Kinetic Analysis of Competition between Aerosol Particle Removal and Generation by Ionization Air Purifiers

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Ionization air purifiers are increasingly used to remove aerosol particles from indoor air. However, certain ionization air purifiers also emit ozone. Reactions between the emitted ozone and unsaturated volatile organic compounds (VOC) commonly found in indoor air produce additional respirable aerosol particles in the ultrafine (<0.1 μm) and fine (<2.5 μm) size domains. A simple kinetic model is used to analyze the competition between the removal and generation of particulate matter by ionization air purifiers under conditions of a typical residential building. This model predicts that certain widely used ionization air purifiers may actually increase the mass concentration of fine and ultrafine particulates in the presence of common unsaturated VOC, such as limonene contained in many household cleaning products. This prediction is supported by an explicit observation of ultrafine particle nucleation events caused by the addition of α-limonene to a ventilated office room equipped with a common ionization air purifier.

Introduction

Ultrafine (diameter <0.1 μm; PM₀.₁), fine (<2.5 μm; PM₂.₅), and coarse (<10 μm; PM₁₀) aerosol particles significantly contribute to the toxicity of urban air pollution (1, 2). The adverse health effects of particulate matter (PM) include exacerbation of asthma symptoms (3, 4), cardiovascular problems (5, 6), increased mortality (7, 8), and increased incidence of lung cancers (9, 10). To address the health impacts of airborne PM, the Environmental Protection Agency (EPA) established the national ambient air quality standards for PM₂.₅ at 15 (annual mean) and 65 μg/m³ (24-h mean). The standards for PM₁₀ are 50 and 150 μg/m³, respectively. No official standards for ultrafine particles have been established yet in spite of the increasing evidence for their toxicity and innate ability to penetrate into the blood circulation (11).

A significant fraction of urban PM can be classified as secondary organic aerosol (SOA) produced by oxidation of volatile organic compounds (VOC) (12). A particularly important group of aerosol-forming VOC are terpenes (13, 14), a class of hydrocarbons emitted by coniferous plants and used extensively as additives to many household cleaning products. The SOA yields, reaction mechanisms, and particle composition have been extensively studied for oxidation of α-pinene, β-pinene, limonene, and other monoterpenes in smog chambers under atmospherically relevant conditions (15–26) and in simulated indoor environments (13, 14, 27–31). The observed SOA yields resulting from oxidation by ozone can be quite high (>50% by mass), but the yields depend in a complicated way on multiple factors including presence of NOₓ, presence of OH scavengers, concentration of preexisting aerosol particles, concentrations of reactants, humidity, temperature, radiation level, and reaction time.

Stand-alone air purification devices for indoor use have gained widespread popularity in recent years. However, certain air purifiers emit ozone during operation, either intentionally or as a byproduct of air ionization (32–35). Ozone, a criterion air pollutant regulated by multiple health standards, represents a serious health concern by itself (36). In addition, ozone can react with certain indoor surfaces (37–41) and indoor VOC (30, 42–44) generating secondary products with potential adverse health effects. For example, terpene oxidation products are known eye and airway irritants (45, 46).

Ionization air purifiers present an interesting dilemma in this respect. On one hand, they remove PM from the air. On the other hand, ozone emitted by certain ionization air purifiers in the presence of unsaturated VOC increases both the mass and number concentration of aerosol particles. The main objective of this study is to verify whether the mass emission rate of fine and ultrafine PM resulting from an ionization air purifier operation can exceed the purifier’s PM removal rate under conditions characteristic of a private residence.

Experimental Section

A common residential ionization air purifier (IAP) was used in experiments. A commercial ozone generator (OG) marketed as an “air cleaner” despite its lack of any particle filtration capabilities, was used for comparison. Rates of ozone emission and particle removal (Table 1) for these two devices were quantified as described in the Supporting Information.

The measured ozone emission rates for the IAP and OG are 2.2(2) and 108(14) mg h⁻¹, respectively. Parentheses contain 2σ uncertainties in the last significant digits.

