensitivity studies (not shown) show no change in model predictions when varying C_w above C_w = 0.1 mg m^{-3}.

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In the initial version of the model, after all the α-pinene is consumed, vapor wall deposition was assumed to continue to deplete the gas-phase oxidation products and aerosol mass evaporates to maintain gas-particle equilibrium. SOA evaporation was not observed experimentally (i.e., the SOA mass concentration does not decrease significantly over time after peak SOA growth has been achieved in these chamber experiments (Fig. 2)). In order to represent these observations in the model, a first-order, particle-phase reaction is introduced by which aerosol species are converted into non-volatile absorbing organic mass with a timescale of τ_{olig}. This mechanism (which is not included in the model used in McVay et al. (2014)) is similar to that used by the sequential equilibrium partitioning model, in which aerosol is converted from an absorbing to non-absorbing, non-volatile phase in order to explain the inhibited diffusion and evaporation observed in α-pinene ozonolysis SOA (Cappa and Wilson, 2011). Although we assume here that the converted non-volatile aerosol mass still participates in partitioning, either mechanism invokes a particle-phase process to retard SOA evaporation.

Model parameters α_w, α_p, τ_{olig} and the branching ratios between the oxidation products are optimized to best-fit the predictions with the experimental observations. Specifically, model predictions are compared to experimental data: SOA mass concentration vs. reaction time, α-pinene concentration vs. reaction time, and O_3 concentration vs. reaction time. Figure S6 compares reaction profiles of measured and modeled O_3 and α-pinene concentrations for the base model case. Sensitivity tests were also performed on each model parameter, shown in Figs. S7-S10. Table 2 summarizes the parameters used. While the optimized parameters provide a good fit to the data, we caution that the parameters are interconnected, and other fits may also be possible. We are confident that our conclusions derived using these parameters are robust.

4. Results

Figure 1 shows the size-dependent particle wall deposition coefficients inferred from seed-only deposition experiments. The initial total AS seed surface area concentration in the low AS-seed only and high AS-seed only experiments (which are conducted using 0.015 M AS and 0.05 M AS solutions, respectively) are similar to those

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used in the α-pinene ozonolysis experiments (i.e., ~1000 and ~3000 μm^2 cm^{-3}, respectively). While there are differences in the particle wall deposition coefficients from the low and high AS-seed only experiments, this difference is likely the result of uncertainties arising from the low particle number concentrations for the larger particles in the low AS-seed only experiment. As shown in Fig. 1, both sets of particle wall deposition coefficients generally fall within the range of those measured in routine monthly AS-seed only experiments conducted in the chamber.

The particle wall deposition corrected number concentration data provide a test of the appropriateness of the particle wall deposition correction. This is because the corrected number concentration should level off at a constant value (i.e., the initial particle number concentration), assuming no significant coagulation, when particle wall deposition is properly accounted for since the wall-deposited particle number distribution is added to the suspended particle number distribution during particle wall loss correction. We account for particle wall deposition in nucleation and low AS experiments using deposition coefficients determined from the low AS-seed only experiments, while particle deposition in high AS experiments are accounted for using coefficients determined from the high AS-seed only experiments. Figures S1 and S2 show the particle wall deposition-corrected aerosol number and volume concentrations. Over all experiments, the particle wall deposition-corrected final particle number concentration (i.e., at the end of the reaction) is 9 to 17 % less than the initial particle number concentration for the low AS and high AS experiments (Table S1), respectively, indicating that the particle wall deposition-corrected volume concentrations are slightly underestimated. It is currently unclear why the particle wall deposition-corrected final particle number concentrations are somewhat smaller than the initial particle number concentrations, though this could be due to variations in particle wall deposition rates in the AS-seed only and α-pinene ozonolysis experiments. As a sensitivity test, we used the average of the low AS-seed only and high AS-seed only particle wall deposition coefficients to account for particle wall deposition in all the experiments (Figs. S3 and S4). While there is a negligible difference in the particle wall deposition corrected volume concentrations (Figs. S3 and S4 vs. Figs. S1 and S2), a larger spread (1 to 22 %) exists in the difference between the initial and final particle number concentrations when

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the average particle wall deposition coefficients are used (Table S1). Therefore, all subsequent nucleation and low AS data presented here are particle wall deposition-corrected using coefficients determined from the low AS-seed only experiments, and all high AS data are corrected using particle wall deposition coefficients determined from the high AS-seed only experiments.

Figure 2 shows the reaction profiles of the α-pinene ozonolysis experiments. SOA growth typically starts within 10 to 20 min of the start of the reaction. At either initial O_3 concentration, the molar ratio of O_3 reacted to α-pinene reacted is approximately 1:1 (i.e., 50 ppb α-pinene reacted with 50 ppb O_3), which indicates that O_3 reacts only with α-pinene and not its oxidation products. As anticipated, the α-pinene oxidation rates in the 100 ppb O_3 experiments are significantly slower than those in the 500 ppb O_3 experiments. Figures 2a-c show that peak SOA levels are typically reached at reaction time ~300 to 350 min in the 100 ppb O_3 experiments, during which ≥ 95 % of the injected α-pinene has reacted. In contrast, all the α-pinene reacts within 80 to 90 min of the start of reaction in the 500 ppb O_3 experiments, and peak SOA levels are achieved at reaction time ~100 min (Figs. 2d-f). These results indicate that the O_3 concentration dictates both the rate of α-pinene oxidation and the time it takes to achieve peak SOA growth.

Figure 3 shows the time-dependent growth curves (SOA mass concentration vs. α-pinene reacted (Ng et al., 2006)) for the 100 and 500 ppb O_3 experiments. Only SOA growth data up to SOA peak concentrations are shown. SOA growth essentially stops once all the α-pinene has reacted. This is expected, as α-pinene has only one double bond; the first step of α-pinene ozonolysis is rate-limiting and the first-generation products are condensable (Ng et al., 2006; Chan et al., 2007). The time-dependent SOA growth curves for experiments corresponding to different seed aerosol concentrations overlap for both low and high O_3 concentrations. This indicates that the initial AS seed surface area does not influence the SOA growth rate within the range of AS seed surface area concentration used. It is important to note that while it appears that the SOA growth rate is faster in the 100 ppb O_3 relative to the 500 ppb O_3 experiments based on the time-dependent growth curves shown in Fig. 3, this is not the case. Instead, the observed time-

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dependent growth curves can be explained by the higher concentration of α-pinene having reacted during the 10 to 20 min delay of SOA formation in the 500 ppb O_3 experiments compared to the 100 ppb O_3 experiments (Fig. 2).

