Supporting Information for Influence of vapor wall-loss in laboratory chambers on yields of secondary organic aerosol

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Section 1. Materials and Methods

The Supplementary information contains an overview of the new and historical chamber experiments (S1.1), optimization of $k_w$ and $\alpha$ (S1.2), the statistical oxidation model (S1.3), the treatment of vapor wall loss within the SOM and a discussion of vapor-particle equilibrium timescales (S1.4), and the fitting of historical chamber data (S1.5).

S1.1. Experiments

S1.1.1. Toluene Photooxidation Experiments

Toluene SOA formation experiments were conducted in the new Caltech dual 24-m$^3$ Environmental Chambers, in which the temperature (T) and relative humidity (RH) are automatically controlled. Prior to each experiment, the Teflon chambers were flushed with clean, dry air for 24 h until the particle number concentration < 10 cm$^{-3}$ and volume concentration < 0.01 $\mu$m$^3$ cm$^{-3}$. Ammonium sulfate (AS) seed aerosol was injected into the chamber by atomizing 0.015 or 0.1 M aqueous (NH$_4$)$_2$SO$_4$ solution into the chamber for 30 to 120 min. The resulting total AS seed surface area ranged from $\sim 1 \times 10^3$ $\mu$m$^2$ cm$^{-3}$ up to $\sim 1 \times 10^4$ $\mu$m$^2$ cm$^{-3}$, and the corresponding particle-to-wall surface area ratio ranged from $\sim 1 \times 10^{-3}$ to $7 \times 10^{-3}$. Hydrogen peroxide (H$_2$O$_2$) was used for the OH source by evaporating 120 $\mu$L of 50% wt aqueous solution into the chamber with 5 L min$^{-1}$ of purified air for $\sim$ 100 min, resulting in an approximate starting H$_2$O$_2$ concentration of 2.0 ppm. 3 $\mu$L toluene (Sigma-Aldrich, 99.8% purity) was injected into a glass bulb, which was connected into the Teflon chamber. 5 L min$^{-1}$ of purified air flowed through the glass bulb into the chamber for $\sim$ 15 min, introducing $\sim$ 40 ppb toluene into the chamber. For experiments at elevated NO$_x$ (i.e. high-NO$_x$ conditions) NO and NO$_2$ were added to the chamber at the start of a given experiment until the concentrations were $\sim$17 ppb and 30 ppb, respectively. The initial [VOC]/[NO$_x$] in the high-NO$_x$ experiments ranged from 4.8-6.0 ppbC/ppb. After $\sim$ 90 min mixing, photooxidation was initiated by irradiating the chamber with black lights with output wavelength ranging from 300 to 400 nm. The irradiation leads to photolysis of H$_2$O$_2$ to produce OH radicals with an approximately constant concentration throughout the entire experiment. Temperature and relative humidity of all experiments were $\sim$298 K and $\sim$3%,
respectively. The initial O$_3$ concentration was below detection limit in all experiments. H$_2$O$_2$ exerts an interference on the O$_3$ detection, increasing the O$_3$ monitor readout by ~2-3 ppb in the current study. NO was continuously injected into the chamber over the course of each experiment at 80 ppb h$^{-1}$ for the first 2.5 h of reaction, then 50 ppb h$^{-1}$ for the next 4.5 h of reaction, and then 30 ppb h$^{-1}$ for the remainder of the reaction. Experimental conditions (e.g. [VOC], seed surface area, [NO$_x$]) for each experiment are reported in Table S1.

A suite of instruments was used to monitor toluene SOA formation and evolution. T, RH, NO, NO$_x$ and O$_3$ were continuously monitored. Toluene concentration was monitored using a gas chromatograph with flame ionization detector (GC/FID, Agilent 6890N), equipped with a HP-5 column (15 m × 0.53 mm ID × 1.5 μm thickness, Hewlett-Packard). Particle size distribution and number concentration were measured by a cylindrical differential mobility analyzer (DMA; TSI Model 3081) coupled to a condensation particle counter (TSI Model 3010). The DMA was operated in a closed system with a recirculating sheath and excess flow of 2.67 L min$^{-1}$ and a 5.4 : 1 ratio of sheath to aerosol flow rate. The column voltage was scanned from 15 to 9850 V over 45 s.

**S1.1.2. Historical Experiments**

All the other SOA formation experiments used in SOM optimal fitting were carried out in the Caltech dual 28-m$^3$ Environmental Chamber. Details of experimental protocols can be found in (1-6). Experimental conditions are reported in Tables S2 and S3 and differences in methodology from the above toluene photooxidation experiments are highlighted below. An identical suite of instrumentation was used as in the toluene photooxidation experiments. The historical experiments typically had seed $SA$ around 1-2 x 10$^3$ cm$^{-3}$, corresponding to the lowest seeded experiments in the toluene photooxidation experiments. The majority of the historical low-NO$_x$ experiments examined in this study used similar methods and conditions as the new toluene experiments, i.e. used H$_2$O$_2$ as the OH source. The experimental procedures associated with the high-NO$_x$ experiments differed from the new toluene experiments. Specifically, for the historical high-NO$_x$ experiments the primary OH source was HONO photolysis, as opposed to H$_2$O$_2$ photolysis. This has the practical implication of leading to reaction conditions where (i) the OH concentration is initially ~O(10$^7$ molecules cm$^{-3}$) and decays rapidly over a period of ~1-3 hours and (ii) the initial [VOC]/[NO$_x$] ratio tends to be much smaller compared to the current experiments. Thus, the timescales of SOA
formation during the historical high-NOx experiments were, in general, very different than for
the toluene photooxidation experiments: rapid formation over approximately 1-2 hours vs.
continuous formation over 18 hours. For high-NOx experiments, NOx was added prior to the
lights being turned on both from the HONO injection, which introduces some NO2, and from
addition of NO. Additional NO was produced upon photolysis of HONO. Typical initial NOx
concentrations were on the order of 500 ppb, corresponding to initial [VOC]/[NOx] of ~0.5
ppbC/ppb (Table S3).