IAP works by capturing a certain fraction of particles from the air passing through the purifier. The particle capture probability, γ, is related to the first-order particle removal rate constant, kᵣᵢₚ, the mass flow rate through the air purifier, F, and room volume, V, as follows:

\[ kᵣᵢₚ = γF/V \]  (1)

The γF product, which is related to the clean air delivery rate (CADR) of the air purifier, can be used to predict the effective particle removal rate constant in a well-mixed room of an arbitrary volume. The measured value of γF (see Supporting Information) is 342(20) SLM = 20(1) m³ h⁻¹ for the IAP. This value of γF was measured for particles that were predominantly in the 0.15–0.30 μm size range. This work assumes that the γF value is the same for all particle sizes of interest. It is certainly possible that IAP has different efficiencies for ultrafine and coarse particles (47), but this is not going to strongly affect the main conclusions of this work. OG was found to have no measurable effect on the particle count (γF ≈ 0) because it has no built-in particle filtration capabilities.

The actual tests were performed in a sparingly furnished office room with a floor area of 11.1 m² and overall volume of 27.1 m³. The floor material was linoleum, the walls were...
painted drywall, and the ceiling consisted of industrial fiberglass ceiling tiles. The room was ventilated through an HVAC system with a measured whole air exchange rate of \(\sim 5 \text{ h}^{-1}\). This exchange rate is higher than for an average private residence but typical for an office room. The air purifiers were positioned on the floor in the middle of the room. The ozone monitor and particle counters were installed in an adjacent room and air was sampled approximately 1 m away from the air purifiers.

A scanning mobility particle sizer (SMPS) was used to measure the particle size distribution in the 0.010–0.90 \(\mu \text{m}\) size range, and a laser particle counter sampled particles in the 0.15–5.0 \(\mu \text{m}\) size range. A large fan was placed in the room for a better mixing of the air across the room volume. The time to acquire one particle size distribution with SMPS was 7 min and that for laser particle counter was 5 min. In a typical run, the data were logged with a Labview-based program for 5–20 h with the air purifier turned off and then for another 5–20 h with the air purifier turned on. At certain time intervals, a measurement of \(\text{d}_{\text{limonene}}\) vapor (5–60 mg) was injected in the room at a rate of 3 mg min\(^{-1}\) for a brief period of time.

**Kinetic Model.** The following model is used to describe concentrations in a single well-mixed indoor environment that exchanges air with the exterior atmosphere:

\[
\frac{d[X]}{dt} = \kappa_X[X]_{\text{out}} + \frac{E_X(t)}{V} + R_X - \lambda[X] - S \frac{V}{V_{\text{ex}}}[X] \tag{2}
\]

\([X]\) and \([X]_{\text{out}}\) are concentrations of species \(X\) indoors and outdoors, respectively; \(\lambda\) is the whole air exchange rate; \(\kappa_X\) is outdoor-to-indoor penetration efficiency; \(V\) is the volume; \(S\) is the interior surface area; \(E_X\) is the emission rate for \(X\) by all indoor sources; \(R_X\) is the combined rate of production of \(X\) by gas-phase chemistry; \(\kappa_X\) is an effective first-order rate constant for the removal of \(X\) by chemical reactions; \(V_{\text{ex}}\) is the deposition velocity of \(X\) on indoor surfaces. The constants \(\lambda\), \(\kappa_X\), and \(k_{\text{ex}}\) all have units of inverse time, \(\kappa_X\) is unitless, and \([X]\) has mass concentration units (\(\mu \text{g m}^{-3}\)) to simplify comparison of concentrations of gas-phase and aerosolized species.

Three species are included in the model: ozone, an unsaturated VOC (\(\text{d}-\text{limonene}\)), and PM. Ozone is emitted indoors by the air purifier and also penetrates from outdoors by means of air exchange. Aerosol particles are brought indoors by the HVAC system, and also chemically generated via reaction

\[\text{VOC} + O_3 \rightarrow \chi \text{PM} + \text{volatile organics} \tag{3}\]

where \(\chi\) is the mass yield of aerosol resulting from the ozonolysis of VOC. The model implicitly assumes that all involatile products of VOC oxidation by ozone quickly partition themselves in the particle phase. The aerosol particles are not differentiated by size or composition; reaction 3 is simply assumed to increase the total mass concentration of PM in the room volume.