Figure 4 shows the time-dependent SOA mass yields as a function of initial total AS seed surface area for the 100 and 500 ppb O_3 experiments. Regardless of the O_3 concentration, the SOA mass yields stay roughly constant despite the increase in AS seed surface area. This indicates that the surface area concentration of AS seed aerosol does not noticeably influence the partitioning of gas-phase α-pinene ozonolysis products to the particle phase within the range of AS seed surface area concentration used. Higher SOA mass yields are observed in the 500 ppb O_3 experiments, which indicates that the α-pinene oxidation rate controls the absolute amount of SOA formed. It is important to note that these conclusions are robust even when the average of the low AS-seed only and high AS-seed only particle wall loss coefficients are used to account for particle wall loss in all the experiments (Fig. S5). The enhancement of SOA mass yields at higher O_3 concentrations and the lack of a SOA mass yield dependence on AS seed surface area (within the range of AS seed surface area concentration used in this study) will be discussed further in Section 5.

The α-pinene ozonolysis SOA mass yields obtained in this study are compared to those reported in previous studies in Fig. 5. Table S2 lists the experimental conditions employed in these studies. To facilitate comparison between the different studies, all the SOA mass yield and concentration data (including this study) are adjusted to an organic density of 1.0 g cm^{-3}. As shown in Fig. 5, the SOA mass yields obtained at peak SOA growth in this study are generally consistent with those of previous studies where the chamber was operated in batch mode (that in this study).

The competition between the condensation of SOA-forming vapor to aerosol particles vs. to chamber walls is investigated using the coupled vapor-particle dynamics model described in Section 3. As noted earlier, optimal model values for α_p, α_w, τ_{olig} and the branching ratios between the oxidation products were determined for the 100 and 500 ppb O_3 experiments by comparing the observed and best-fit time-dependent SOA, α-pinene, and O_3 concentrations profiles (Figs. S6-S10). Sensitivity tests were performed

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for each parameter to establish that the set of optimal model values provide the best overall agreement with time-dependent SOA formation profiles observed for all experiments (Figs. S7-S10). Predictions from the coupled vapor-particle dynamics model show that the optimal parameters are: $\alpha_w = 10^{-6}$, $\alpha_p = 1$, $\tau_{olig} = 4$ h, branching ratios = 0.57, 0.35, 0.04, 0.015 and 0.025 for oxidation products with vapor pressures $>10^3$, 10^2, 10, 1 and 0.1 μg m^{-3}, respectively. The best-fit $\alpha_w = 10^{-6}$ (Fig. S7) corresponds to a first-order vapor-wall deposition rate constant ($k_{wall,on}$) of 10^{-4} s^{-1}. This $k_{wall,on}$ value is comparable to that reported by Matsunaga and Ziemann (2010) for a 8.2 m^3 chamber.

5. Discussion

α-pinene ozonolysis has been carried out at two O_3 mixing ratios (100 and 500 ppb) under varying AS seed aerosol surface area concentrations (0, ~1000 and ~3000 μm^2 cm^{-3}).

5.1 Seed aerosol surface area effect

Figure 3 shows that the time-dependent SOA growth curves for experiments with different seed area concentrations overlap at both O_3 concentrations, which indicates the AS seed surface area does not affect the rate of SOA growth within the range of AS seed surface area concentration used in this study. This observation differs from findings by Pathak et al. (2007b) for the O_3+α-pinene system, who showed that even though the final SOA mass yields measured in the reaction of 7.3 ppb α-pinene with 1500 ppb O_3 were similar in their seeded and unseeded experiments, SOA growth was considerably slower in unseeded experiments compared to seeded experiments. The authors suggested that the slow SOA formation rate in their unseeded experiment was the result of SOA formation being limited by the mass transfer of semi-volatile oxidation products to newly formed particles (via nucleation) during the early stages of the experiment. These newly formed particles have a significantly smaller aerosol surface area for gas-particle partitioning as compared to that of seed aerosol particles in the seeded experiments. Consequently, the semi-volatile oxidation products accumulated in the gas phase during the early stages of the unseeded experiments, resulting in slower SOA growth compared to the seeded experiments. The observation that the presence of seed aerosol does not influence the

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SOA growth rate in the present study may be explained by the relatively high concentrations of α-pinene reacted and SOA mass loadings obtained. Previous studies have shown that the delay between the onset of VOC oxidation and SOA formation in unseeded experiments is most pronounced at low aerosol loadings (Kroll et al., 2007). We note that the concentrations of α-pinene reacted and SOA mass loadings obtained in this study are significantly larger than those reported by Pathak et al. (2007b). Therefore, it is possible that due to the relatively large concentrations of α-pinene reacted in this study, substantial concentrations of gas-phase oxidation products are generated, which results in rapid partitioning into the particle phase even in the absence of seed aerosol. This is evident from the large increase in the particle number concentration during the early stages of the unseeded 100 and 500 ppb O_3 experiments, where the particle number concentration increased to ~8000 and ~10000 particles/cm^3 during the first 45 min of the 100 and 500 ppb O_3 experiments, respectively (Fig. S1a and S2a). Thus, the SOA growth rates are not controlled by the presence of AS seed in this study.

Figure 4 shows that for both initial O_3 mixing ratios used, the time-dependent SOA mass yield is similar at any given AS seed surface area (see also Table 1). The absence of a SOA growth dependence on the AS seed surface area is similar to observations reported by McVay et al. (2016) for the α-pinene photooxidation (OH-driven chemistry) system, but differ from those reported by Zhang et al. (2014) for the toluene photooxidation system in which the SOA mass yield increased with the surface area concentration of seed aerosol.