**S1.1.3. Particle Wall-Loss Correction**

Particle wall losses during an experiment must be accounted for. Two limiting assumptions
have been made for the interactions between those particles that have deposited on the wall
and suspended vapors in determining the corrected suspended SOA concentrations (5, 7, 8).
In one case, particles deposited on the wall are assumed to cease interaction with the
suspended vapors and no loss of vapors to the walls is accounted for. This case gives the
lower bound of the total organic mass concentration, since particles remain the same size as at
the moment they deposited on the wall for the remainder of the experiment. SOA
concentrations determined from this case are used for the primary analysis in the manuscript,
which is appropriate because vapor loss to the walls is treated separately. In the second
limiting case, particles deposited on the wall are assumed to continue to interact with the
suspended vapors as if they had remained suspended, with the wall-bound particles assumed
to grow at the same rate as suspended particles in the chamber. The corrected SOA
concentrations in this case are larger than in the first case because of the additional uptake of
vapors to wall-bound particles. This case provides an upper-bound on the actual SOA formed
under the assumption that the vapors interact with wall-bound particles, but not the Teflon
walls (5, 7, 8). However, traditional application of this second case does not account for the
substantially differing timescales of gas-particle vs. gas-wall transport, nor does it account for
loss of vapors to the chamber walls and the substantially larger amount of effective absorbing
mass of the walls ($C_w$) compared to the deposited particles. Compared with $C_w$ (10 mg m$^{-3}$),
which is assumed as a constant from the onset of the experiment, the total organic mass
deposited on the chamber wall over the course of 18 h photooxidation is ~ 3 orders of
magnitude lower. As such, this “upper bound” can underestimate the actual SOA formation,
as it accounts for only a subset of the overall vapor wall-loss correction. Nonetheless, the “upper bound” corrected results are provided for reference to previous experiments.

For either case, the Aerosol Parameter Estimation (APE) model (9), derived on the basis of the aerosol general dynamic equation (10), is employed to calculate these two limits. The suspended particle population evolves as a result of three processes: coagulation, condensation, and wall-loss. The change of suspended particle number-size distribution due to coagulation is well constrained. The size-dependent wall loss rate is determined by experimentally monitoring the decay of dry inert (NH₄)₂SO₄ particles assuming first-order kinetics. The condensation rate is the only free parameter in the model, which can be obtained by optimal fitting of the APE model predictions to the DMA measured particle size distribution at each time step. Once the condensation rate values are estimated, they can be applied to parameterize the growth of particles on the walls due to condensation of gaseous vapor and deposition of suspended particles. A factor that describes the extent of interactions between deposited particles and suspended vapors is applied when summing aerosol masses in the chamber core and on the walls. A value of 0 for this factor corresponds to no condensation to deposited particles. A value of 1 for this factor corresponds to the case where the condensation rate of gaseous vapors to deposited particles is the same as those suspended. The primary analysis in this work utilizes the corrected particle mass under the assumption of no condensation to deposited particles because vapor wall loss is treated separately. The evolution of the wall-loss corrected particle size distributions is shown for each experiment in Fig. S1 for the lower limit case. The time-dependent aerosol growth, from which the aerosol yield can be calculated, is shown for each experiment in Fig. S2 for both limiting cases.

S1.2. Optimizing \( k_w \) and \( \alpha \)

The optimal values of \( k_w \) and \( \alpha \) were determined using the general procedure as outlined below. There were a total of 6 experiments conducted for each NOₓ condition, 5 with seed aerosol and 1 without. Only the seeded experiments are considered in the optimization method because of difficulties associated with specification of nucleation. The SOM was fit to one of these 5 seeded experiments for a variety of \( k_w \) and \( \alpha \) values. For each \( k_w/\alpha \) pair a set of best-fit SOM parameters (i.e. \( \Delta LVP, m_{frag} \) and the \( P_{func} \) array) were determined. Specifically,
the experiments with seed SA = 5.5 x 10^3 μm^2 cm^-3 (low-NO_x) and SA = 3.5 x 10^3 μm^2 cm^-3 (high-NO_x) were used for fitting. These best-fit SOM parameters and the associated k_w/α pair were then used to simulate SOA formation for the other 4 seeded experiments. Reduced goodness of fit metric ($\chi^2_{red}$) values were calculated for each experiment as:

$$\chi^2_{red} = \frac{1}{n-6-1} \sum \left( \frac{C_{OA,obs}(t)-C_{OA,model}(t)}{\sigma_{OA,obs}(t)} \right)^2$$

where $n$ is the number of data points per experiment, 6 is the number of model degrees of freedom and $\sigma_{OA,obs}$ is the uncertainty in the observations. For each experiment, the minimum $\chi^2_{red}$ across all $k_w/\alpha$ pairs was determined, and the set of $\chi^2_{red}$ values for each experiment was normalized by the minimum in that set. Normalization ensures that the different experiments carry equal weight in the next step. The composite $\chi^2_{red}$ across all seeded experiments was then determined as:

$$\chi^2_{red,composite}(k_w, \alpha) = \sum_{i=1}^{5} \chi^2_{red,norm,i}(k_w, \alpha)$$

where the sum is over the normalized $\chi^2_{red}$ for all seeded experiments. Smaller values of the composite $\chi^2_{red}$ indicate overall better agreement across all of the seeded experiments for a given set of best-fit SOM parameters, $k_w$ and $\alpha$. A contour diagram of the calculated composite $\chi^2_{red}$ as a function of $k_w$ and $\alpha$ (Fig. S3) illustrates that only certain combinations of $k_w$ and $\alpha$ provide for good agreement across all experiments. There is almost no seed effect when $\alpha > 0.1$, and therefore the overall agreement is poor no matter what $k_w$ is used. As $\alpha$ is lowered, a seed effect becomes evident. However, only when $\alpha$ is O(10^{-3}) and $k_w$ is O(10^{-4}) can overall good agreement with all experiments be obtained. Since the $k_w$ and $\alpha$ values were not determined from a specific fitting algorithm, we refer to the values that provide for best agreement as the “optimal” values rather than “best fit” values. These are: $k_w = 2.5 \times 10^{-4}$ s^{-1} and $\alpha = 2 \times 10^{-3}$ for low-NO_x experiments and $k_w = 2.5 \times 10^{-4}$ s^{-1} and $\alpha = 1 \times 10^{-3}$ for high-NO_x experiments.
S1.3. The Statistical Oxidation Model

The SOM simulates the oxidation of a given hydrocarbon as a trajectory through a 2-D grid of carbon and oxygen atoms in which “species” are considered particular carbon/oxygen combinations (e.g. C$_{12}$O$_4$). Specific rules define the movement through this space, describing the probability that a reaction leads to functionalization or fragmentation, how many oxygen atoms are added per reaction, and the decrease in vapor pressure that occurs upon addition of a single oxygen atom. SOM effectively simulates the multi-generational chemistry that characterizes photooxidation experiments. Full details are provided in (6, 11). The fragmentation probability ($P_{\text{frag}}$) depends on the oxygen content of the reacting species and is parameterized as:

$$P_{\text{frag}} = \left(\frac{N_O}{N_C}\right)^{m_{\text{frag}}}$$  \hspace{1cm} (S3)

where $m_{\text{frag}}$ is an adjustable parameter, and $N_O$ and $N_C$ are the number of oxygen and carbon atoms comprising an SOM species, respectively. The $P_{\text{frag}}$ is always constrained to be $\leq 1$. (Recently, a “bug” in the SOM code was found related to how the fragmentation was being treated. Rather than the probability of fragmentation depending on the oxygen content of the reacting species, it was being determined based on the oxygen content of the product species. This has now been fixed. The SOM was originally written in the IGOR programming language. The SOM has now been independently implemented in Fortan using the framework outlined in (11) and the IGOR and Fortan versions produce equivalent results, suggesting that no further “bugs” of this sort exist. The best-fit SOM parameters for the alkanes differ from those reported in (6) as a result of this update and because vapor wall-loss has been included.)