With these assumptions, the time evolution of ozone, reactive VOC, and aerosol concentrations can be written as follows.

\[
\frac{d[O_3]}{dt} = \lambda \kappa_{O_3}[O_3]_{\text{out}} + \frac{E_{O_3}}{V} - (\lambda + k_{dO_3} + k_{\text{VOC}})[O_3] \tag{4}
\]

\[
\frac{d[\text{VOC}]}{dt} = \lambda \kappa_{\text{VOC}}[\text{VOC}]_{\text{out}} + \frac{E_{\text{VOC}}}{V} - (\lambda + k_{d\text{VOC}} + k_{\text{ap}})[\text{VOC}] \tag{5}
\]

\[
\frac{d[\text{PM}]}{dt} = \lambda \kappa_{\text{PM}}[\text{PM}]_{\text{out}} + \chi k_{\text{ap}}[O_3]_{\text{out}} - (\lambda + k_{d\text{PM}} + k_{\text{ap}})[\text{PM}] \tag{6}
\]

In the last equation, we separated the removal of aerosol particles by wall deposition (\(k_{d\text{PM}}\)) and by the air purifier (\(k_{\text{ap}}\)). The latter can be calculated from eq 1. These equations will be used below to simulate the indoor VOC, PM, and ozone concentrations either analytically or numerically.

**Results**

**Steady-State Kinetic Model.** In the experiments and simulations described here, and also in many realistic indoor environments, the ozone removal is often dominated by either air exchange or surface deposition. Gas-phase reactions normally make a much smaller contribution to the ozone removal rate. Under such conditions, the term \(k_{\text{VOC}}\) in eq 4 can be neglected compared to \(\lambda\) and \(k_{dO_3}\). With this simplifying assumption, the equations can be easily solved in steady-state (ss) for the case of time-independent emission rates \(E_{O_3}\) and \(E_{\text{VOC}}\). The steady-state concentration of ozone depends on whether the air purifier is turned on or off:

\[
[O_3]_{\text{ON ss}} = \frac{E_{O_3}/V + \lambda \kappa_{O_3}[O_3]_{\text{out}}}{\lambda + k_{dO_3}} \tag{7}
\]

\[
[O_3]_{\text{OFF ss}} = \frac{\lambda \kappa_{O_3}[O_3]_{\text{out}}}{\lambda + k_{dO_3}} \tag{8}
\]

This dependence propagates into the steady-state concentrations of VOC and aerosol particles.

\[
[VOC]_{\text{ON/OFF ss}} = \frac{\lambda \kappa_{\text{VOC}}[\text{VOC}]_{\text{out}} + E_{\text{VOC}}/V}{\lambda + k_{d\text{VOC}} + k_{\text{ap}}} \tag{9}
\]

\[
[\text{PM}]_{\text{ON/OFF ss}} = \frac{\lambda \kappa_{\text{PM}}[\text{PM}]_{\text{out}} + \chi k_{\text{ap}}[O_3]_{\text{out}}}{\lambda + k_{d\text{PM}} + k_{\text{ap}}} \tag{10}
\]

The time it takes for the concentrations to approach their steady-state values is inversely proportional to the corresponding removal rates, i.e., values in the denominators of eqs 8–10. For the base conditions listed in Table 2, these times are 0.3, 1.4, and 2 h for ozone, particles, and VOC, respectively.

To quantify the effect of the air purifier on particle concentration in the room, we define an efficiency parameter \(K\), as the ratio of the steady-state PM concentrations obtained when the air purifier is turned on to that when it is off.

\[
K = \frac{[\text{PM}]_{\text{ON ss}}}{[\text{PM}]_{\text{OFF ss}}} = \frac{\lambda + k_{d\text{PM}} + k_{\text{ap}}}{\lambda + k_{d\text{PM}} + k_{\text{ap}}} \times \frac{\lambda \kappa_{\text{PM}}[\text{PM}]_{\text{out}} + \chi k_{\text{ap}}[O_3]_{\text{out}}[VOC]_{\text{ON ss}}}{\lambda \kappa_{\text{PM}}[\text{PM}]_{\text{out}} + \chi k_{\text{ap}}[O_3]_{\text{out}}[VOC]_{\text{OFF ss}}} \tag{11}
\]
TABLE 2. Kinetic Model Parameters