The best-fit $\alpha_p = 1$ (Fig. S8) suggests the absence of significant limitations to vapor-particle mass transfer in the present α-pinene ozonolysis study, and that SOA formation is governed by quasi-equilibrium growth (McVay et al., 2014), which occurs when SOA-forming vapors are produced at a rate that is significantly slower than that required to establish gas-particle equilibrium (Shiraiwa and Seinfeld, 2012; Zhang et al., 2012). Moreover, the characteristic timescale to establish gas-particle equilibrium is less than those for reaction and vapor-wall deposition. When the vapor and particle phases maintain equilibrium, gas-particle equilibrium is controlled by the amount of organic matter in the VOC system. As a result, the rate of condensation of SOA-forming vapors

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is independent of the seed aerosol surface area (McVay et al., 2014). The best-fit $\alpha_p = 1$ is within the approximate range of α_p coefficients determined from α-pinene ozonolysis SOA thermodenuder studies ($\alpha_p = 0.1$) (Saleh et al., 2013) and α-pinene photooxidation chamber studies ($\alpha_p = 0.1$ or 1) (McVay et al., 2016). Notably, this result differs markedly from that for toluene photooxidation (Zhang et al., 2014), where α_p was determined to be 0.001, and for which, since the SOA mass yield was strongly dependent on the seed aerosol surface area, the condensation of SOA-forming vapors onto seed aerosol particles was kinetically limited (McVay et al., 2014). Kinetically-limited SOA growth occurs when the timescale for gas-particle equilibrium is competitive with or exceeds the timescale for reaction and vapor wall deposition, and may reflect imperfect accommodation of gas-phase organics to the particle phase. The markedly different behavior of the α-pinene and toluene SOA systems could be due to differences in SOA volatility and aerosol physical phase state (McVay et al., 2016).

5.2 Oxidation rate effect

At higher O_3 concentrations, the α-pinene oxidation rate increases, leading to higher SOA mass yields (the "oxidation rate effect"). This behavior was previously observed by Ng et al. (2007) for the *m*-xylene photooxidation system, for which the oxidation rate effect was attributed to the loss of semi-volatile condensable products to chamber walls in competition with condensation onto seed particles to form SOA.

SOA formation from α-pinene ozonolysis is presumed to be driven by a range of semi- and low-volatility first-generation products arising from reaction of O_3 with the single C=C double bond (Ng et al., 2006). These products are subject to two competing routes: condensation to particles to form SOA or deposition on the chamber walls. Each process can be represented in terms of a first-order rate constant: $k_{wall,on}$ and $k_{particle,on}$ (s^{-1}). The rate of vapor-wall deposition of condensable species A is then $k_{wall,on} \times [A]$ (molec cm^{-3} s^{-1}) and the rate of condensation onto particles is $k_{particle,on} \times [A]$ (molec cm^{-3} s^{-1}). Increasing the rate of reaction increases the concentration of [A], but the relative rates of vapor-wall deposition and condensation onto particles will remain the same. In general, however, both vapor-wall deposition and vapor-particle condensation are reversible

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processes (McVay et al., 2014; Zhang et al., 2014). The first-order rate constant for evaporation from the wall can be represented as (Matsunaga and Ziemann, 2010):

$$k_{wall,off} = k_{wall,on}\left(\frac{C_i^*}{C_w}\right) \tag{13}$$

where C_i^* is the saturation concentration and C_w is the assumed equivalent wall organic concentration. The rate of evaporation from particles is:

$$k_{particle,off} = k_{particle,on}\left(\frac{C_i^*}{C_{aer}}\right) \tag{14}$$

where C_{aer} is the organic aerosol concentration ($C_{aer}=\Sigma A_k+M_{init}$).

The difference between C_{aer} and C_w is the key to explaining the oxidation rate effect. At the beginning of the experiment, C_{aer} is very small because the inorganic seeds are essentially non-absorbing. Therefore, $k_{particle,off}$ is large, and the net SOA growth is small. In contrast, C_w is considered to be substantial (on the order of 10 mg m^{-3}) and to be essentially constant throughout the experiment (Matsunaga and Ziemann, 2010; McVay et al., 2014; Zhang et al., 2014). Model predictions are insensitive to the value of C_w since, in any event, C_w is significantly larger than C_{aer} (Zhang et al., 2014). Therefore, $k_{wall,off}$ is small at the beginning of the experiment and the net vapor wall loss rate is fast. As C_{aer} increases, the net SOA condensation rate increases relative to the net vapor wall loss rate. When the reaction rate increases corresponding to higher O_3 concentrations, C_{aer} grows more quickly because more condensable species are available to form SOA, and the net condensation rate increases more rapidly. Therefore, the observed oxidation rate effect is due to vapor wall deposition, and arises because vapor-particle and vapor-wall condensation are essentially reversible processes. This explanation is consistent with simulations varying the O_3 concentration in which all species are non-volatile (i.e., do not evaporate from the particles or the wall). In this case, no oxidation rate effect is observed as the O_3 concentration increases. The growth curves for different O_3 concentrations overlap, and the same yield is obtained regardless of O_3 concentration (Fig. S11).

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Sensitivity tests were performed to determine the point at which SOA formation is no longer influenced by the O_3 concentration. In these simulations, the initial α-pinene concentration is fixed at 48 ppb, while the O_3 concentration is varied from 75 to 1000 ppb. The rate of O_3 injection is assumed to remain constant as the O_3 concentration is increased to mimic the experimental protocol (i.e., O_3 injection time is increased to achieve higher O_3 concentrations). The O_3 injection rate used in these simulations is fixed at 500/54.25 ppb min^{-1}, which is the same as that used to analyze results from the 500 ppb O_3 experiments. Model predictions in Fig. S12 show that the maximum SOA mass concentration increases with increasing O_3 concentration up to approximately 500 ppb O_3. Beyond this O_3 concentration, the SOA growth curves overlap and the maximum SOA mass concentration does not increase even when more O_3 is added. This plateau arises due to the lengthening time required to inject increasing amounts of O_3. More than 1 h is required to inject > 500 ppb of O_3, and by this time, virtually all of the α-pinene has reacted. Increasing the O_3 concentration after all of the α-pinene has reacted does not lead to any changes in the SOA mass concentration. However, if a faster injection rate of O_3 is used, the oxidation rate effect will persist to higher O_3 concentrations (i.e., > 500 ppb O_3) (Fig S13). With a faster injection rate, 500 ppb O_3 is injected before all of the α-pinene has reacted. Continuing to inject O_3 to a higher concentration (i.e., 750 ppb) will cause α-pinene to decay faster and SOA to grow faster than when the O_3 injection stops at 500 ppb. The oxidation rate effect is then apparent at higher O_3 concentrations. If, instead of using an injection rate of O_3, simulations are run using fixed initial O_3 (not possible experimentally), the rate effect persists to even higher O_3 concentrations. The relative increase in yield with increasing O_3 concentrations slows at very high O_3 concentrations because the rate of reaction becomes substantially faster than the vapor wall deposition rate, and there is less marginal effect to increasing the reaction rate.

