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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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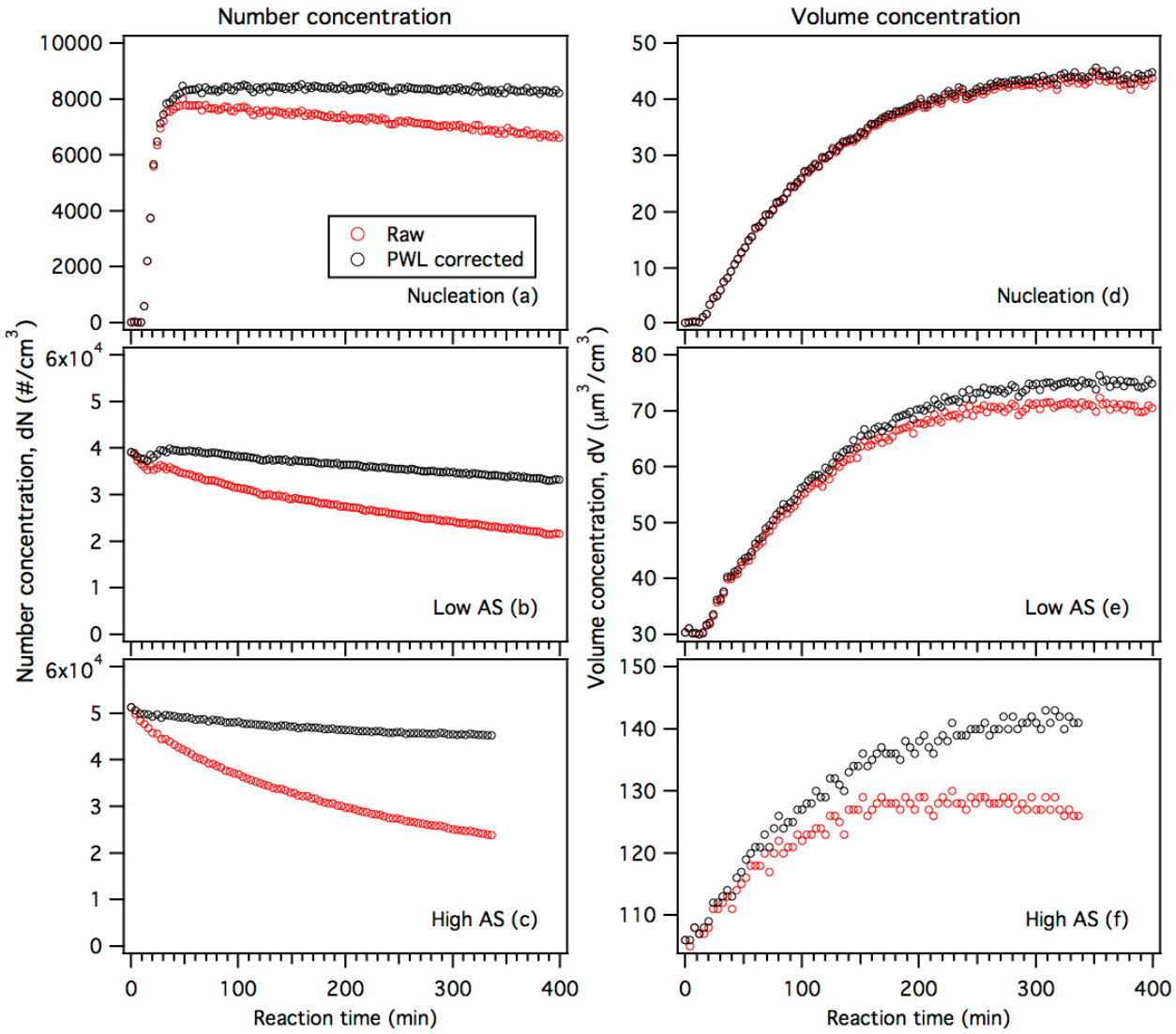


Figure S1: Raw and particle wall loss (PWL) corrected number and volume concentration data for the 100 ppb O_3 experiments. Raw nucleation (panels a and d) and low AS (panels b and e) data are particle wall loss corrected using particle wall loss rates determined from the low AS-seed only experiments. Raw high AS (panels c and f) data are particle wall loss corrected using particle wall loss rates determined from the high AS-seed only experiments.

