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Effects of an ozone-generating air purifier on indoor secondary particles in three residential dwellings

Abstract The use of indoor ozone generators as air purifiers has steadily increased over the past decade. Many ozone generators are marketed to consumers for their ability to eliminate odors and microbial agents and to improve health. In addition to the harmful effects of ozone, recent studies have shown that heterogeneous and homogeneous reactions between ozone and some unsaturated hydrocarbons can be an important source of indoor secondary pollutants, including free radicals, carbonyls, carboxylic acids, and fine particles. Experiments were conducted in one apartment and two detached single-family dwellings in Austin, TX, to assess the effects of an ozone generator on indoor secondary organic aerosol concentrations in actual residential settings. Ozone was generated using a commercial ozone generator marketed as an air purifier, and particle measurements were recorded before, during, and after the release of terpenes from a pine oil-based cleaning product. Particle number concentration, ozone concentration, and air exchange rate were measured during each experiment. Particle number and mass concentrations increased when both terpenes and ozone were present at elevated levels. Experimental results indicate that ozone generators in the presence of terpene sources facilitate the growth of indoor fine particles in residential indoor atmospheres. Human exposure to secondary organic particles can be reduced by minimizing the intentional release of ozone, particularly in the presence of terpene sources.

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Key words: Ozone generators; Particulate matter; Ozone; Terpenes; Secondary organic aerosol.

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Practical Implications

Past studies have shown that ozone-initiated indoor chemistry can lead to elevated concentrations of fine particulate matter, but have generally been completed in controlled laboratory environments and office buildings. We explored the effects of an explicit ozone generator marketed as an air purifier on the formation of secondary organic aerosol mass in actual residential indoor settings. Results indicate significant increases in number and mass concentrations for particles <0.7 microns in diameter, particularly when an ozone generator is used in the presence of a terpene source such as a pine oil-based cleaner. These results add evidence to the potentially harmful effects of ozone generation in residential environments.

Introduction

There is a growing public awareness of the risks associated with poor indoor air quality. In the past two decades, cases of asthma have risen significantly in the general population and 'sick buildings' have received significant media attention. Consequently, numerous companies market air purifiers to the public, and claim that their products can provide relief from a myriad of respiratory ailments, decrease odors, and destroy microbial agents. However, many air purifiers, including those marketed as electrostatic precipitators, negative ion generators, and ozone generators, produce ozone.

Exposure to ozone has been associated with chest pain, coughing, and irritation of the respiratory system (Lippmann, 1989; U.S. Environmental Protection Agency, 1997). Ozone exposure has also been shown to worsen chronic asthma and other respiratory diseases, as well as compromise the body's ability to fight respiratory infections (Lippmann, 1989; U.S. Environmental Protection Agency, 1997). Ozone is a particularly potent lung irritant for at-risk groups, such as the elderly, young, and people with asthma and other lung diseases (Boeniger, 1995). These are groups that spend a considerable amount of time indoors (Klepeis et al., 2001) and, therefore, are more likely to have increased ozone exposure when an ozone generator is employed. Several government agencies in the US have warned against their use. Additionally, ozone generators, when operating at safe ozone levels, may not destroy microbes, reduce odor sources, or reduce indoor pollutants enough to provide any consequential health benefits (Esswein and Boeniger, 1994; Foarde et al., 1997).

To assess the potential significance of ozone generators on indoor air quality we considered a simple steady-state mass balance on a well-mixed residential dwelling in the absence of outdoor ozone or any significant indoor homogeneous chemistry, e.g. titration reactions of ozone by nitric oxide. For these conditions the indoor concentration of ozone is given by the following equation:

$$C = f\left[\frac{E/V}{\lambda + v_\mathrm{d}(A/V)}\right], \tag{1}$$

where C = concentration of ozone (parts per billion by volume = ppb), $f = 5.1 \times 10^5$ = unit conversion factor for ozone concentration at 25°C (ppb/g/m^3), E = emission rate for ozone generator (g/h), V = volume of well-mixed building (m^3), λ = air exchange rate (h^{-1}), v_d = deposition velocity for ozone (m/h), and A/V = surface to volume ratio for an interior environment (1/m). Kissel (1993) reported ozone emission rates of 0.04–1.114 g/h for nine ozone generators. Murray and Burmaster (1995) reported a median value of λ of 0.5 h^{-1} for homes in the US. A typical home floor area in the US is 157 m^2 (U.S. Bureau of the Census, 2001). Multiplying this value by an assumed ceiling height of 2.4 m yields a typical indoor residential house volume of 377 m^3. Lee et al. (1999) reported a central tendency of 2.8 h^{-1} for v_d(A/V) in the living rooms of 43 residential homes in Southern California. Substituting these values into Equation 1 leads to increases in indoor ozone concentrations ranging from 16 to 453 ppb due to the use of explicit ozone generators. The upper end of this range exceeds the 8-h National Ambient Air Quality Standard in the US by an approximate factor of 6 and is clearly an unacceptable condition if occupants are present in a building. However, even the lower end of this range reflects a considerable increase in ozone concentrations if it is placed in the context of an equivalent increase in outdoor ozone concentration.

The increase in outdoor ozone concentration that would contribute the same amount of ozone as an explicit ozone generator is given by Equation 2:

$$C_\mathrm{outdoor} = f\left(\frac{E}{p\lambda V}\right), \tag{2}$$

where C_outdoor = equivalent increase in outdoor ozone concentration (ppb), p = fractional penetration of ozone through a building envelope (–), and all other variables are as described previously. Liu and Nazaroff (2001) reported a mean value of $p = 0.53$ for an idealized fiberglass insulated wall. Using this value for the ozone penetration factor and $\lambda = 0.5$ h^{-1}, V = 377 m^3, and E = 0.04 to 1.114 g/h yields equivalent increases in outdoor ozone concentrations of 204 ppb to 5.7 ppm. An outdoor ozone concentration equal to 5.7 ppm is clearly unrealistically high. However, even the lower bound equivalent is in the range of ozone concentrations observed in the most polluted cities in the industrialized world.

In addition to the harmful effects of ozone itself, indoor ozone can also drive indoor chemistry, reacting heterogeneously with building materials and furnishings, as well as homogeneously with unsaturated organic compounds, nitric oxide, and some free radicals. Such reactions have been shown to be important, especially with respect to reaction products (Long et al., 2000; Rohr et al., 2002; Wainman et al., 2002; Weschler and Shields, 1999). There is evidence that the by-products may often be more irritating than the original reactants (Wolkoff et al., 1997, 1999). Clausen et al. (2001) exposed mice to a mixture of high concentrations of ozone and limonene. The mice experienced a 33% reduction in respiratory rate. The individual compounds that were measured in the air samples could not explain this reduction. It was hypothesized that other, more irritating products than those measured, were also produced. By-products resulting from indoor ozone chemistry include free radicals, aldehydes, ketones, alcohols, carboxylic acids, and fine particulate matter (Sarwar et al., 2003).

Weschler and Shields (1999) found a direct correlation between elevated indoor O_3 and terpene concentrations and indoor fine particles by selectively introducing limonene, α-terpinene and a terpene-based cleaner into two adjacent unoccupied and identical offices. In the first office, an ozone generator was used to raise the indoor O_3 levels to 200–300 ppb; the second office did not have an ozone generator. The authors reported a significant increase in particle number concentrations in the submicron range in the office with elevated ozone. The authors attributed the formation and growth of indoor particles to O_3/terpene reactions and condensation of the resulting by-products. In subsequent experiments conducted in these same adjacent offices, the authors depended on outdoor-to-indoor transport as the source of ozone – typically between 2 and 40 ppb. In these experiments one of the offices contained a limonene source; the other did not. The particle concentration in both offices increased when the indoor ozone level increased, although the office with the limonene source had a significantly greater increase in submicron particles. The difference in particle mass concentrations between the two offices tracked the indoor ozone levels and was approximately 15–20 μg/m^3 when indoor ozone was in the range of 25–30 ppb.

Long et al. (2000) reported evidence that indoor chemical reactions involving ozone can be a significant source of indoor ultra-fine particles. The authors conducted six sampling events using a pine oil-based cleaner to mop floors and clean toilets in Boston homes. Ozone was present in these homes solely because of outdoor-to-indoor transport. Five of the six sampling events demonstrated significant fine particle formation. Particle number concentrations increased by 7–10 times relative to the original particle number concentrations. More than 50% of the particles (by volume) generated during these five events were ultra-fine in nature.