5.3 Interplay of the seed aerosol surface area effect and the oxidation rate effect

In this study, we observe an oxidation rate effect but not a seed aerosol surface area effect. In Zhang et al. (2014), a seed aerosol surface area effect was observed, but the variation of the oxidation rate was not studied. A key aspect of vapor wall deposition is the potential interplay between the seed aerosol surface area effect and the oxidation

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rate effect. To examine this interplay in the α-pinene ozonolysis system, simulations were carried out by varying the seed aerosol surface area and the O_3 concentration simultaneously, while using the branching ratios, oligomerization rate, and vapor wall deposition rate parameters obtained in the present study. The initial α-pinene concentration was set to 50 ppb, and a fixed O_3 concentration was used in place of a linear injection. α_p was varied at 0.001, 0.01, and 1 in these simulations. Figure 6 shows the SOA mass yield at peak SOA growth as a function of both the seed aerosol surface area and O_3 concentration for α_p = 1, 0.01, and 0.001. For α_p = 1, the oxidation rate dominates: SOA mass yield increases significantly as O_3 concentration increases while the seed aerosol surface area has a negligible effect. For α_p = 0.01, both effects can be observed in different regions: at low O_3 concentrations and high seed aerosol surface areas, the oxidation rate effect dominates; at low seed aerosol surface areas and high O_3 concentrations, the seed surface area dominates. At low seed aerosol surface areas and low O_3 concentrations, both effects are present. For α_p = 0.001, the seed aerosol surface area effect dominates except at very high seed aerosol surface areas. These observations show that the presence of an oxidation rate effect and/or seed aerosol surface area effect depends on a complex interplay of factors, such as α_p, the rate of hydrocarbon oxidation, and the amount of seed surface area present.

6. Implications

In this study, we systematically examine the roles of gas-particle partitioning and VOC oxidation rate in the presence of vapor-wall deposition in α-pinene ozonolysis. We show that despite the presence of vapor-wall deposition, SOA mass yields at peak SOA growth remain approximately constant regardless the seed aerosol surface area (within the range of AS seed surface area concentration used in this study). This observation is consistent with SOA formation in the α-pinene ozonolysis system being governed by quasi-equilibrium growth, for which there are no substantial limitations to vapor-particle mass transfer. This result was demonstrated in a previous modeling study which showed that increasing the seed-to-chamber surface area ratio will lead to increased SOA growth only in cases in which the condensation of SOA-forming vapors onto seed aerosol

particles is kinetically limited as a result of imperfect accommodation of gas-phase organics to the particle phase (McVay et al., 2014).

An important implication of this study is that diverting vapor-wall deposition in chamber studies via the addition of ever-increasing quantities of seed aerosol particles is not effective in VOC systems for which SOA formation is governed by quasi-equilibrium growth. This study also underscores the importance of accounting for particle wall deposition appropriately in chamber studies, to avoid erroneous conclusions regarding the role of gas-particle partitioning (quasi-equilibrium vs. kinetically-limited SOA growth) in influencing vapor wall loss in the VOC system.

We note that the present study shows that the SOA mass yield is independent of seed aerosol surface area concentration for values ranging from 0 to ~3000 $\mu m^2\ cm^{-3}$. This corresponds to a seed-to-chamber surface area ratio of 0 to ~1×10^{-3}, which is substantially smaller than the range used by Zhang et al. (2014) to study the influence of vapor-wall deposition on toluene photooxidation SOA formation in the Caltech chamber (i.e., 0 to ~5×10^{-3}). It is possible that a SOA mass yield dependence on the seed surface area may have become more apparent had a larger range of seed aerosol surface area (i.e., > 3000 $\mu m^2\ cm^{-3}$), and hence a larger range of seed-to-chamber surface area ratio, been used here. One consideration is that coagulation may become increasingly important, and will need to be accounted for, when higher seed aerosol number concentrations (relative to those used in this study) are used (Seinfeld and Pandis, 2006; Pierce et al., 2008). A detailed analysis of the effect of seed aerosol surface area concentrations > 3000 $\mu m^2\ cm^{-3}$ on α-pinene ozonolysis SOA mass yields will be the subject of forthcoming work.

Higher SOA mass yields at peak SOA growth are observed in the present study when O_3 is increased from 100 to 500 ppb. This is because α-pinene is oxidized more quickly, which leads to gas-phase oxidation products being formed more rapidly, and consequently partitioning more quickly onto AS seed aerosol particles before they are lost to the chamber walls. Therefore, the oxidation rate effect (i.e., higher SOA mass yields as a result of faster hydrocarbon oxidation rates) is a consequence of vapor-wall deposition. An important implication of this study is that SOA mass yields can be affected by vapor-wall deposition in VOC systems that are not characterized by slow

mass accommodation of gas-phase organics to the particle phase (Zhang et al., 2014). Thus, this work demonstrates that the effect of vapor-wall deposition on SOA mass yields can be mitigated through the use of excess oxidant concentrations. It should be noted that the α-pinene ozonolysis SOA mass yields (absolute values) increased by 5 to 9 % when O_3 is increased from 100 to 500 ppb (for an initial α-pinene concentration of ~50 ppb), where SOA formation is governed by quasi-equilibrium growth. In the absence of vapor-wall deposition, SOA mass yields are predicted by the model used here to approximately double from those observed experimentally. In contrast, Zhang et al. (2014) showed that the presence of vapor-wall deposition led to underestimation of SOA formation by factors as much as four in the toluene photooxidation system, where the condensation of SOA-forming vapors onto seed aerosol is kinetically limited. Taken together, these results indicate that the magnitude by which vapor-wall deposition affects SOA mass yields depends on the extent to which the VOC system is governed by kinetically-limited SOA condensational growth.