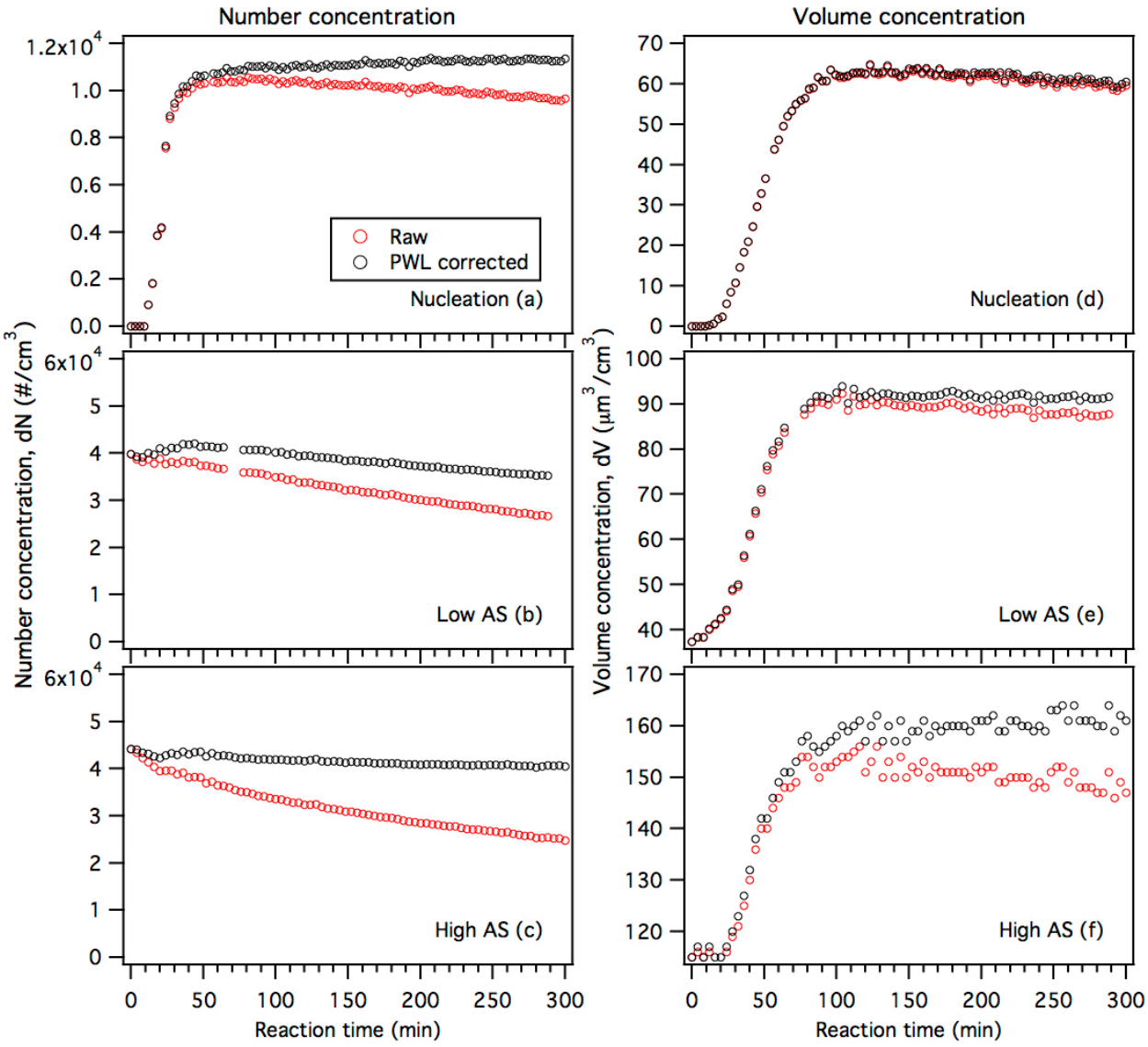


Figure S2: Raw and particle wall loss (PWL) corrected number and volume concentration data for the 500 ppb O_3 experiments. Raw nucleation (panels a and d) and low AS (panels b and e) data are particle wall loss corrected using particle wall loss rates determined from the low AS-seed only experiments. Raw high AS (panels c and f) data are particle wall loss corrected using particle wall loss rates determined from the high AS-seed only experiments.