Sarwar et al. (2003) investigated mass increases for fine particles in seven size ranges when terpenes were introduced to an 11 m^3 chamber in the presence of an ozone generator. Initial ozone concentrations were approximately 100–150 ppb in the chamber. When pure α-pinene was allowed to evaporate from a vial placed in the chamber, fine particle levels increased. This initially occurred as a large, immediate increase in the smallest size range measured, 0.02–0.1 microns, followed by a decrease in the number of particles in this size range and an increase in the number of particles in the next largest size range, 0.1–0.2 microns, approximately 1.5 h later. This particle growth wave continued to the 0.5–0.7 micron size range, approximately 10 h later. Similar results were observed when several terpene-based consumer products were used in the presence of elevated ozone with maximum increases in secondary organic aerosol concentrations exceeding 100 μg/m^3 for particle diameters <0.7 μm.

Weschler and Shields (2003) further explored the effect of air exchange rate on indoor secondary particle size distribution and mass concentrations. They introduced limonene into two adjacent unoccupied and identical offices. In one of the offices, an ozone generator was operated to raise the indoor O_3 levels to 50–425 ppb. The other office did not have an ozone generator. Lower air exchange rates led to increased time for homogeneous chemical reactions and gaseous product–particle interaction. This lead to increased particle mass concentrations and shifted the resulting secondary particle size distribution toward larger sizes.

Such findings might provide an explanation for the 'unexplained' indoor fine particles reported in previous studies (Pope and Dockery, 1996). While the mechanisms and products of ozone/terpene reactions are not fully understood, low vapor pressure compounds, such as carbonyls, are known to be generated from ozone-initiated reactions (Atkinson et al., 1995). It was hypothesized that these products condense onto seed particles present in the air, leading to increases in both particle size and number (Weschler and Shields, 1997).

In this study, we explored the effects of indoor ozone originating from a commercial ozone generator in the presence of a common terpene source on indoor fine particles in actual homes.

Experimental methodology

Two experimental events were conducted in each of three residences (six events) in central Texas. The residences included one apartment (apartment X), one house built in 1915 (house Y), and one house built in 1966 (house Z). Apartment X had a floor space of 37 m^2 and was located on the third floor of a complex built in 1984. The apartment had one bedroom, one main door, one sliding glass door, and three windows. The volume was 90 m^3 and the average air exchange rate (ACH) was determined to be 1.0 h^{-1}. House Y was a two-bedroom, two-bathroom house with two main doors, two French doors, and eight windows. The volume was approximately 325 m^3 and the average ACH was 0.95 h^{-1}. House Z had four bedrooms and two bathrooms. There were eight doors, including a garage door and four sets of French doors. The house had seven windows and a volume of approximately 680 m^3. The average ACH was found to be 0.27 h^{-1}. The air exchange rates described above are averages over two sampling events. The actual air exchange rates varied slightly between events at each location, as listed in Table 1. Air exchange rate measurements are specific to the individual dwellings and environmental conditions (indoor/outdoor temperature gradients, ambient winds, etc.) that prevailed during each event. All three homes had central air conditioning and were in normal operation during each experiment.

Each experiment was completed over a 1-day period in each home, and the two events at each home were completed on sequential days. Baseline indoor and ambient outdoor conditions were first measured for 30 min before a commercial corona discharge ozone generator (Living Air, BORA-IV, Alpine Industries, Inc., Greenville, TN, USA) was placed in each home and operated on the highest setting for approximately 1 h prior to the introduction of a terpene source (pine oil-based cleaner). Lidded containers measuring $13 \times 13 \times 5$ cm were filled one-quarter full with the terpene source and were placed in one to four locations in each home. Lids were removed from each container at a specified time, allowing for continuous evaporation of terpenes. Attempts were made to quantify terpene concentrations during experiments by collection on Tenax-TA with subsequent thermal desorption and identification/quantification using gas chromatography/mass spectrometry. However, because of instrumentation problems we were unable to accurately determine terpene concentrations. It is reasonable to state that peak total terpene concentrations exceeded