<table>
<thead>
<tr>
<th>parameter</th>
<th>definition</th>
<th>base values for calculation of K</th>
<th>values for simulation of particle bursts</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>room volume</td>
<td>50 m³</td>
<td>27.1 m³ (measured)</td>
</tr>
<tr>
<td>[O₃]ᵢₒᵤᵣ</td>
<td>outside ozone</td>
<td>30 ppb</td>
<td>5 ppb (measured)</td>
</tr>
<tr>
<td>[PM]ᵢₒᵤᵣ</td>
<td>outside PM</td>
<td>10 μg m⁻³</td>
<td>0.59 μg m⁻³ ([PM₁₀])</td>
</tr>
<tr>
<td>[VOC]ᵢₒᵤᵣ</td>
<td>outside VOC</td>
<td>0.0 μg m⁻³</td>
<td>0.0 μg m⁻³ (assumed)</td>
</tr>
<tr>
<td>λ</td>
<td>air exchange rate</td>
<td>0.5 h⁻¹</td>
<td>5.0 h⁻¹ (measured)</td>
</tr>
<tr>
<td>kₒ₃ₒ₃</td>
<td>ozone surface deposition</td>
<td>2.8 h⁻¹</td>
<td>1.0 h⁻¹ (estimated)</td>
</tr>
<tr>
<td>kₒ₃ₚₘ</td>
<td>PM surface deposition</td>
<td>0.2 h⁻¹</td>
<td>0.2 h⁻¹ (assumed)</td>
</tr>
<tr>
<td>kₒ₃₋ₒ₃ ›</td>
<td>VOC surface deposition</td>
<td>0.0 h⁻¹</td>
<td>0.0 h⁻¹ (assumed)</td>
</tr>
<tr>
<td>kₒ₃₋ₚₘ ›</td>
<td>VOC + O₃ rate constant</td>
<td>2.0 × 10⁻¹⁶ cm³ s⁻¹</td>
<td>2.0 × 10⁻¹⁶ cm³ s⁻¹</td>
</tr>
<tr>
<td>γ</td>
<td>aerosol mass yield</td>
<td>1.0</td>
<td>1.0 (assumed)</td>
</tr>
<tr>
<td>kₒ₃₋ₚₘ ›</td>
<td>all penetration efficiencies</td>
<td>1.0</td>
<td>1.0 (assumed)</td>
</tr>
<tr>
<td>Eₒ₃</td>
<td>VOC indoor emission rate</td>
<td>5 mg h⁻¹</td>
<td>5 min pulse at 3 mg h⁻¹</td>
</tr>
<tr>
<td>Eₒ₃</td>
<td>ozone indoor emission rate</td>
<td>variable 0−10 mg h⁻¹</td>
<td>2.2 mg h⁻¹ (SI637)</td>
</tr>
<tr>
<td>γ/F</td>
<td>clean air delivery rate</td>
<td>variable 0−100 m³ h⁻¹</td>
<td>20 m³ h⁻¹ (SI637)</td>
</tr>
</tbody>
</table>

aThe third column lists the base parameters used for steady-state calculation of the air purifier efficiency, K, from eq 11. The forth column lists parameters used in the simulation of particle bursts observed in the office room with operating IAP. [PM]ᵢₒᵤᵣ refers to the [PM₁₀],[PM₀.12] and [PM₂.₅] in columns 3 and 4, respectively.

Operation of an effective air purifier should result in conditions corresponding to K < 1. When K > 1, the device actually increases particle numbers rather than removes, thus acting as a net particle emitter. The situation with K = 1 corresponds to the exact cancellation of the particle removal and generation rates.

The first term in this equation describes the effect of the air purifier in the absence of any indoor chemistry.

$$K_{base} = \left(1 + \frac{k_{ap}}{\lambda + k_{ap}}\right)^{-1} \quad (12)$$

The more effective the air purifier the smaller is the values of $K_{base}$. It is close to unity for an ineffective air purifier ($k_{ap} \ll \lambda + k_{ap}$). A similar parameter was used to characterize air cleaners in ref 48.

The second term in eq 11 corresponds to the effect of indoor particle generation from the VOC oxidation by ozone. It is unity for air purifiers that emit no ozone or for rooms containing negligible amounts of reactive VOC, but it can be substantially larger than unity if both ozone and reactive VOC are present. In such cases, the effect of indoor chemistry can make the overall value of K > 1 (air contamination) even if $K_{base} < 1$.