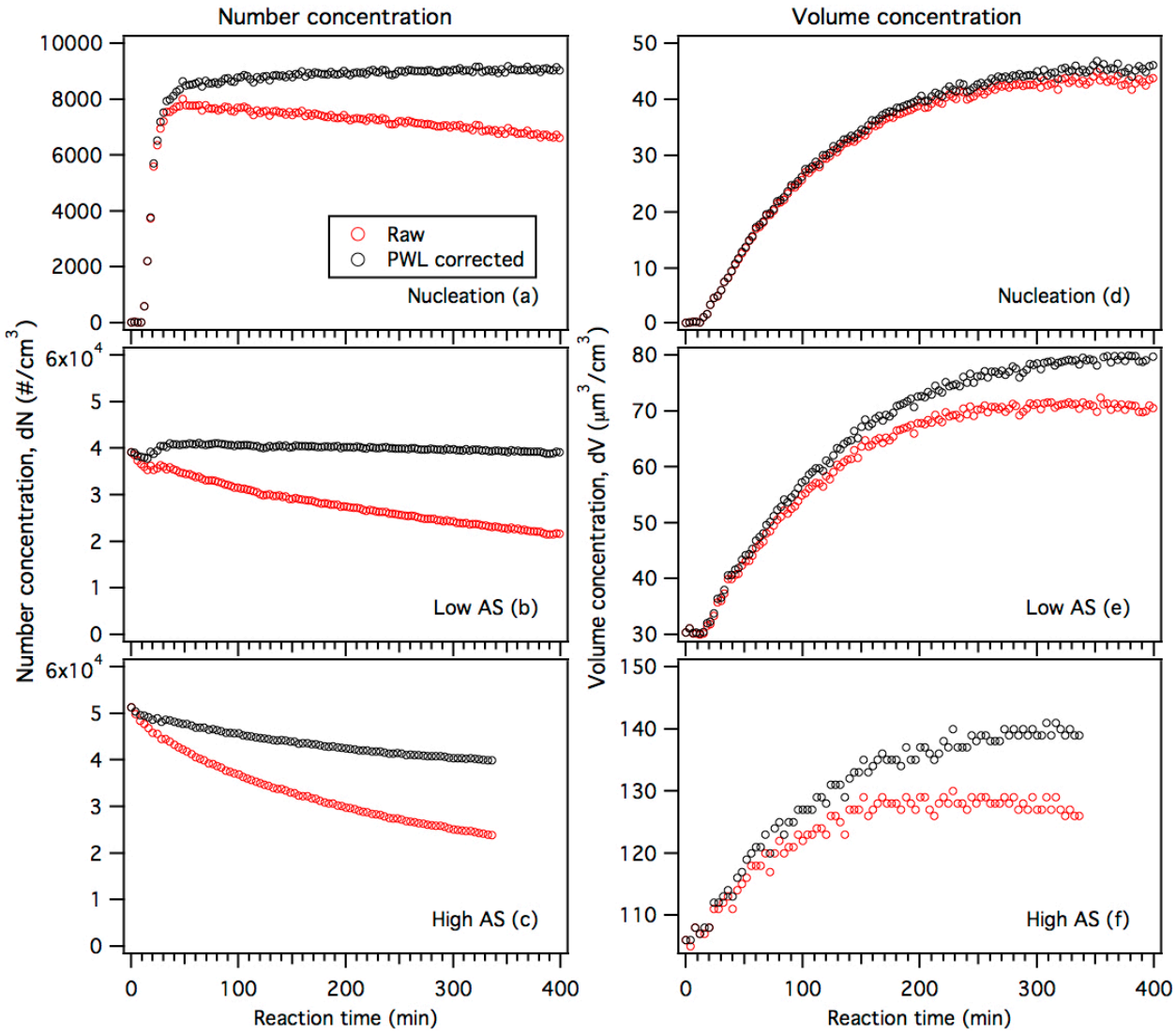


Figure S3: Raw and particle wall loss (PWL) corrected number and volume concentration data for the 100 ppb O_3 experiments. All the raw data are particle wall loss corrected using the average particle wall loss rates (i.e. average of the particle wall loss rates obtained from low AS-seed only and high-AS seed only experiments).

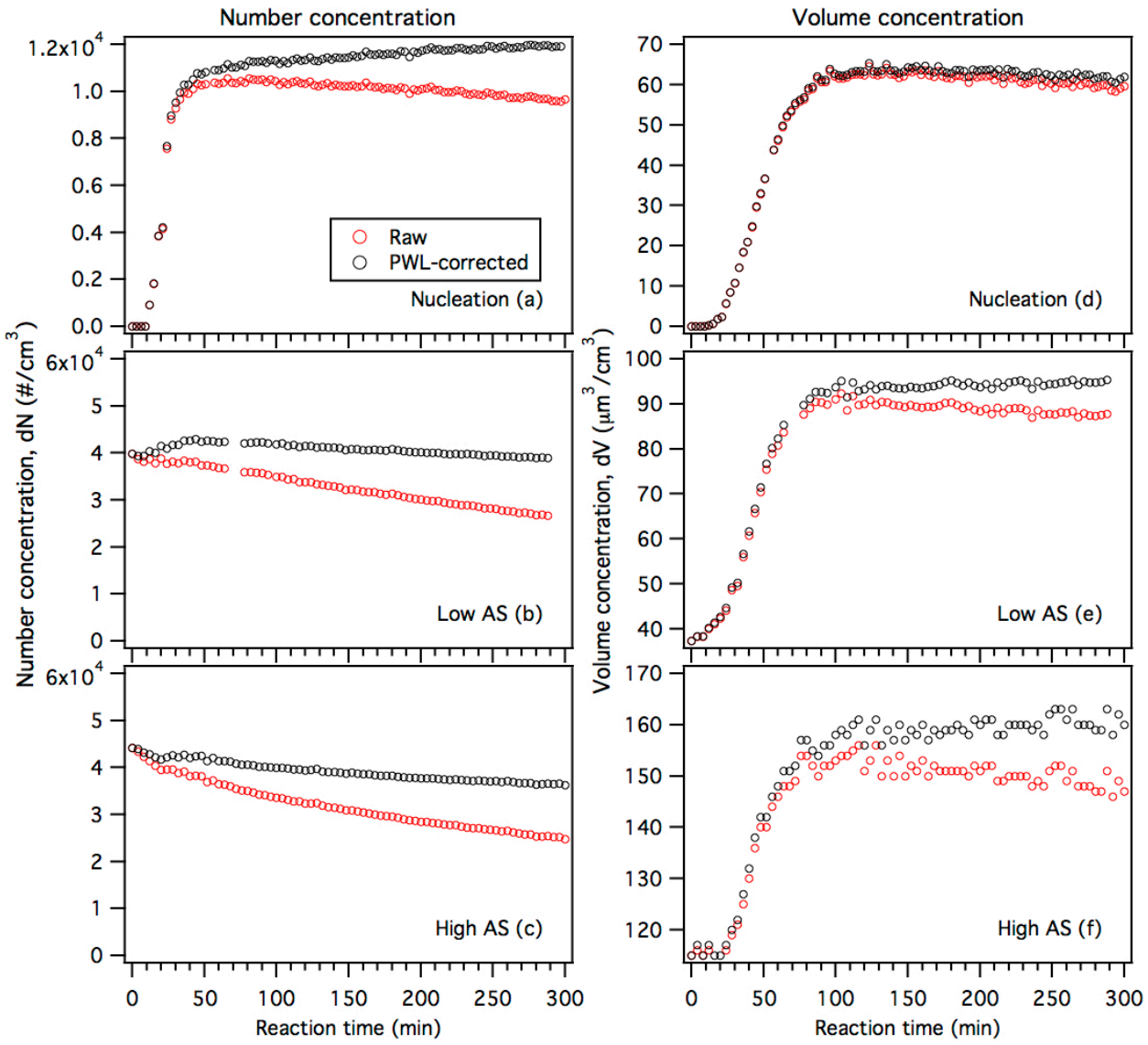


Figure S4: Raw and particle wall loss (PWL) corrected number and volume concentration data for the 500 ppb O_3 experiments. All the raw data are particle wall loss corrected using the average particle wall loss rates (i.e. average of the particle wall loss rates obtained from low AS-seed only and high-AS seed only experiments).