The functionalization probability ($P_{\text{func}}$) describes the likelihood of adding 1, 2, 3 or 4 oxygen atoms per reaction, and each can be adjusted independently, subject to the constraint that they are positive and must sum to 1. The decrease in vapor pressure (or more specifically, in the log of the saturation concentration, $C^*$, in $\mu$g m$^{-3}$) per oxygen added is referred to as $\Delta$LVP, and ranges from ~0.7 to 2.5, depending on the type of functional group added. Thus, there are
6 total adjustable (tunable) parameters in the base model: (i) fragmentation, (ii) volatility
decrease per oxygen added and (iii-vi) oxygen addition probability. For this study,
heterogeneous OH reactions are not simulated.

The reaction rate coefficient matrix associated with reactions of product species with OH
radicals has been updated from the original SOM on the basis of comparison with output from
the GECKO-A model for simulations of the outflow from Mexico City (12). The reaction rate
coefficient of the parent hydrocarbon with OH, $k_{OH}$ (cm$^3$ molecules$^{-1}$ s$^{-1}$), is specified to be
consistent with literature results, e.g. for toluene $k_{OH} = 5.2 \times 10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. For all
other species within the SOM grid, the $k_{OH}$ are determined referenced to the reaction rate
coefficient for species with the same number of carbon atoms but zero oxygen atoms as:

$$\log(k_{OH,base}) = A_1 + A_2 \times N_C^{A_3}$$ \hspace{1cm} (S4)

and where $A_1 = -15.103$, $A_2 = -3.9481$, and $A_3 = -0.79796$. For a given $N_C$, the $k_{OH}$ is
temperature dependent and varies with $N_O$ as

$$k_{OH}(T) = k_{OH,base} \times T^2 \times \exp\left(-1 \times \frac{6a}{8.314 \times T}\right) \times \left[1 + \frac{b_1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{1(ln(N_O+0.01)-ln(b_2))^2}{2\sigma^2}\right)\right]$$ \hspace{1cm} (S5)

and where the variables $b_1$, $b_2$, and $\sigma$ are functions of $N_C$, with

$$\sigma(N_C \leq 15) = 0.0214 \times N_C + 0.5238; \ \sigma(N_C > 15) = -0.115 \times N_C + 2.695 , \ (S6)$$

$$b_1 = -0.2583 \times N_C + 5.8944 , \ \ (S7)$$

And
Within the SOM gas-particle partitioning is treated through the framework of absorptive partitioning theory (13), in which compounds partition between the gas and particle phases according to their Raoult’s Law adjusted vapour pressures. Unlike in previous usages of the SOM, which assumed instantaneous gas-particle equilibrium, the SOM here treats gas-particle mass transfer dynamically. The net flux of molecules to/from the particle is calculated at each timestep as:

\[
\frac{\partial c_{OAI}}{\partial t} = 4\pi D_{gas,i} R_p N_p F_{FS} (c_{gas,i}^{\infty} - \chi_i c_i^*)
\]  

where \( D_{gas,i} \) is the gas-phase diffusivity, \( R_p \) is particle radius, \( N_p \) is particle number concentration, \( F_{FS} \) is the Fuchs-Sutugin correction for noncontinuum mass transfer, \( c_{gas,i}^{\infty} \) is the gas-phase concentration, \( \chi_i \) is the mass fraction and \( c_i^* \) is the saturation concentration of species \( i \). The entire SOA mass is considered absorbing in the calculation of \( \chi_i \). It is assumed that \( D_{gas,i} \) varies with molecular weight (MW) and is equal to \( D_{CO2} (MW_{CO2}/MW_i) \), with \( D_{CO2} = 1.38 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \). The Fuchs-Sutugin correction is equal to:

\[
F_{FS} = \frac{0.75\alpha(1+Kn)}{Kn^2+Kn+0.283Kn\alpha+0.75\alpha}
\]  

where \( \alpha \) is the mass accommodation coefficient onto particles and \( Kn \) is the Knudsen number, defined as:

\[
Kn = \lambda/R_p
\]  

and \( \lambda \) is the gas mean free path, which is equal to:
\[ \lambda_i = 3 \cdot \frac{D_{gas,i}}{c_i} \]  

(S12)

with \( \bar{c}_i \) equal to the root mean square speed of the gas, which is equal to:

\[ \bar{c}_i = \left( \frac{8N_A kT}{\pi MW_i} \right)^{\frac{1}{2}} \]  

(S13)

with \( N_A \) = Avagadro’s number, \( k \) = the Boltzmann constant and \( T \) = temperature. The results obtained with the dynamic partitioning SOM are equivalent to those obtained using the instantaneous equilibrium assumption when \( \alpha > 0.1 \) and with seed aerosols present. It should be noted that \( \alpha \) as used in Eqn. S8 represents the net mass transfer and can include resistances both in the gas-phase and at the particles surface. Full accommodation of vapors into the bulk particle can be limited by diffusion within the particles when particles are highly viscous (14). The dynamic SOM utilized here uses monodisperse particles with a size equal to the number mean diameter and the number concentration adjusted to give the desired initial seed surface area \( (S_A) \). Although the ideal model would use the actual seed size distribution as input, we have established that for particle diameters larger than \( \sim 50 \) nm the model results are sufficiently insensitive to the selected particle diameter for a fixed seed \( S_A \). As such, the results here are not limited by the simplification of using monodisperse particles. Nucleation is not explicitly simulated by the SOM. Therefore, dynamic SOM calculations for the nucleation experiments have been carried out assuming an initial seed size of 5 nm and a seed concentration equal to that observed at the end of the experiment. Given that there is substantial uncertainty associated with this assumption the nucleation experiments have not been quantitatively assessed.
S1.4. Vapor Wall-Loss