We have calculated values of K for a typical indoor environment as a function of the ozone emission rate and clean air delivery rate from the air purifier ($\gamma/F$). Figure 1 lists the calculation parameters. The outside ozone, PM, and unsaturated VOC concentrations are 30 ppb, 10 μg/m³, and 0 μg/m³, respectively. Characteristic of reasonably clean air. The whole air exchange rate $\lambda = 0.5$ h⁻¹ comes from an analysis of multiple residences (49, 50). The value $k_{ap} = 2.8 \text{ h}^{-1}$ is adopted for a typical surface removal rate constant for ozone (44, 51). The corresponding rate constant for particles is $k_{ap} = 0.2 \text{ h}^{-1}$, a value suitable for a sparsely furnished room (49, 52). It is known that particle deposition rates depend on particle size (47, 52), but this dependence is not explicitly considered in this model in order to keep it simple. All penetration efficiencies are set to $\kappa = 1$ (setting them to smaller values would only make the predicted K higher).

The VOC emission rate is assumed to be $E_{VOC} = 5 \text{ mg} / \text{h}$ (this corresponds to the evaporation of 0.5 g of a cleaning solution containing 1% limonene in 1 h). This value is comparable to the combined emission rate of aerosol-forming terpenes in realistic indoor environments (28, 42). The rate constant for the reaction between VOC and ozone corresponds to that for limonene (12). The aerosol mass yield is difficult to estimate as it depends on a complicated way on the preexisting PM concentration, concentrations of reactants, and many other factors. This model assumes that $\chi = 1$, but we also show results for a 1 order of magnitude reduction in the yield. Surface deposition of VOC is neglected. The ozone emission rate is varied over the range expected for a typical ionization air purifier, 0–10 mg/h (34).

Figure 1 shows the calculated $K = 1$ curves for several different scenarios. Everything above the $K = 1$ curve corresponds to $K < 1$ (air purification) and everything below the curves corresponds to $K > 1$ (air contamination). In addition to the base conditions listed in Table 2, Figure 1 also presents calculations for [O₃]ᵢₒᵤᵣ, [PM]ᵢₒᵤᵣ, or air exchange rate, $\lambda$, scaled by 1 order of magnitude. Although it is not directly obvious from eq 11, an increase in [PM]ᵢₒᵤᵣ by a certain factor is exactly equivalent to a decrease in the VOC emission rate, $E_{VOC}$, or to a decrease in the aerosol mass yield, $\chi$, by the same factor. For example, the bottom curve in panel b is equivalent to the base conditions with $\chi$ changed to 0.1, a more realistic SOA yield for low concentrations of reactants (53).

Ozone-free air purifiers fall on the vertical axes ($E_{O₃} = 0$) in Figure 1. They are always characterized by $K \leq 1$ as predicted by eq 12. Pure ozone generators fall on the horizontal axes ($\gamma/F = 0$), and always have $K > 1$. The ionization air purifiers that both remove particles and emit ozone represent the most interesting case. For example, the IAP used here ($\gamma/F = 20(1) \text{ m}^3 \text{ h}^{-1}$ and $E_{O₃} = 0.2(12) \text{ mg} \text{ h}^{-1}$) falls slightly below the $K = 1$ curve for the base-case scenario. With the predicted value of $K = 1.12$, this device would not act as a purifier under the base conditions listed in Table 2. Decreasing the outside concentrations of PM or ozone, decreasing the air exchange rate, or increasing the indoor VOC emission rate would make the situation even worse.

**Indoor SOA Nucleation Events.** Aerosol particle generation was tested for both IAP and OG in a 27.1 m³ office room. Figure 2 shows a sample data run. Operation of OG normally increased the ozone steady-state concentration by some 250 ppb above the 5 ppb background. Operation of IAP increased it by ~5–15 ppb above the background, in rough proportion to its ozone emission rate (34). The triangles in Figure 2 indicate the time when a certain amount (5–60 mg) of limonene vapor was injected into the room.

Continuous operation of IAP in the absence of limonene resulted in a slight (~20%) reduction in the average particle concentration. For the 27.1 m³ room volume, the expected particle removal rate constant by IAP is $k_{ap} = 0.76 \text{ h}^{-1}$. The measured air exchange rate for this room is $\lambda \sim 5 \text{ h}^{-1}$. Neglecting the particle wall deposition, eq 12 predicts 10–
15% reduction in the particle count, in agreement with our observations. As expected, operation of OG had no detectable effect on the particle concentration.