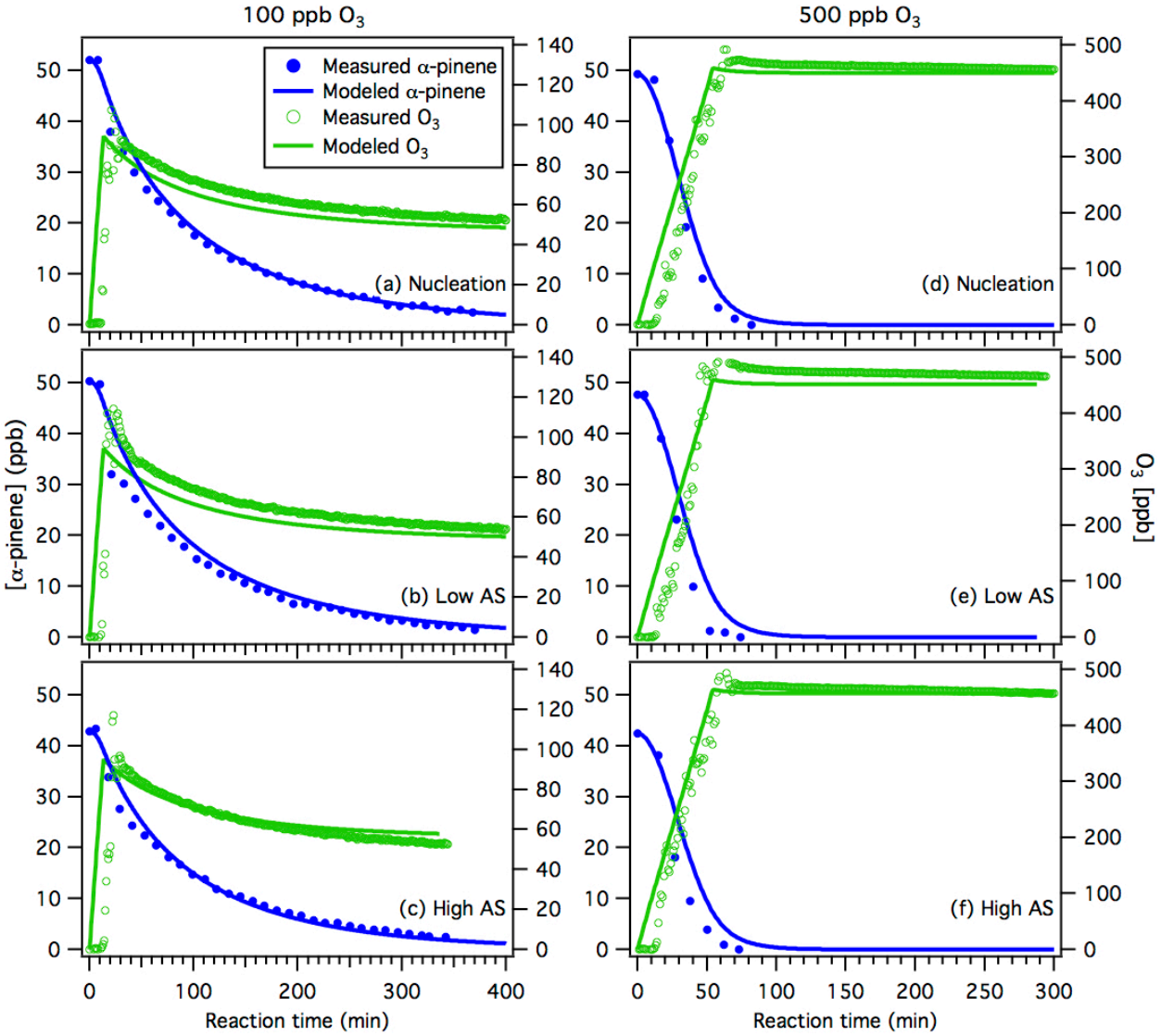


Figure S5: Reaction profiles of the measured and modeled O_3 and α-pinene concentration in the α-pinene ozonolysis experiments. Panels (a), (b) and (c) show results from the nucleation, low AS and high AS 100 ppb O_3 experiments, respectively. Panels (d), (e) and (f) show results from the nucleation, low AS and high AS 500 ppb O_3 experiments, respectively. The blue lines that fit the α-pinene concentration measurements and the green lines that fit the O_3 concentration measurements are model simulation results that come from the coupled vapor-particle dynamics model described in Section 3.