Given these observations of how gas-particle partitioning can influence the magnitude by which vapor-wall deposition affects SOA mass yields, an overriding question is: what controls the gas-particle partitioning behavior of SOA formed in different VOC systems? α_p describes the overall mass transfer of vapor molecules into the particle phase (McVay et al., 2014; Zhang et al., 2014). Thus, α_p affects the vapor-particle equilibrium timescale, which, depending on the extent to which it is competitive with the timescales for reaction and vapor-wall deposition, determines whether SOA formation is governed by kinetically-limited or quasi-equilibrium growth. Markedly different α_p values could arise from the physical phase state of the SOA formed. As discussed by McVay et al. (2014, 2016), if the SOA formed exists in a semi-solid state (Vaden et al., 2010; Virtanen et al., 2010; Cappa and Wilson, 2011; Vaden et al., 2011; Virtanen et al., 2011; Kuwata and Martin, 2012; Perraud et al., 2012; Saukko et al., 2012; Abramson et al., 2013; Renbaum-Wolff et al., 2013), a low value of α_p might be expected owing to retarded surface accommodation and particle-phase diffusion (Zaveri et al., 2014). Quantification of α_p is challenging experimentally, and reported α_p values for the same system can vary by several orders of magnitude (Grieshop et al., 2007; Stanier et al., 2007; Vaden et al., 2011; Miles et al., 2012; Saleh et al., 2013). Therefore, α_p of SOA

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formed in different VOC systems need to be better constrained through a combination of experimental and modeling efforts.

The SOA mass yield from the ozonolysis of monoterpenes in the GEOS-CHEM chemical transport model (19 % at 10 μg m^{-3}) is currently based on that measured in α-pinene ozonolysis studies by Shilling et al. (2008) (Pye et al., 2010). Shilling et al. (2008) measured these SOA mass yields in a teflon chamber operated in continuous-flow mode, as opposed to batch mode, which is how experiments in the present study and most of those shown in Fig. 5 and Table S2 were conducted. While it is not possible to directly compare our results with those of Shilling et al. (2008) due to differences in SOA mass concentrations, the SOA mass concentrations and yields measured in the current study are generally consistent with those of previous batch chamber studies. The SOA mass yields at ~10 μg m^{-3} SOA mass concentration measured by Shilling et al. (2008) are generally higher than those measured in chambers operated in batch mode (Griffin et al., 1999; Cocker et al., 2001b; Presto et al., 2005; Presto and Donahue, 2006; Pathak et al., 2007b) (Fig. 5). One possible explanation for the higher SOA mass yields in the continuous-flow, steady state, mode is that the SOA-forming vapors are in equilibrium with the organic mass present on the chamber walls and seed aerosol, hence minimizing the irreversible loss of SOA-forming vapors to the chamber walls (Shilling et al., 2008). However, the extent to which SOA mass yields obtained in a continuous-flow reactor are influenced by vapor wall loss is unclear. Using a continuous-flow reactor, Ehn et al. (2014) observed α-pinene ozonolysis SOA mass yields to increase with increasing seed aerosol surface area but required $\alpha_p = 1$ to fit the observed SOA growth. The observed vapor-wall deposition rate constant in their continuous-flow reactor (0.011 s^{-1}) is two orders of magnitude larger than that of the GTEC chamber (10^{-4} s^{-1}). The estimated timescales for gas-particle and gas-wall partitioning are also approximately equal in their continuous-flow reactor. This indicates that SOA condensational growth is kinetically limited in their continuous-flow reactor even at $\alpha_p = 1$ (Ehn et al., 2014; McVay et al., 2014), which suggests that SOA mass yields measured in their continuous-flow reactor may be significantly affected by vapor-wall deposition.

Previous studies on SOA formation from the OH and NO_3 oxidation of biogenic VOCs have similarly reported higher SOA mass yields in the presence of higher oxidant concentrations. For example, in the NO_3 oxidation of β-pinene, Boyd et al. (2015) reported SOA mass yields 10 to 30 % higher than those previously reported by Fry et al. (2009, 2014). In addition to differences in the experimental conditions of the two studies, Boyd et al. (2015) hypothesized that the higher SOA mass yields could also be a result of the higher NO_3 concentrations used in their study (which led to faster β-pinene oxidation rates) compared to those used by Fry et al. (2009, 2014). The oxidation rate effect was also observed in the *m*-xylene photooxidation system, where Ng et al. (2007) showed that the SOA mass yields were dependent on the *m*-xylene oxidation rate, with higher OH concentrations (and hence faster oxidation rates) resulting in higher SOA mass yields Together, these studies show that faster hydrocarbon oxidation rates can alleviate the effects of vapor-wall deposition on SOA mass yields in different VOC systems.

This gives rise to the question: should chamber SOA experiments on different VOC systems be performed under as rapid oxidation conditions as possible (i.e., large oxidant concentrations) to reduce the effects of vapor-wall deposition? A recent study by McVay et al. (2016) reported similar SOA growth under low and high OH levels for α-pinene photooxidation. The authors hypothesized that the autoxidation mechanism likely becomes a more important pathway at low OH levels (Crounse et al., 2013), and thus contributes substantially to SOA growth. Therefore, it is possible that certain reaction pathways and mechanisms (which are important in the atmosphere) are biased when unusually high levels of oxidants are used in chamber experiments (e.g. autoxidation). Thus, this underscores the need to design chamber experiments that simultaneously mitigate the magnitude of vapor-wall deposition while ensuring that reaction conditions, and consequently reaction pathways and oxidation products, are atmospherically relevant.