Loss of vapors to the chamber walls is simulated as a first-order process, characterized by the first-order wall-loss coefficient $k_w$ (s$^{-1}$). Vapor wall-losses are assumed to be reversible, characterized by the gas-wall partitioning coefficient, $K_w$, which is dependent upon compound vapor pressure,

$$K_w = \frac{RT}{M_w \gamma_w P_{sat}}$$  \hspace{1cm} (S14)

where $R$ is the ideal gas constant, $T$ is temperature (assumed 298 K), $M_w$ is the effective molecular weight of the wall material, $\gamma_w$ is the activity coefficient, and $P_{sat}$ is the saturation concentration of the species of interest. It is convenient to use the saturation concentration, $C^*$ ($\mu$g m$^{-3}$), instead of the saturation vapor pressure, where

$$C^* = \frac{1}{K_p} = \frac{M_p \gamma_p P_{sat}}{RT}$$  \hspace{1cm} (S15)

with $K_p$ the gas-particle partitioning coefficient, $M_p$ the average molecular weight of the organic species comprising the particles and $\gamma_p$ is the activity coefficient. The rate coefficient for transfer of gas-phase species onto the walls is given as $k_{w,on}$, while that for evaporation from the walls is given as $k_{w,off}$. The $k_{w,on}$ is specified as a model input parameter (and is equivalent to the $k_w$ in the main text). The $k_{w,off}$ is obtained from detailed balance as:

$$k_{w,off} = k_{w,on} C_w = k_{w,on} \left( \frac{C^* M_w \gamma_w}{C_w M_p \gamma_p} \right)$$  \hspace{1cm} (S16)

and where $C_w$ is the equivalent wall OA concentration ($\mu$g m$^{-3}$). If one makes the simple assumption that $M_w = M_p$ and $\gamma_w = \gamma_p$, then $C_w$ can be viewed as an effective concentration that accounts for differences in molecular weight and activity between the particles and walls.
The $C_w$ must therefore be estimated from experiments. Matsunaga and Ziemann (15) report a range of $C_w$ values that are constant within a given class of molecules (e.g. ketones vs. alkanes), with $C_w = 2, 4, 10$ and $24 \text{ mg m}^{-3}$ for alkanes, alkenes, alcohols and ketones. For all reported simulations here it has been assumed that $C_w = 10 \text{ mg m}^{-3}$. Results are reasonably insensitive to the choice of $C_w$ over the previously determined range because $C_w \gg C_OA$. The sensitivity of our results to the assumed $C_w$ is discussed further below in Section S1.4.3.

It is assumed that $k_{w, on}$ is not dependent on compound identity. Consequently, the $k_{w, off}$ terms vary with compound identity, specifically with $C^*$. The value of $k_{w, on}$ can be estimated from consideration of just the gas-phase transport terms within a chamber. McMurry and Grosjean (16) report an expression for $k_{w, on}$,

$$k_{w, on} = \left( \frac{A}{V} \right) \frac{\alpha_w \bar{c}}{1.04 \left( \frac{\alpha_w \bar{c}}{4} \right)^{4/5} \left( k_e D_{gas} \right)^{0.5}}$$  \hspace{1cm} \text{(S17)}$$

where $A/V$ is the surface to volume ratio of the chamber (equal to $6/L$ for a square chamber, and where $L$ is the length of one side), $\alpha_w$ is the mass accommodation coefficient of vapors onto the chamber walls, $\bar{c}$ is the mean thermal speed of the molecules, $k_e$ is the coefficient of eddy diffusion, and $D_{gas}$ is the molecular diffusivity. It should be noted that $\alpha_w$ is not necessarily equal to $\alpha$ for uptake onto particles. For the type of molecules here, $D_{gas}$ is $\sim 3\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $\bar{c} \sim 200 \text{ m s}^{-1}$. This leaves $k_e$ and $\alpha_w$ as the two key unknowns. Values of $k_{w, on}$ have been calculated as a function of $k_e$ for $\alpha_w$ ranging from $10^{-7}$ to 1, where 1 is perfect accommodation. $k_e$ values from $10^{-3} \text{ s}^{-1}$ to 1 $\text{ s}^{-1}$ have been used, which corresponds to mixing timescales of 17 min to 1 s (Fig. S4). McMurry and Grosjean (16) reported values for their actively mixed chambers of 0.02 s$^{-1}$ (60 $\text{ m}^3$ chamber) and 0.12 s$^{-1}$ (4 $\text{ m}^3$ chamber). Since the Caltech chamber is not actively mixed it is expected that the characteristic $k_e$ value is considerably smaller.

The value of $k_e$ for the Caltech chamber is estimated based on observed size-dependent deposition rates of particles in the chamber. The minimum in the $k_w$ for particles as a function of size is dependent upon $k_e$. This minimum occurs at a diameter of $\sim 350 \text{ nm}$ for the $24 \text{ m}^3$
Caltech chamber and at ~250 nm for the 28 m$^3$ chamber (5). For particles in a cubic chamber, the $k_w$ is related to the eddy diffusion coefficient through the equation (17):

$$k_w = \frac{1}{l} \left[ \frac{8\sqrt{k_e D}}{\pi} + v \cdot \coth \left( \frac{x}{2} \right) \right]$$  \hspace{1cm} (S18)

where $v$ is the particle terminal settling velocity (m s$^{-1}$) and $x$ is defined as:

$$x = \frac{\pi v}{2\sqrt{k_e D}}$$  \hspace{1cm} (S19)

From Eqn. S5, $k_w$ has been calculated as a function of particle diameter and the $k_e$ value adjusted until the minimum occurs at 250 nm or 350 nm. The required $k_e$ in the 24 m$^3$ chamber is 0.075 s$^{-1}$ and in the 28 m$^3$ chamber is 0.015 s$^{-1}$, similar to the values reported by McMurry and Grosjean for 60 m$^3$ ($k_e = 0.12$ s$^{-1}$) and 4 m$^3$ ($k_e = 0.02$ s$^{-1}$) chambers (16). Therefore, it is expected that the maximum $k_w$ ~ 6.0 x 10$^{-4}$ s$^{-1}$ for the 24 m$^3$ chamber and ~ 3 x 10$^{-4}$ for the 28 m$^3$ chamber from consideration of Fig. S4. Since the accommodation coefficient for the condensing species on the Teflon chamber walls is not known, it is not possible to definitively put a lower bound on the $k_w$. However, the experimental results of Matsunaga and Ziemann (15) clearly demonstrate that vapors are taken up to their chamber walls quite rapidly, and they estimate that $\alpha_w \sim 10^{-5}$, which suggests that $k_w \sim 3 \times 10^{-4}$ s$^{-1}$ (24 m$^3$) or ~ 2 x 10$^{-4}$ s$^{-1}$ (28 m$^3$). This theoretical estimate is in very good agreement with the optimal $k_w$ (= 2 x 10$^{-4}$ s$^{-1}$) for the 24 m$^3$ chamber.