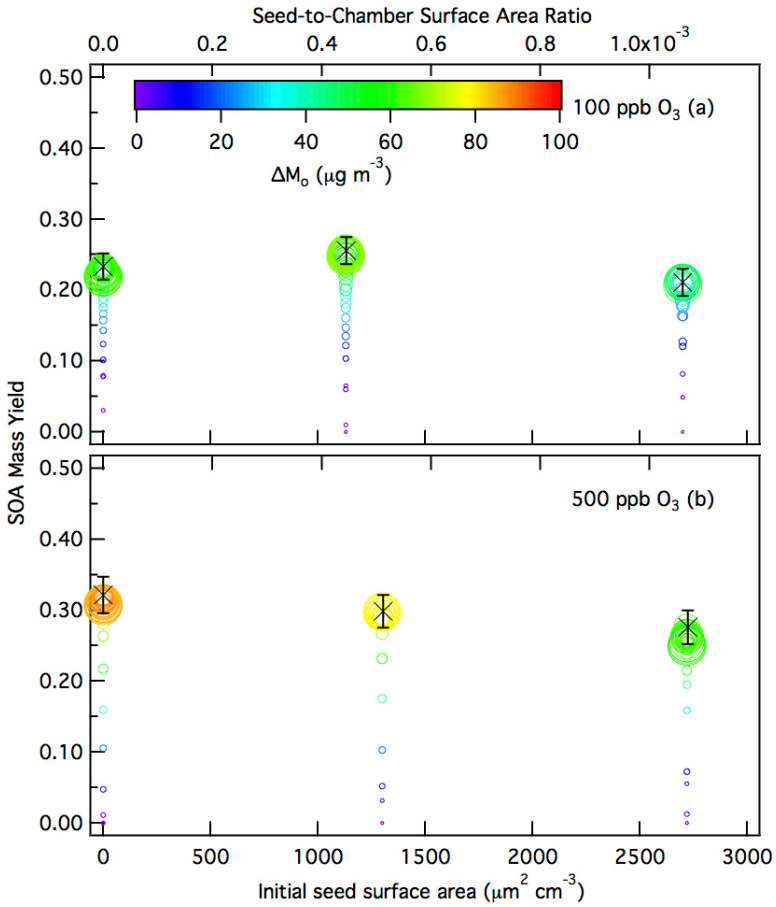
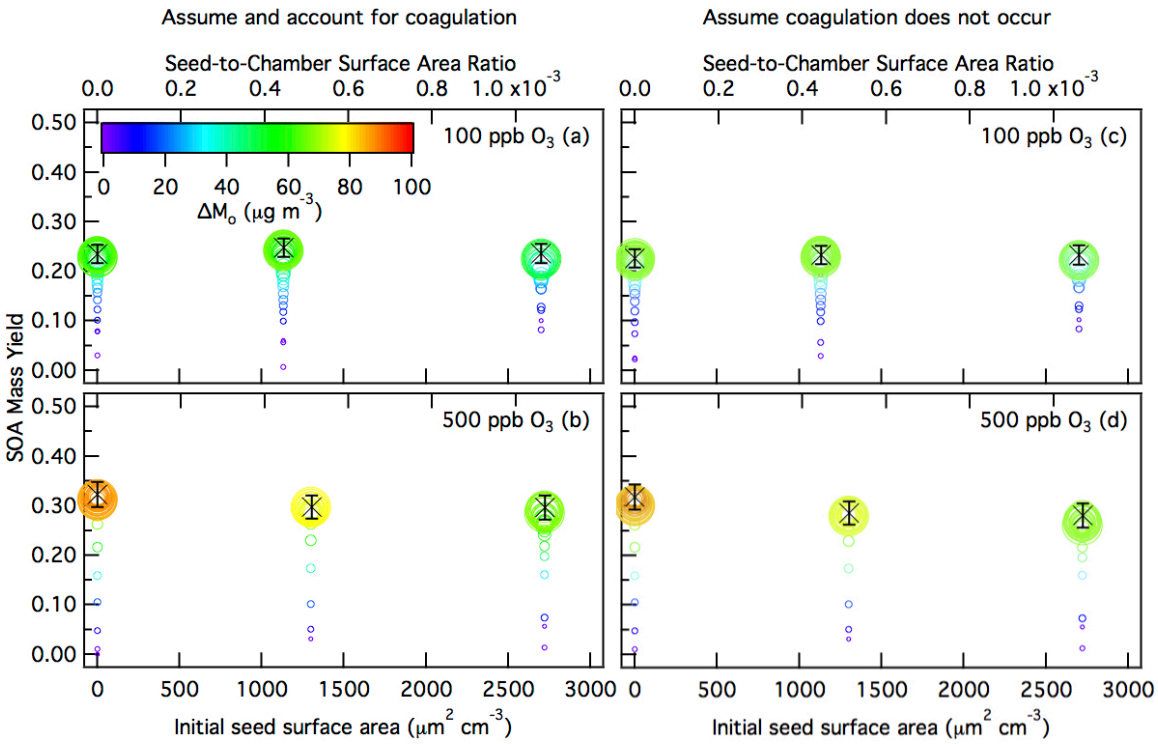


Figure S6: 10 min-averaged SOA mass yields over the course of an α-pinene ozonolysis experiment as a function of initial total AS seed surface area concentration for the (a) 100 ppb O_3 experiments, and (b) 500 ppb O_3 experiments. Here, all the data have been particle wall loss corrected using the average particle wall loss rates (i.e. average of the particle wall loss rates measured from low AS-seed only and high-AS seed only 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. The y-axis error bars represent the uncertainty in the peak SOA mass yield, which originates from the α-pinene injection and the aerosol volume concentration measured by the SMPS at peak SOA growth (one standard deviation). As discussed in the main text, the use of average measured particle wall loss rates for particle wall loss correction does not change the conclusions of this work: 1) SOA mass yields are enhanced at higher O_3 concentrations, and 2) there is a lack of a SOA mass yield dependence on the seed surface area within the range of AS seed surface area concentration used in this study.