Injections of limonene into the room during operation of either OG (injections 1–4 in Figure 2) or IAP (injections 5 and 6) reproducibly increased the particle number concentration by 1–2 orders of magnitude. On the contrary, injections of limonene without operating air purifiers (e.g., injection 7 in Figure 2) produced little change in the particle concentration; a small increase was observed only in injection 7 in Figure 2) produced little change in the particle number concentration would occur 15% of such injections. Very infrequently, a spontaneous increase in the particle number concentration would occur (Figure 2). These spontaneous bursts were of an external origin and penetrated into the room through the HVAC system.

The limonene injection rate (3 mg min⁻¹) was higher than one could expect for a typical indoor source. However, the injection lasted only a short time, and the total mass of injected limonene was comparable to what one could get from a room cleaning using a limonene-containing cleaning solution (27).

Steady-state ozone concentration decreased at most 10–20% for a short period of time following the injection. (The spikes in [O₃] in Figure 2 are artifacts resulting from the contribution of particles to the overall UV absorption sensed by the ozone monitor.) This small effect on the ozone concentration is due to the relatively small rate of reaction (3). Indeed, an instantaneous 10-mg limonene injection into the 27.1-m³ room volume would correspond to the initial concentration of 1.6 × 10¹² molecules/cm⁻³. Even at this high concentration, the VOC + O₃ reaction’s contribution to the ozone removal rate is only 1.2 h⁻¹. The air exchange rate, λ ≈ 5 h⁻¹, and ozone deposition rate, k₉₅ = 2.8 h⁻¹ (44, 51) are considerably higher. The effect of VOC on the ozone concentration is expected to be even smaller if VOC are emitted over an extended period of time. The same arguments were used to justify neglecting the k₅[VOC] term in eq 4 in the steady-state model described above.

Figure 2c shows the total particle mass concentration computed from the particle size distribution assuming spherical particles with a density of 1 g/cm³. While limonene injections 1–4 occurring at [O₃] = 250 ppb produce clear peaks in the total particle mass concentration, injections 5 and 6 occurring at 10–15 ppb ozone increase the number but not the total mass of the particles. This is a clear indication that the limonene oxidation products not only condense onto pre-existing particles but also nucleate homogeneously. A similar conclusion was reached in a chamber study of ozone reacting with selected household products (28). The resulting new particles are in the ultrafine size domain (~0.1 μm), and therefore do not significantly contribute to the total mass.

Figure 3 shows a filled contour plot of two particle bursts corresponding to injections 1 and 2 in Figure 2. In the first case, corresponding to the addition of 15 mg of limonene over 5 min, the particle size distribution peaks below 0.1 μm. In the second case, corresponding to the addition of 30 mg of limonene over 10 min, the resulting particle size distribution is bimodal, reflecting complicated particle nucleation and growth dynamics. The structure of these particle bursts bears a resemblance to the particle nucleation events frequently observed outdoors (54–56). The main difference is that the size distribution evolves considerably faster under the present conditions of large concentrations of reactants and fast air exchange rates.

![Figure 1](image1.png)

**FIGURE 1.** Conditions resulting in an exact cancellation of particle generation and removal by ozone-emitting air purifiers. Solid lines are K = 1 curves for the base conditions listed in Table 2. Areas above and below the K = 1 curves correspond to air purification (K < 1) and contamination (K > 1), respectively. Panels a–c display K = 1 curves for 10-fold deviations from the base conditions in [O₃]⁰, [PM]⁰, and λ, respectively. An increase in [PM]⁰ is exactly equivalent to a decrease in E_{03} or λ by the same factor. Panel a includes the parameters of the IAP used in this work.

![Figure 2](image2.png)

**FIGURE 2.** Sample measurements of ozone (a) and particle (b) concentrations in a ventilated office. Two plateaus in [O₃] correspond to the OG and IAP operation. Spikes in [O₃] are experimental artifacts (see text). Panels b and c display the total number and mass concentrations of particles in the 0.01–0.9 μm size range. Triangles represent injections of limonene in the room at a rate of 3 mg min⁻¹; injections 1–7 lasted 5, 10, 15, 20, 5, 15, and 15 min, respectively.
Figure 4 displays the time evolution in the particle size distribution resulting from an addition of 15 mg of limonene in 5 min into the room with IAP turned on. Each size distribution took 6 min to acquire, with SMPS scanning in the direction of increasing particle diameter. New particles appear immediately after the limonene addition. They grow from their initial diameter of 0.02–0.03 μm to 0.08–0.1 μm before being driven out of the room by the HVAC air flow.