Loza et al. (18) report observations of vapor wall-loss rates for two compounds: 2,3-epoxy-1,4-butanediol (BEPOX) and glyoxal. BEPOX is the butadiene derivative of an epoxydiol of isoprene. The uptake of both compounds to the chamber walls was observed to depend strongly on RH and whether a “new” or “old” chamber was used, with the measured values ranging from ~2-7 x 10$^{-5}$ s$^{-1}$ (18). Such new vs. old dependence was not observed by Matsunaga and Ziemann (15), who investigated wall-losses of alkanes, alkenes, 2-ketones and 2-alcohols. This suggests that the mechanism involved in the uptake of BEPOX and glyoxal
was somewhat different than that for the hydrocarbons considered by Matsunaga and Ziemann (15), or may alternatively indicate complications associated with capturing fast initial decay during the fill period in the much larger Caltech chamber. Such fill and mixing complications likely also explain the strong differences between the wall-loss rate coefficients for 2-dodecanol determined by Loza et al. (19) and Matsunaga and Ziemann (15). Since the vapor uptake to the Teflon chamber walls is reversible, care must be taken in the interpretation of observed wall-loss rates. Only measurements made in the very early stages of uptake will correspond directly to the first-order wall-loss rate coefficient, since as the system approaches equilibrium net vapor uptake will slow. As such, we suggest that the estimates of $k_w$ using the $\alpha$ from Matsunaga and Ziemann (15) may be more relevant to the current study given the nature of the compounds involved.

### S1.4.1. Gas-Particle Partitioning Timescales

The timescale associated with reaching gas-particle equilibrium varies with seed $SA$, and for a distribution is approximately:

$$\tau_{g-p} \approx \left(2\pi N_p \overline{D_p} D_{\text{gas}} \overline{F_{PS}}\right)^{-1}$$  \hspace{1cm} (S20)

where $N_p$ is the particle number concentration, $\overline{D_p}$ is the number mean diameter, $D_{\text{gas}}$ is the gas-phase diffusivity and $\overline{F_{PS}}$ is the correction to the mass transfer flux due to noncontinuum effects and imperfect accommodation given in Eqn. S8. Values for $\tau_{g-p}$ have been calculated for the low-NOx experiments based on the initial seed number concentration and mean diameter as a function of $\alpha$ (Fig. S5), using $D_{\text{gas}} = 1 \times 10^{-5}$ m$^2$ s$^{-1}$ and $\lambda = 150$ nm. The $\tau_{g-p}$ vary approximately inversely with $\alpha$. The optimal $\alpha$ was determined to be $\alpha \approx 0.002$, corresponding to an optimal $k_w = 2 \times 10^{-4}$ s$^{-1}$, or a lifetime with respect to wall loss of $\tau_w = 1/k_w = 83$ min. The $\tau_{g-p}$ for the experiment with the smallest seed concentration ($1.4 \times 10^3$ $\mu$m$^2$ cm$^3$) when $\alpha = 0.001$ is 230 min, very similar to $\tau_w$. As seed $SA$ increases, the $\tau_{g-p}$ decrease to $\sim 30$ min for the highest seed $SA$. This difference in the relative values of $\tau_{g-p}$ vs. $\tau_w$ explains why the seed effect is seen most strongly when seed $SA$ is less than $\sim 3 \times 10^3$ $\mu$m$^2$ cm$^3$, because this is the point at which the two timescales become highly competitive. Similarly, it
helps to explain why larger values of $\alpha$ do not lead to a noticeable seed $S_A$ dependence; when $\alpha > 0.1$ the $\tau_{g-p} = 2$ min for the experiment with the smallest seed $S_A$.

**S1.4.2. Dependence on VOC and OH concentrations**

Calculations were performed to determine the magnitude of the wall-loss bias ($R_{\text{wall}}$) as a function of the initial [toluene] and [OH] based on the best-fit of the SOM to the low-NO$_x$ set of experiments. Fig. S6 shows the variation in the end of experiment SOA concentration as a function of initial toluene and OH, and corresponds to the results shown in Fig. 3 in the main text.

**S1.4.3. Sensitivity to $C_w$**

As discussed in the main text, the sensitivity of our results to the assumed $C_w$ is has been established by performing fits to the observations for varying values of $C_w$, from 0.01 to 10 mg m$^{-3}$ for the suite of low-NO$_x$ toluene photooxidation experiments (c.f. Fig. 4). Here, it was assumed that $k_w = 2 \times 10^{-4}$ s$^{-1}$ and $\alpha = 2 \times 10^{-3}$, consistent with the optimized values determined in the main text. Good fits are obtained over the entire range of $C_w$. Above $C_w = 0.2$ mg m$^{-3}$ (= 200 $\mu$g m$^{-3}$) the calculated wall-loss bias, $R_{\text{wall}}$, is constant. Below 0.2 mg m$^{-3}$ the calculated $R_{\text{wall}}$ falls off, reaching a second plateau at small $C_w$ that is still above unity. The best-fit SOM parameters vary systematically with $C_w$ (Fig. S7), apparently compensating for the varying levels of vapor wall-loss.

**S1.5. Fitting of Historical Chamber Data**

Beyond the toluene experiments, which are the focus of the manuscript, best-fit SOM parameters have been determined for a suite of historical photooxidation experiments conducted using a variety of other precursor compounds, both under low- and high-NO$_x$ conditions. The historical experiments were all carried out in the prior 28 m$^3$ Caltech chamber. Experimental conditions are given in Tables S2 and S3. Fitting of the SOM to the observations is performed for these experiments assuming that $k_w = 1 \times 10^{-4}$ s$^{-1}$, $\alpha = 2 \times 10^{-3}$ and $C_w = 10$ mg m$^{-3}$. The results are relatively insensitive to $C_w$ when varied over the range 2-24 mg m$^{-3}$, as discussed above. The value of $k_w$ for the historical chamber is estimated to be slightly smaller than the optimal value determined for the new 24 m$^3$ chamber based on
consideration of the size-dependent particle wall-loss rates, as discussed in Section S1.4. Best fit SOM parameters for low-NOx and high-NOx conditions are given in Table S4. Wall-loss bias values were calculated in the same manner as for the toluene experiments. Experimental data and simulation results are shown in Fig. S8-9.