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66 **Figure S7:** 10 min-averaged SOA mass yields over the course of an α-pinene ozonolysis
67 experiment as a function of initial total AS seed surface area concentration. Panels (a)
68 and (b) show the SOA mass yields obtained using the coagulation-corrected size-
69 dependent particle wall deposition coefficients for the 100 and 500 ppb O_3 experiments,
70 respectively. Panels (c) and (d) show the SOA mass yields obtained using the measured
71 size-dependent particle wall deposition coefficients (that account for coagulation) for the
72 100 and 500 ppb O_3 experiments, respectively (also shown in Fig. 4 of the main text).
73 Symbol color indicates the SOA mass concentration and symbol size indicates the time
74 after O_3 is injected into the chamber. The × symbols are the SOA mass yields at peak
75 SOA growth. The y-axis error bars represent the uncertainty in the peak SOA mass yield,
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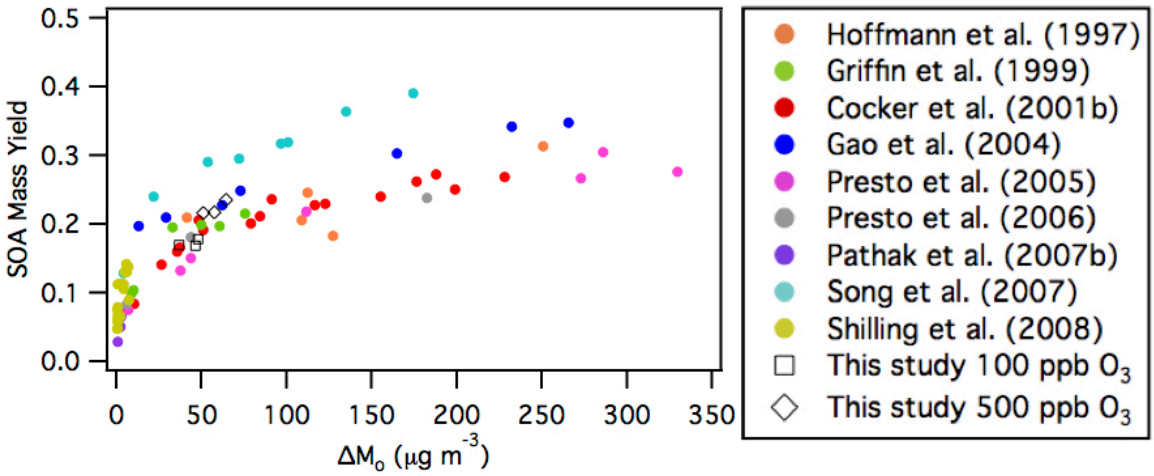

Figure S8: Comparison of SOA mass yields obtained using the coagulation-corrected size-dependent particle wall deposition coefficients to those of previous dark α-pinene ozonolysis studies (Table S2). The SOA mass yields and concentrations of majority of these previous studies (Hoffmann et al., 1997; 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.

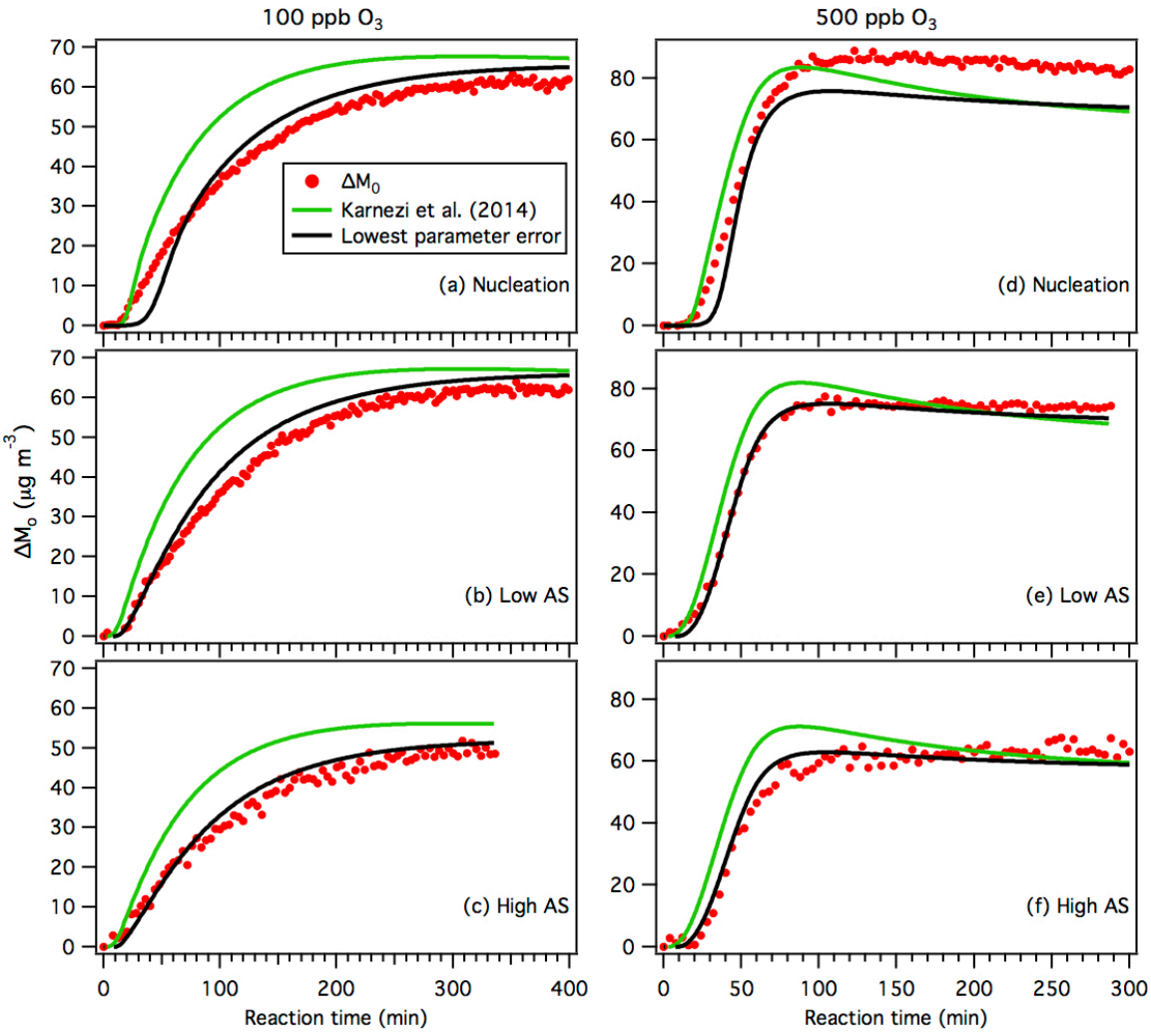

Figure S9: Reaction profiles for measured and modeled SOA concentration, using both the Karnezi et al. (2014) parameters and the lowest-error combination of parameters (see Table S4). Panels (a), (b) and (c) show results from the nucleation, low AS and high AS 100 ppb O_3 experiments, respectively. Panels (d), (e) and (f) show results from the nucleation, low AS and high AS 500 ppb O_3 experiments, respectively.