**Model Evaluation.** The observed particle bursts were fitted to the kinetic model described above in one of the following ways. The first approach was a numeric solution of eqs 4–6 using a stiff differential equation solver. The injection of limonene was treated as a 3 mg min⁻¹ limonene source turned on for a certain period of time. The second approach was an analytical solution of eqs 4–6, under the simplifying assumptions of an instantaneous jump in VOC concentration by the amount of [VOC]added (i.e., the amount that is added over the entire injection period) and a constant ozone concentration in the room. Once again, the second assumption means that [O₃]ss is not strongly affected by the presence of limonene. The resulting solutions are

\[
[VOC](t) = [VOC]_{ss}^{ON} + [VOC]_{added}e^{-k_{VOC}t} \quad (13)
\]

\[
[PM](t) = [PM]_{ss}^{ON} + \frac{k_{r}[VOC]_{added}[O₃]_{ss}^{ON}}{k_{PM} - k_{VOC}} (e^{-k_{VOC}t} - e^{-k_{PM}t}) \quad (14)
\]

\[
k_{VOC} = \lambda + k_{dVOC} + k_{r}[O₃]_{ss}^{ON} \quad (15)
\]

\[
k_{PM} = \lambda + k_{dPM} + k_{ap} \quad (16)
\]

The initial steady-state concentrations are calculated from eqs 7–10.

Figure 5 shows the results of the simulations. The experimental data points represent the total mass concentration of particles following an injection of 15 mg of limonene over 5 min into the room with an operating IAP. Because the particles are small, the total mass is calculated only for particles below 0.12 μm in diameter under the usual assumptions of particles’ sphericity and unit density. The simulation parameters (Table 2) are explicitly measured, estimated, or taken from the literature. For example, the outdoor particle concentration, [PM]₀₁₂μm, is chosen to match the background particle mass concentration for particles with Dₚ < 0.12 μm for that particular measurement. The only adjustable parameter in the fit is the mass yield of aerosol particles, χ.

Figure 5 shows that both exact and approximate simulations provide a satisfactory fit to the data. The fitted mass yield of aerosol particles is χ = 0.13 for this particular measurement. The fitted yield becomes higher for elevated [O₃]₀₁₂μm or larger amounts of injected limonene. This explains why the particle bursts resulting from injections 1–4 in Figure 2 are stronger than the ones from injections 5 and 6. These results are in qualitative agreement with published chamber
studies of SOA yields, which find that the yields increase with the concentration of both VOC and \( \text{O}_3 \) (15, 53, 57, 50).

**Discussion**

Concerns about ozone-emitting air purifiers have been and continue to be raised by scientists and government officials (32, 34, 35, 44, 59). Thus, in a recent report to the California Legislature, the California Air Resources Board officially recommended that the public avoid using these devices indoors (33). This important report reviewed both direct and indirect health effects of the artificially elevated indoor ozone concentrations.

This paper evaluates a simple kinetic model that can be used to quantify the indirect effect of ozone—VOC chemistry on the level of indoor PM. This model includes only three chemical species, but it grasps all the key elements of the ozone—VOC chemistry. It should be directly applicable under conditions when the reactive VOC emissions are dominated by one molecule or by several molecules with comparable reactivities toward ozone. In more complicated VOC emission scenarios, the model can be expanded to include multiple SOA-forming reactions between ozone and VOC.

The most striking prediction of the model is the small magnitude of the air purifier’s ozone emission rate needed to significantly increase the PM level in the air under realistic indoor conditions. Indeed, under the base conditions listed in Table 2, an air purifier with \( E_{\text{O}_3} > \text{f} \) ratio exceeding ~0.1 mg m\(^{-3}\) (i.e., 0.1 mg of ozone emitted into every cubic meter of air processed by the air purifier) may increase the respirable PM mass concentration instead of reducing it as advertised by the manufacturer. It is also of concern that this condition is actually fulfilled by IAP used in this work: an appliance that had a broad commercial availability as recently as 2005. Reduction of the ozone emission rate (ideally to zero level) and increasing the air flow through the air purifier are the most important factors for achieving the maximum possible reduction in the indoor PM level. Operation of ozone-emitting air purifiers in indoor environments with elevated concentrations of unsaturated VOC should be avoided.

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**Supporting Information Available**

Supporting information describes characterization of the ozone emission rates and particle removal rates for the two air purifiers used in this study.

**Literature Cited**