S1.6. References


Fig. S1: Time-dependent volume distributions ($dV/d\log D_p$) of AS seed and organic aerosols after 0 - 18 h of photoxidation of toluene under (top panels) high-NOx and (bottom panels) low-NOx conditions. Distributions are colored according to the time after lights were turned on. The lower bound wall-loss correction is used here. For the experiments at higher seed $SA$, the influence of coagulation on the particle evolution is evident.
Fig. S2: Time-dependent SOA growth curves for toluene photooxidation under high-NO$_x$ (HNO$_x$) and low-NO$_x$ (LNO$_x$) conditions. Error bars come from the 95% confidence interval associated with determining the size-dependent first-order wall-loss rate for dry inert ammonium sulfate ((NH$_4$)$_2$SO$_4$) particles.
Fig. S3: Calculated composite reduced chi-square values for (A) high-NO\textsubscript{x} and (B) low-NO\textsubscript{x} toluene experiments as a function of the mass accommodation coefficient, $\alpha$, and the first order wall-loss rate coefficient, $k_w$. The colors indicate the magnitude of the calculated composite reduced goodness of fit metric, with the contours based on the circles. The black x indicates the optimal value: $k_w = 2.5 \times 10^{-4}$ s\textsuperscript{-1} and $\alpha = 1 \times 10^{-3}$ (high-NO\textsubscript{x}) and $k_w = 2.5 \times 10^{-4}$ s\textsuperscript{-1} and $\alpha = 2 \times 10^{-3}$ (low-NO\textsubscript{x}).
Fig. S4: Calculated wall-loss coefficients $k_w$ as a function of the coefficient of eddy diffusion, $k_e$, which characterizes the state of turbulent diffusion in the chamber, for different values of the mass accommodation coefficient onto the walls, $\alpha_w$. The top axis shows the time-scales corresponding to the eddy diffusion coefficients.
**Fig. S5:** Calculated gas-particle equilibration time as a function of the gas-particle mass accommodation coefficient, $\alpha$, for different seed surface areas corresponding to the low-NO$_x$ experiments. The horizontal gray line indicates the timescale associated with vapour wall-loss for $k_w = 2.5 \times 10^{-4}$ s$^{-1}$. The vertical dashed gray lines indicate the optimal values of $\alpha$ determined here for the high- and low-NO$_x$ toluene systems. For the nucleation experiments, it is assumed that the particles are 10 nm diameter.
Fig. S6: Calculated end-of-experiment SOA mass concentrations corresponding to the results shown in Figure 3. The SOA concentration is shown as a function of initial toluene concentration and OH concentration when $k_w = 2.5 \times 10^{-4}$ s$^{-1}$ and $C_w = 10$ mg m$^{-3}$. The SOA concentrations for a given [toluene] and [OH] are indicated by colors and contours. Results are based on the optimal fit of the SOM to the low-NO$_x$ experiments.
Fig. S7: The best-fit SOM parameters determined at each $C_w$ corresponding to the results shown in Fig. 4 in the main text. The fragmentation probabilities, $P_{\text{frag}}$, were calculated from the best-fit $m_{\text{frag}}$ values and Eqn. S3 using O:C = 0.5. $\Delta$LVP corresponds to the decrease in vapor saturation concentration per oxygen added and $P_{\text{func}}$ corresponds to the probability of adding 1, 2, 3 or 4 oxygen atoms per reaction.
Fig. S8: Results from historical low (left panels) and high (right panels) NO<sub>x</sub> SOA formation experiments for alkane photooxidation (open circles). The solid red lines are best-fit SOM results when wall losses are accounted for assuming that $k_w = 1 \times 10^{-4}$, $\alpha = 1$ and $C_w = 10 \mu g m^{-3}$. The blue dashed lines are the simulated SOA concentrations when wall-loss is turned off, but the SOM parameters determined from the best-fit with wall-loss on are retained.
Fig. S9: Same as Fig. S3, but for aromatics. Importantly, the toluene experimental results are from Ng et al. (3), not from the current set of experiments. For each experiment, data collected over the full experiment time is shown. However, the SOM fitting has been restricted to the periods shown as colors other than gray (orange or blue). The gray points are data that were collected, but not used in fitting. These data have been excluded to be consistent with the range of data considered in Ng et al. (3) and Chan et al. (1), where 2product fits have been performed. For m-xylene, low-NOx, fits to data from Ng et al. (3) and Loza et al. (5) are shown separately.
Fig. S10: Same as Fig. S8, but for α-pinene (4) and isoprene (4) photooxidation.
Fig. S11: Calculated time-dependent $R_{\text{wall}}$ values for historical experiments based on the results shown in Fig. S8 - Fig. S10. Results are grouped according to species type and NO$_x$ level. Left panels are low-NO$_x$ and right panels high-NO$_x$ results. Note that the toluene results in the top panels are based on data presented in Ng et al. (3), not from the current set of experiments. Results are shown for m-xylene, low-NO$_x$ for two separate experimental data sets: Ng et al. (3) and Loza et al. (5). The presented results are limited to the period where $C_{\text{OA}} > 0.5 \mu$g m$^{-3}$. 
Table S1. Experimental conditions for toluene SOA photooxidation experiments in the 24 m³ Caltech chamber.

<table>
<thead>
<tr>
<th>Exp. (#)</th>
<th>[HC]₀ (ppb)</th>
<th>[NO]₀ (ppb)</th>
<th>[NO₂]₀ (ppb)</th>
<th>Initial ([\text{VOC}]/[\text{NOx}]) (ppbC/ppb)</th>
<th>Additional NO injection</th>
<th>Initial seed surface area (µm² cm⁻³)</th>
<th>Initial surface area ratio (Aerosol/Wall)</th>
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</thead>
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<tr>
<td><strong>High NOₓ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>~36.8</td>
<td>~19.0</td>
<td>~34.4</td>
<td>4.8</td>
<td>yes</td>
<td>~0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>~38.7</td>
<td>~19.6</td>
<td>~32.2</td>
<td>5.2</td>
<td>yes</td>
<td>1.69 x 10³</td>
<td>8.57 x 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>~37.9</td>
<td>~15.5</td>
<td>~34.9</td>
<td>5.3</td>
<td>yes</td>
<td>3.51 x 10³</td>
<td>1.88 x 10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>~37.9</td>
<td>~17.5</td>
<td>~31.7</td>
<td>5.4</td>
<td>yes</td>
<td>6.70 x 10³</td>
<td>3.32 x 10⁻³</td>
</tr>
<tr>
<td>5</td>
<td>~38.2</td>
<td>~13.1</td>
<td>~31.5</td>
<td>6.0</td>
<td>yes</td>
<td>8.51 x 10³</td>
<td>4.83 x 10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>~38.7</td>
<td>~16.8</td>
<td>~35.3</td>
<td>5.2</td>
<td>yes</td>
<td>1.15 x 10⁴</td>
<td>5.72 x 10⁻³</td>
</tr>
<tr>
<td><strong>Low NOₓ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>~33.9</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>2</td>
<td>~37.6</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>1.41 x 10³</td>
<td>1.03 x 10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>~37.3</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>3.10 x 10³</td>
<td>2.13 x 10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>~36.8</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>5.47 x 10³</td>
<td>4.07 x 10⁻³</td>
</tr>
<tr>
<td>5</td>
<td>~38.7</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>7.95 x 10³</td>
<td>5.17 x 10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>~37.9</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>--</td>
<td>--</td>
<td>9.41 x 10³</td>
<td>6.70 x 10⁻³</td>
</tr>
</tbody>
</table>