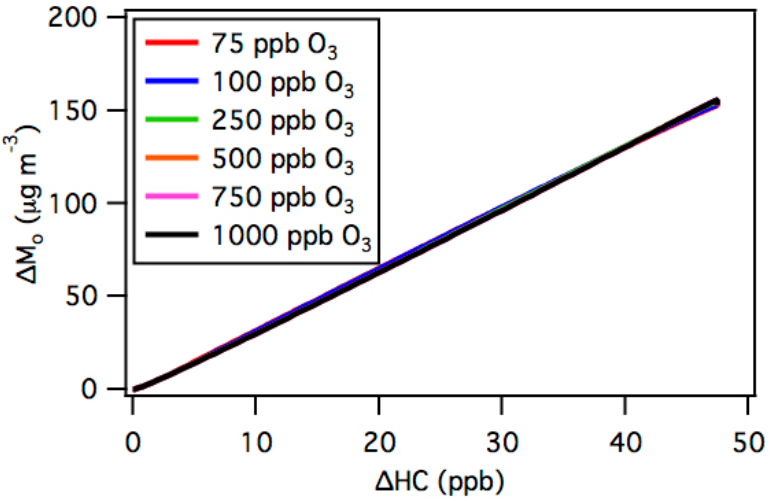

Figure S10: Results from the coupled vapor-particle dynamics model showing how SOA mass concentration (ΔM_o) changes as a function of reacted α-pinene at different O_3 concentrations, assuming all the α-pinene oxidation products are non-volatile. In these model simulation runs, the initial α-pinene concentration is fixed at 48 ppb, while the O_3 concentration is varied from 75 to 1000 ppb. The O_3 injection rate used in these model simulation runs is 500/54.25 ppb min^{-1}.

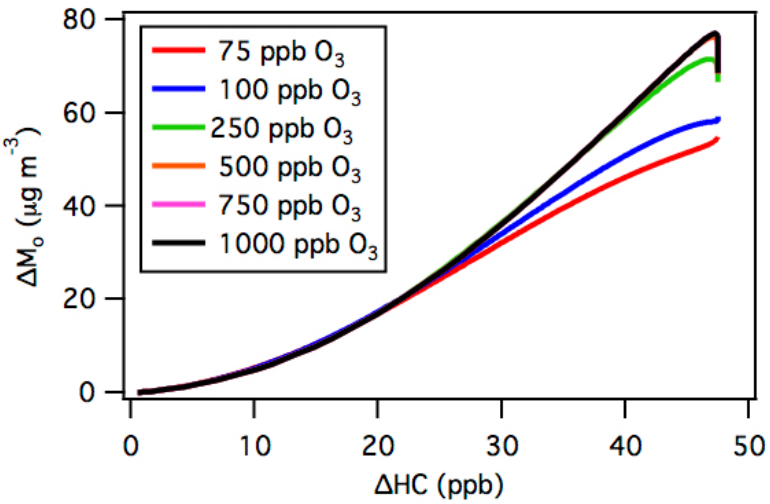

Figure S11: Predictions from the coupled vapor-particle dynamics model showing time-dependent growth curves for SOA formation from α-pinene ozonolysis at different O_3 concentrations. In these model simulation runs, the initial α-pinene mixing ratio is fixed at 48 ppb, while the O_3 mixing ratio is increased from 75 to 1000 ppb. In the model, the O_3 injection rate is assumed to be fixed at 500/54.25 ppb min^{-1}, and the injection time is increased to achieve the desired O_3 concentration (i.e., 75, 100, 250, 500, 750 or 1000 ppb) in the chamber. The predicted ΔM_o decreased slightly at the end of the experiment at the higher O_3 concentrations (250, 500, 750 and 1000 ppb) due to SOA evaporation. It is important to note that SOA evaporation is predicted at high O_3 concentrations in the coupled vapor-particle dynamics model, but not observed in chamber experiments.