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Table 1: Experimental conditions and results for the α-pinene ozonolysis experiments

Experiment	Initial Seed Surface Area ($\mu m^2\ cm^{-3}$)	Initial [α-pinene][a] ($\mu g\ m^{-3}$)	ΔM_0[b] ($\mu g\ m^{-3}$)	SOA Mass Yield[c] (%)
100 ppb O_3 nucleation	0	290.2±23.2	62.0±1.2[d]	22.6±1.9
100 ppb O_3 low AS	1130	280.5±22.4	63.0±0.8[d]	23.3±1.9
100 ppb O_3 high AS	2700	238.7±19.1	50.6±1.6[d]	23.3±1.9
500 ppb O_3 nucleation	0	274.4±21.9	87.3±0.3[e]	31.8±2.5
500 ppb O_3 low AS	1300	264.9±21.2	75.7±0.6[e]	28.6±2.3
500 ppb O_3 high AS	2720	236.1±18.9	66.3±1.9[e]	28.1±2.4

[a]Concentration of α-pinene injected into the chamber. All the α-pinene reacted in the 500 ppb O_3 experiments, but not the 100 ppb O_3 experiments.
[b]Uncertainties in the peak SOA mass concentration (ΔM_0) are calculated from one standard deviation of the aerosol volume as measured by the scanning mobility particle sizer.
[c]SOA mass yields at peak SOA growth are reported.
[d]The SOA mass concentration is calculated using the density = 1.39 g cm^{-3} obtained from the 100 ppb O_3 nucleation experiment.
[e]The SOA mass concentration is calculated using the density = 1.37 g cm^{-3} obtained from the 500 ppb O_3 nucleation experiment.

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Table 2: Coupled vapor-particle dynamics model parameters

Parameter	Definition	Value
α_p	Vapor-particle mass accommodation coefficient	1
α_w	Vapor-wall mass accommodation coefficient	10^{-6}
τ_{olig}	Timescale of oligomerization	4 h
C^*	Saturation vapor pressures and branching ratios of oxidation products	[0.57 (>10^3), 0.35 (10^2), 0.04 (10), 0.015 (1) and 0.025 (0.1)]
D_i	Gas-phase molecular diffusivity	3×10^{-6} m^2 s^{-1}
A/V	Surface area-to-volume ratio of the chamber	2.5 m^{-1}
C_w	Equivalent organic mass concentration in the wall	10 mg m^{-3}
k_e	Eddy diffusion coefficient	0.03 s^{-1}
M_i	Molecular weight of the diffusing gas-phase molecule i	168, 184, 192, 200 and 216 g $mole^{-1}$
M_{init}	Initially absorbing organic material in seed aerosol	0.01 μg m^{-3}
P	Pressure	1×10^5 Pa
T	Temperature	298 K
ρ_{seed}	Density of inorganic seed	1700 kg m^{-3}
ρ_{org}	Density of organic material on seed particle	1300 kg m^{-3}

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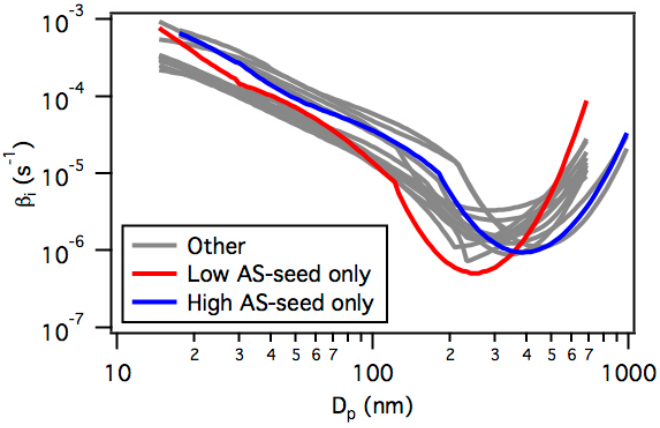

Figure 1: Particle wall deposition coefficients (β_i) measured during the low AS-seed only and high AS-seed only experiments in GTEC. Also shown are the particle wall deposition coefficients (labeled "Other") measured in previous routine monthly AS-seed only experiments in the chamber. These previous routine monthly AS-seed only experiments were performed using either a 0.008 M AS or a 0.1 M AS solution.

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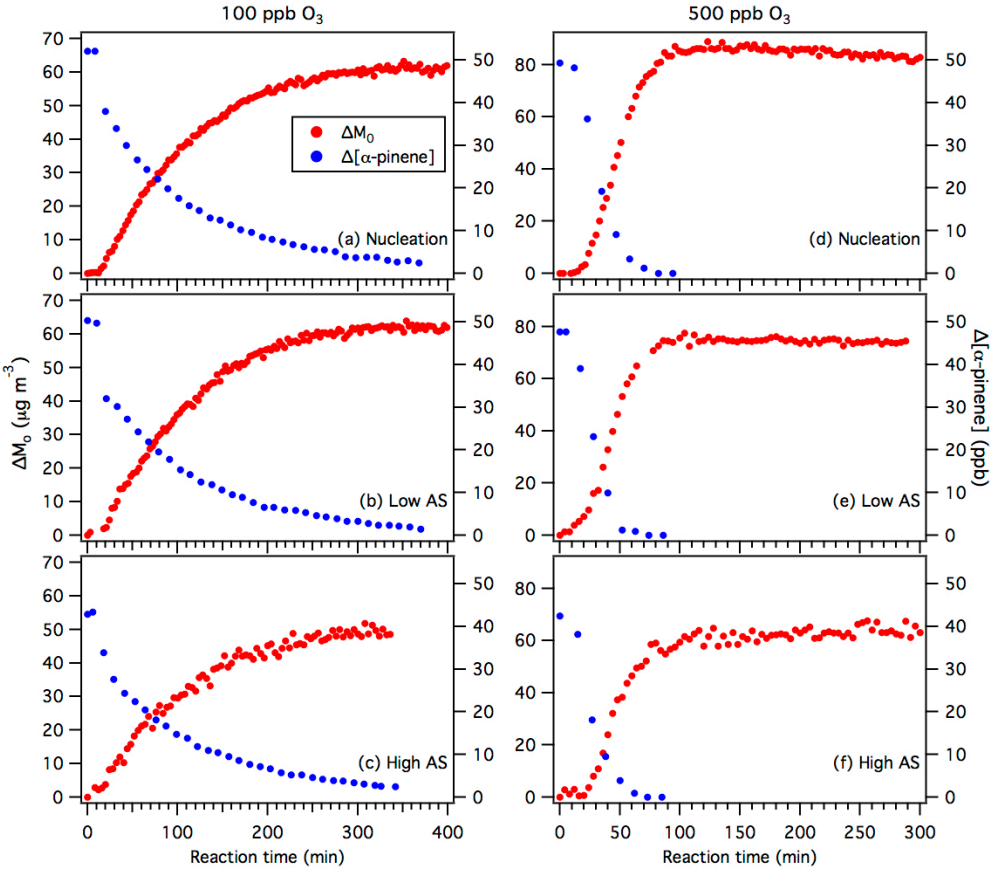