* Detection limits (DL) for O₃, NO, and NO₂ are 0.5 ppb, 0.4 ppb, and 0.4 ppb, respectively.
**Table S2.** Conditions for low-NOx experiments in the 28 m³ Caltech chamber.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Ref</th>
<th>Date [mm/dd/yy]</th>
<th>[VOC]₀ [ppb]</th>
<th>[NOx]₀ [ppb]</th>
<th>Initial [VOC]/[NOx]₀ (ppbC/ppb)</th>
<th>[OH]ᵃ (molecules/cm³)</th>
<th>% Yield at C&lt;sub&gt;OA&lt;/sub&gt; = 10 µg m⁻³</th>
<th>k&lt;sub&gt;OH&lt;/sub&gt; (cm³ molecules⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>(6)</td>
<td>03/16/11</td>
<td>34.0</td>
<td>&lt;2</td>
<td>--</td>
<td>2.5x10⁶</td>
<td>6.1</td>
<td>1.34x10⁻¹¹</td>
</tr>
<tr>
<td>methylundecane</td>
<td>(6)</td>
<td>02/25/11</td>
<td>28.1</td>
<td>&lt;2</td>
<td>--</td>
<td>2.4x10⁶</td>
<td>7.2</td>
<td>1.34x10⁻¹¹</td>
</tr>
<tr>
<td>cyclohexadecane</td>
<td>(6)</td>
<td>02/23/11</td>
<td>9.8</td>
<td>&lt;2</td>
<td>--</td>
<td>2.7x10⁶</td>
<td>17.2</td>
<td>1.34x10⁻¹¹</td>
</tr>
<tr>
<td>hexylcyclohexane</td>
<td>(6)</td>
<td>03/21/11</td>
<td>15.6</td>
<td>&lt;2</td>
<td>--</td>
<td>3.0x10⁶</td>
<td>15.4</td>
<td>1.34x10⁻¹¹</td>
</tr>
<tr>
<td>benzene</td>
<td>(3)</td>
<td>11/04/06</td>
<td>414</td>
<td>&lt;2</td>
<td>--</td>
<td>3x10⁶</td>
<td>23.8</td>
<td>1.22x10⁻¹²</td>
</tr>
<tr>
<td>toluene</td>
<td>(3)</td>
<td>10/24/06</td>
<td>52.7</td>
<td>&lt;2</td>
<td>--</td>
<td>3.3x10⁶</td>
<td>26.7</td>
<td>5.63x10⁻¹²</td>
</tr>
<tr>
<td>m-xylene</td>
<td>(3)</td>
<td>10/27/06</td>
<td>19.3</td>
<td>&lt;2</td>
<td>--</td>
<td>3x10⁶</td>
<td>28.2</td>
<td>2.31x10⁻¹¹</td>
</tr>
<tr>
<td>m-xylene</td>
<td>(5)</td>
<td>10/11/10</td>
<td>29.2</td>
<td>&lt;2</td>
<td>--</td>
<td>2.5x10⁶</td>
<td>21.4</td>
<td>2.31x10⁻¹¹</td>
</tr>
<tr>
<td>naphthalene</td>
<td>(1, 2)</td>
<td>08/13/08</td>
<td>31.5</td>
<td>2</td>
<td>--</td>
<td>2x10⁶</td>
<td>19.0</td>
<td>2.44x10⁻¹¹</td>
</tr>
<tr>
<td>α-pinene</td>
<td>(4)</td>
<td>06/02/10</td>
<td>66.2</td>
<td>&lt;2</td>
<td>--</td>
<td>3x10⁶</td>
<td>36.8</td>
<td>5.3x10⁻¹⁰</td>
</tr>
<tr>
<td>isoprene</td>
<td>(4)</td>
<td>02/25/09</td>
<td>49</td>
<td>&lt;2</td>
<td>--</td>
<td>2x10⁶</td>
<td>4.3ᵇ</td>
<td>1x10⁻¹⁰</td>
</tr>
</tbody>
</table>

ᵃ Average over the experiment
ᵇ Maximum yield, since maximum C<sub>OA</sub> < 10 µg m⁻³.
ᶜ From historical experiments by Ng et al. (2007), not the current set of experiments.
ᵈ m-xylene data are available from two independent sets of experiments.
**Table S3.** Conditions for high-NOx experiments in the 28 m³ Caltech chamber.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Ref.</th>
<th>Date</th>
<th>[VOC]₀ (ppb)</th>
<th>[NO]₀ &amp; [NO₂]₀ (ppb)</th>
<th>Initial [VOC]/[NOx] (ppbC/ppb)</th>
<th>[OH]ⁿ (molecules/cm³)</th>
<th>% Yield at C₀A = 10 µg m⁻³</th>
<th>kOH (cm³ molecules⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>(6)</td>
<td>05/12/11</td>
<td>32.2</td>
<td>343/--</td>
<td>1.13</td>
<td>4.5x10⁷</td>
<td>6.2</td>
<td>1.34x10¹¹</td>
</tr>
<tr>
<td>methylundecane</td>
<td>(6)</td>
<td>03/01/11</td>
<td>72.4</td>
<td>366/--</td>
<td>2.37</td>
<td>3.3x10⁷</td>
<td>5.1</td>
<td>1.34x10¹¹</td>
</tr>
<tr>
<td>cyclododecane</td>
<td>(6)</td>
<td>05/23/11</td>
<td>13.8</td>
<td>362/--</td>
<td>0.46</td>
<td>2.7x10⁷</td>
<td>38.3</td>
<td>1.34x10¹¹</td>
</tr>
<tr>
<td>hexylcyclohexane</td>
<td>(6)</td>
<td>03/22/11</td>
<td>22.1</td>
<td>320/--</td>
<td>0.83</td>
<td>4.1x10⁷</td>
<td>12.3</td>
<td>1.34x10¹¹</td>
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<tr>
<td>benzene</td>
<td>(3)</td>
<td>01/15/07</td>
<td>336</td>
<td>83/86</td>
<td>11.9</td>
<td>3.2x10⁷</td>
<td>15.6</td>
<td>1.22x10¹²</td>
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<td>toluene</td>
<td>(3)</td>
<td>10/14/06</td>
<td>138</td>
<td>373/568</td>
<td>1.03</td>
<td>3.6x10⁷</td>
<td>8.3</td>
<td>5.63x10¹²</td>
</tr>
<tr>
<td>m-xylene</td>
<td>(3)</td>
<td>10/05/06</td>
<td>89.8</td>
<td>469/474</td>
<td>0.76</td>
<td>4.2x10⁷</td>
<td>3.9</td>
<td>2.31x10¹¹</td>
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<td>naphthalene</td>
<td>(1, 2)</td>
<td>08/14/08</td>
<td>48.6</td>
<td>404/171</td>
<td>0.85</td>
<td>2.5x10⁷</td>
<td>11.2</td>
<td>2.44x10¹¹</td>
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<td>α-pinene</td>
<td>(4)</td>
<td>06/03/10</td>
<td>44.9</td>
<td>446/398</td>
<td>0.53</td>
<td>1.4x10⁷</td>
<td>9.5</td>
<td>5.3x10¹¹</td>
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<tr>
<td>isoprene</td>
<td>(4)</td>
<td>04/04/09</td>
<td>268</td>
<td>535/402</td>
<td>1.43</td>
<td>6.6x10⁶</td>
<td>1.0ᵇ</td>
<td>1x10¹¹</td>
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</table>

ᵃ For all high-NOx experiments HONO was used as the OH source. The [OH] was not constant in time, but decreased rapidly from the start of the experiment by at least an order of magnitude. The [OH] derived from the first [VOC] measurement after the lights were turned on is given here.