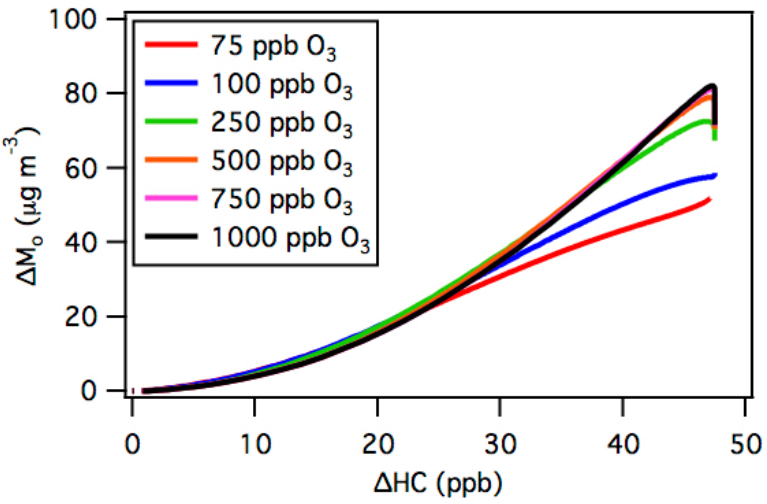

Figure S12: Results from the coupled vapor-particle dynamics model showing how SOA mass concentration (ΔM_o) changes as a function of reacted α-pinene at different O_3 concentrations. In these model simulation runs, the initial α-pinene concentration is fixed at 48 ppb, while the O_3 concentration is varied from 75 to 1000 ppb. Here, the O_3 injection rate is 5 times faster than the base rate used in the model. The base rate is 500/54.25 ppb min^{-1}, the same rate used to analyze results from the 500 ppb O_3 experiments. As discussed in the main text, the oxidation rate effect persists at a higher O_3 concentration when a faster O_3 injection rate is used. It is important to note that SOA evaporation is predicted at high O_3 concentrations in the coupled vapor-particle dynamics model, but not observed in chamber experiments.

Table S1: Initial and particle wall loss corrected final number concentrations[a]

Experiment	Initial Number Concentration (particle/cm^3)	Final Number Concentration (particle/cm^3)[b]	% Change[c]	Final Number Concentration (particle/cm^3)[d]	% Change[c]
100 ppb O_3 nucleation	23	8222	3.5×10^4	9152	3.9×10^4
100 ppb O_3 low AS	39119	32553	-16.8	38689	-1.1
100 ppb O_3 high AS	51254	45280	-11.7	39889	-22.2
500 ppb O_3 nucleation	1	11303	1.6×10^6	11974	1.7×10^6
500 ppb O_3 low AS	39800	35216	-11.5	38905	-2.2
500 ppb O_3 high AS	44196	40191	-9.1	35189	-20.4

[a]Particle number concentrations (dN)

[b]The data shown here correspond to those shown in Figs. S1 and S2. The nucleation and low AS data have been particle wall loss corrected using particle wall loss rates determined from the low AS-seed only experiments. The high AS data have been particle wall loss corrected using particle wall loss rates determined from the high AS-seed only experiments.

[c]$\%\ \text{Change} = \frac{(\text{Difference between initial and particle wall loss corrected final number concentration})}{\text{Initial number concentration}} \times 100\%$

[d]The data shown here correspond to those shown in Figs. S3 and S4. All the data have been particle wall loss corrected using the average particle wall loss rates (i.e. average of the particle wall loss rates obtained from low AS-seed only and high-AS seed only experiments).

Table S2: Discretization of parameters

Parameter	Discretization
α_p	1, 0.1, 0.01, 0.001
α_w	10^{-7}, 10^{-6}, 10^{-5}
τ_{olig}	4, 6, 8
$>10^3$ branching ratio[a]	0.5, 0.6, 0.7, 0.8, 0.9, 1
10^2 branching ratio[a]	0, 0.1, 0.2, 0.3, 0.4, 0.5
10 branching ratio[a]	0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15, 0.2
1 branching ratio[a]	0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15, 0.2
0.1 branching ratio[a]	0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15, 0.2

[a]Only combinations of parameters summing to one were allowed.

Table S3: Comparison of experimental conditions used in this work with those of previous dark α-pinene ozonolysis studies. The SOA mass yields and concentrations of these studies are shown Fig. 5.

Study	Temperature (K)	RH (%)	Seed	OH Scavenger	O_3 (ppb)	ΔHC (ppb)
Cocker et al. (2001)[a]	301.2-302.9	<2, 39-49.2	None, $(NH_4)_2SO_4$ and NH_4HSO_4	2-butanol	130-600	22.6-212.3
Gao et al. (2004)[b]	293	55	$MgSO_4$	cyclohexane	24-270	12-135
Griffin et al. (1999)	303.3-309.9	5	$(NH_4)_2SO_4$	2-butanol	67-260	16.7-65
Hoffmann et al. (1997)	289.3-322.1	N.A.	$(NH_4)_2SO_4$	None	210-327	38-154.1
Pathak et al. (2007b)	288-313	< 10	None, $(NH_4)_2SO_4$	2-butanol	750-3100	3.7-8.5
Presto et al. (2005)[c]	295	< 10	None	2-butanol	160-605	15-210
Presto et al. (2006)[d]	295	< 10	None	2-butanol	260-350	13.4-135
Shilling et al. (2008)[e]	298	40	$(NH_4)_2SO_4$	1- and 2-butanol	50, 300, 535	0.3-22.8
Song et al. (2007)[f]	300.6-301.7	< 2	None	cyclohexane	46-369	5.9-81.1
This study	298	< 5	$(NH_4)_2SO_4$	cyclohexane	100, 500	42.4-52.1

[a]Data collected using aqueous seed aerosol is excluded from our analysis.
[b]Data collected using acidic seed aerosol is excluded from our analysis.
[c]Only dark experiments in which [α-pinene]/[NO_x] > 15 are used in our analysis.
[d]Only dark α-pinene ozonolysis experiments are used in our analysis.
[e]Data collected in batch mode and continuous-flow mode are used in our analysis.
[f]Data collected using organic seed aerosol is excluded from our analysis.

Table S4: Best-fit parameters, using lowest percentage error and Karnezi et al. (2014) method

Parameter	Lowest percentage error	Karnezi et al. (2014) method
α_p	0.1	0.35
α_w	10^{-6}	3.6×10^{-6}
τ_{olig} (h)	4	6
$>10^3$ branching ratio	0.6	0.66
10^2 branching ratio	0.3	0.16
10 branching ratio	0.05	0.06
1 branching ratio	0.05	0.06
0.1 branching ratio	0	0.06
Percentage error for combination	**21%**	**37%**