Figure 2: Reaction profiles of the α-pinene ozonolysis experiments. Panels (a), (b) and (c) show results from the nucleation, low AS and high AS 100 ppb O_3 experiments, respectively. Panels (d), (e) and (f) show results from the nucleation, low AS and high AS 500 ppb O_3 experiments, respectively. As explained in the main text, the SOA mass concentrations (ΔM_o) for the nucleation and low AS experiments are obtained using the particle wall rates obtained from the low AS-seed only experiments, while the SOA mass concentrations (ΔM_o) for the high AS-seed experiments are obtained using the particle wall rates obtained from the high AS-seed only experiments.

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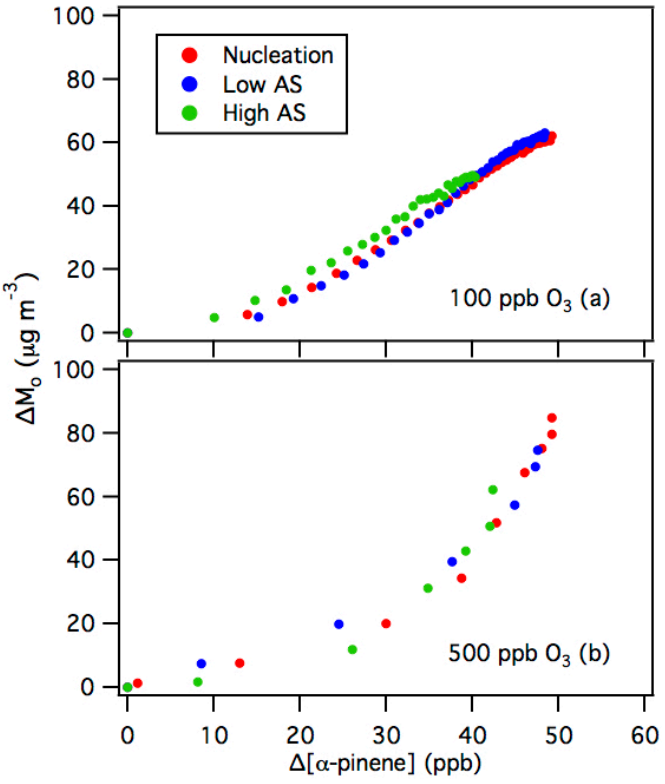

Figure 3: Time-dependent SOA growth curves for α-pinene ozonolysis. Panels (a) and (b) show 10 min-averaged results from the 100 ppb and 500 ppb O_3 experiments, respectively. Only SOA growth data up to the point of SOA peak growth are shown.

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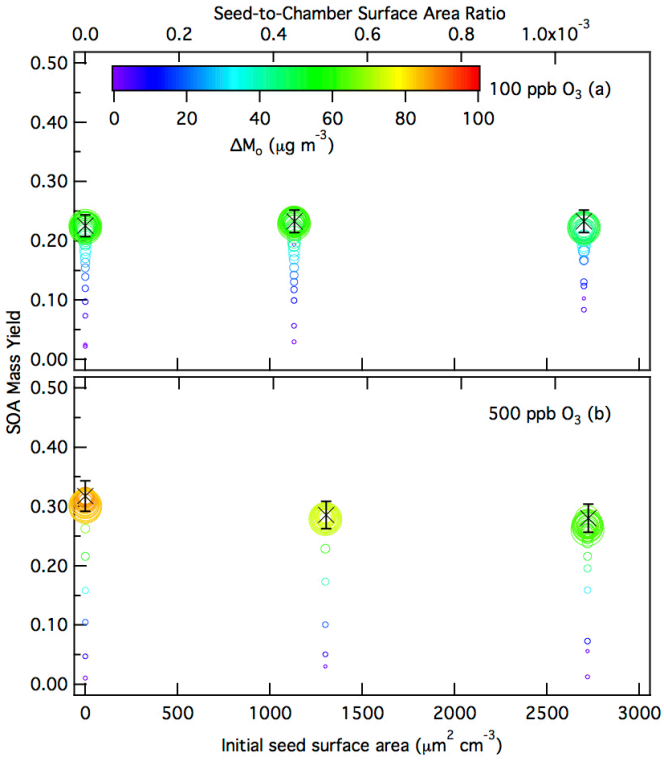

Figure 4: 10 min-averaged SOA mass yields over the course of an α-pinene ozonolysis experiment as a function of initial total AS seed surface area concentration for the (a) 100 ppb O_3 experiments, and (b) 500 ppb O_3 experiments. Symbol color indicates the SOA mass concentration and symbol size indicates the time after O_3 is injected into the chamber. The × symbols are the SOA mass yields at peak SOA growth obtained from the experimental data. The y-axis error bars represent the uncertainty in the SOA mass yield at peak SOA growth, which originates from the α-pinene injection and the aerosol volume concentration measured by the SMPS at peak SOA growth (one standard deviation).