ᵇ Maximum yield, since maximum C₀A < 10 µg m⁻³.

c From historical experiments by Ng et al. (2007), not the current set of experiments.
Table S4. Derived SOM parameters for the experiments when vapor wall-loss is accounted for (assuming $C_w = 10 \, \mu g \, m^{-3}$).

<table>
<thead>
<tr>
<th>VOC$^a$</th>
<th>Fragmentation</th>
<th>ALVP</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>$\chi^2_{\text{red}}$$^b$</th>
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<tr>
<td></td>
<td>$Low , NO_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>toluene (this study)</td>
<td>5</td>
<td>1.83</td>
<td>0.123</td>
<td>0.001</td>
<td>0.002</td>
<td>0.875</td>
<td>1.74</td>
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<td>n-dodecane (6)</td>
<td>0.671</td>
<td>1.58</td>
<td>0.977</td>
<td>0.016</td>
<td>0.003</td>
<td>0.004</td>
<td>1.47</td>
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<td>methylundecane (6)</td>
<td>0.433</td>
<td>1.92</td>
<td>0.997</td>
<td>0.000</td>
<td>0.001</td>
<td>0.002</td>
<td>1.33</td>
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<td>cyclododecane (6)</td>
<td>1.56</td>
<td>1.90</td>
<td>0.994</td>
<td>0.000</td>
<td>0.001</td>
<td>0.005</td>
<td>1.73</td>
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<td>hexylcyclohexane (6)</td>
<td>0.78</td>
<td>1.84</td>
<td>0.885</td>
<td>0.106</td>
<td>0.001</td>
<td>0.008</td>
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<tr>
<td>benzene$^c$ (3)</td>
<td>0.01</td>
<td>2.29</td>
<td>0.284</td>
<td>0.000</td>
<td>0.644</td>
<td>0.072</td>
<td>0.42</td>
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<tr>
<td>toluene$^e$ (3)</td>
<td>0.01</td>
<td>1.88</td>
<td>0.001</td>
<td>0.001</td>
<td>0.727</td>
<td>0.271</td>
<td>1.36</td>
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<td>1.96</td>
<td>0.000</td>
<td>0.085</td>
<td>0.836</td>
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<td>1.88</td>
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<td>0.000</td>
<td>0.613</td>
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<td>0.431</td>
<td>0.161</td>
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<td>1.91</td>
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<td>0.619</td>
<td>0.075</td>
<td>0.044</td>
<td>0.19</td>
</tr>
<tr>
<td>isoprene (4)</td>
<td>0.01</td>
<td>2.23</td>
<td>0.000</td>
<td>0.146</td>
<td>0.826</td>
<td>0.028</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>$High , NO_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>toluene (this study)</td>
<td>1.02</td>
<td>1.42</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
<td>1.10</td>
</tr>
<tr>
<td>n-dodecane (6)</td>
<td>0.188</td>
<td>1.45</td>
<td>0.963</td>
<td>0.000</td>
<td>0.001</td>
<td>0.036</td>
<td>0.07</td>
</tr>
<tr>
<td>methylundecane (6)</td>
<td>0.188</td>
<td>1.12</td>
<td>0.263</td>
<td>0.277</td>
<td>0.455</td>
<td>0.005</td>
<td>0.61</td>
</tr>
<tr>
<td>cyclododecane (6)</td>
<td>0.01</td>
<td>1.69</td>
<td>0.664</td>
<td>0.002</td>
<td>0.004</td>
<td>0.33</td>
<td>0.64</td>
</tr>
<tr>
<td>hexylcyclohexane (6)</td>
<td>0.153</td>
<td>1.75</td>
<td>0.832</td>
<td>0.086</td>
<td>0.055</td>
<td>0.028</td>
<td>0.14</td>
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<tr>
<td>benzene$^c$ (3)</td>
<td>0.912</td>
<td>1.47</td>
<td>0.105</td>
<td>0.001</td>
<td>0.893</td>
<td>0.001</td>
<td>1.15</td>
</tr>
<tr>
<td>m-xylene$^c$ (3)</td>
<td>0.18</td>
<td>1.54</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
<td>0.64</td>
</tr>
<tr>
<td>toluene$^e$ (3)</td>
<td>0.039</td>
<td>1.46</td>
<td>0.001</td>
<td>0.001</td>
<td>0.906</td>
<td>0.094</td>
<td>1.13</td>
</tr>
<tr>
<td>naphthalene$^c$ (1, 2)</td>
<td>0.64</td>
<td>1.41</td>
<td>0.835</td>
<td>0.001</td>
<td>0.002</td>
<td>0.162</td>
<td>0.17</td>
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<tr>
<td>$\alpha$-pinene (4)</td>
<td>0.080</td>
<td>1.81</td>
<td>0.193</td>
<td>0.694</td>
<td>0.101</td>
<td>0.012</td>
<td>0.04</td>
</tr>
<tr>
<td>isoprene (4)</td>
<td>0.322</td>
<td>2.23</td>
<td>0.679</td>
<td>0.321</td>
<td>0.000</td>
<td>0.000</td>
<td>0.79</td>
</tr>
</tbody>
</table>

$^a$ The toluene experiments from this study were conducted in the 24 m$^3$ Caltech chamber (i.e. “new” experiments) and simulated using $k_w = 2.5 \times 10^{-4} \, s^{-1}$ and the experimentally-determined optimal $\alpha$ (-2 x 10$^{-3}$). All other experiments, including the toluene experiments from (3) were conducted in the 28 m$^3$ Caltech chamber (i.e. “historical” experiments”) and simulated using $k_w = 1 \times 10^{-4} \, s^{-1}$ and $\alpha = 1$.

$^b$ The reduced $\chi^2$ associated with the best fit.

$^c$ Fits were performed over the ranges shown in Fig. S9.