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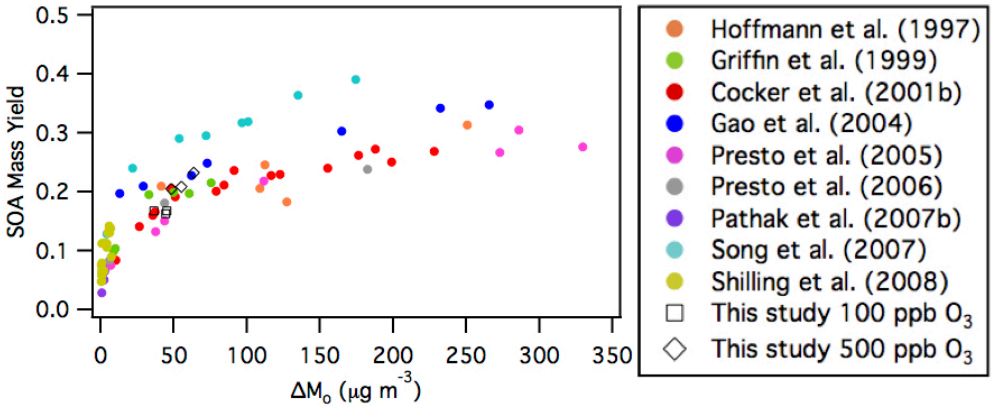

Figure 5: Comparison of SOA mass yields obtained in this study to those of previous dark α-pinene ozonolysis studies (Table S2). The SOA mass yields and concentrations of majority of these previous studies (Hoffmann et al., 1997; Griffin et al., 1999; Cocker et al., 2001b; Gao et al., 2004; Presto et al., 2005; Presto et al. 2006; Pathak et al., 2007b; Song et al., 2007) were previously compiled by Shilling et al (2008). Similar to Shilling et al. (2008), all the data shown here (including those reported in this study) have been adjusted using an organic density of 1.0 g cm^{-3}, and to 298 K using a temperature correction of 1.6 % per K, as recommended by Pathak et al. (2007b) to facilitate easier comparison among the different studies.

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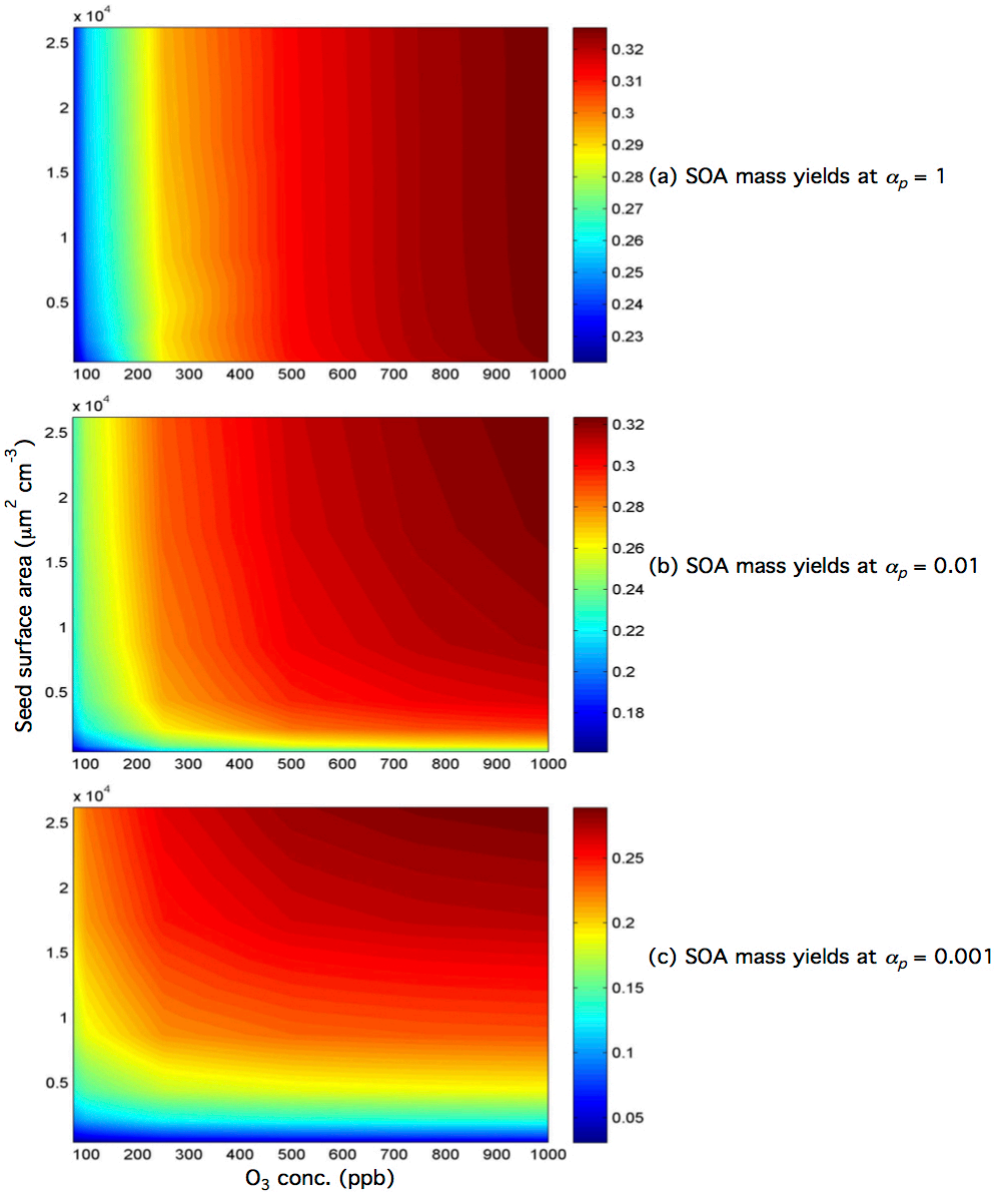

Figure 6: SOA mass yields at peak SOA growth as a function of both the seed surface area and O_3 concentration for α_p = 1, 0.01, and 0.001. The SOA mass yields at peak SOA growth are indicated by colors and contours. Note that the color bars for panels (a), (b) and (c) have different SOA mass yield ranges. Simulations were carried out using the branching ratios, oligomerization rate, and vapor wall deposition rate parameters obtained in this study. The initial α-pinene concentration was set to 50 ppb, and a fixed O_3 concentration was used in place of a linear injection.