Table 1 Summary of relevant conditions during each sampling event

Experiment:	1	2	3	4a[f]	4a[f]	5	6
House:	X	X	Y	Y	Y	Z	Z
V (m^3)	91	91	326	326	326	663	663
λ (h^{-1})[a]	1.19	0.84	0.88	1.02	1.02	0.24	0.3
Temperature (°F)	75.4	76.3	79.3	79.7	79.7	78.9	80.2
RH (%)	52.1	50.0	53.0	53.8	53.8	39.9	38.0
t_{O_3} (h)[b]	3	2	3	5	5	5	5
t_{terp} (h)[c]	0.5	1	1	1	1	3	5
No. of terpene sources	1	1	4	4	4	4	4
Peak O_3 (ppb)[d]	46	52	28	34	34	32	33
Peak ΔPM_1 (μg/m^3)[e]	22.2	14.0	6.0	11.0	11.0	9.4	8.1
Normalized PM_1 mass generation (μg/h per source)	1149	448	220	323	503	257	160

[a] λ = air exchange rate.

[b] t_{O_3} = duration of ozone generation.

[c] t_{terp} = duration of presence of terpene source.

[d] Peak O_3 = peak concentration of ozone recorded.

[e] Peak ΔPM_1 = peak concentration of PM_1 recorded − background PM_1 level.

[f] Terpene source was open for 21-h periods, and closed for 1 h between.

approximately 50–100 ppb for each experiment, and that the terpene mixture was clearly above its odor threshold when the source was open.

The terpene source was either allowed to be open in the presence of the ozone generator for up to 5 h or was opened and closed in 60-min intervals in the presence of an ozone generator. Additionally, in house Z, two burners on a gas stove were switched on for two 15-min periods and resulting ozone and particle levels were recorded. At the end of each experiment, the terpene source was closed and the ozone generator remained on for up to one additional hour. Particle decay was measured during this period. The ozone generator was then switched off and particle measurements continued for up to 30 min.

Particle sampling

Particle number concentrations were simultaneously and continuously measured using a laser-optical particle counter (Particle Analyzer 1 = Particle Measuring Systems Inc., Boulder, CO, USA, LASAIR®; model 1002) and a condensation nuclei counter (Particle Analyzer 2 = TSI™, P-TRAK™; model 8525). Particle Analyzer 2 was used to measure number concentrations of particles between 0.02 and 1.0 μm in diameter. Particle Analyzer 1 was used to measure total particle numbers in eight different channels corresponding to diameters (μm) of 0.1–0.2, 0.2–0.3, 0.3–0.4, 0.4–0.5, 0.5–0.7, 0.7–1.0, 1.0–2.0, and >2.0. The sampling interval of both instruments was set at 60 s. Total particle number in each channel was divided by the total sampling volume to determine the average particle number concentration during the sampling interval. Particle number concentrations from the first six channels of Particle Analyzer 1 were added to obtain the total particle number concentrations for the size range of 0.1–1.0 μm. This total particle number concentration was then subtracted from the particle number concentration detected by Particle Analyzer 2 to estimate the particle number concentration in the range of 0.02–0.1 μm. Thus, the two particle analyzers collectively provided particle number concentrations in nine different diameter ranges.

Mass concentration was estimated using particle number concentrations and an assumed particle density. First, a geometric mean diameter was estimated from the minimum and maximum particle diameters in each size range. The average volume of particles in each size range was determined by assuming that each particle was a sphere with a diameter equal to the geometric mean diameter. The total particle volume in each of the size ranges was estimated by multiplying the average volume of the particle by the particle number concentration in that size range. Particle volumes in each of the size ranges were summed to obtain the total particle volume. Total particle volume was then multiplied by particle material density to obtain particle mass concentration. Based on an evaluation of atmospheric organic aerosols, a material density of 1.2 g/cm^3 was adopted for this study (Turpin and Lim, 2001). This method has been shown to produce approximate particle mass concentrations, albeit underestimates. For example, Fan et al. (2003) concurrently measured particle number and mass concentrations during experiments involving reactions of O_3 with several terpenes. Particle mass concentrations were measured using a filter-based technique, and were also derived using measured particle number concentrations and the geometric mean diameters as described above. The derived particle mass concentrations were 25% lower than the results obtained using the filter-based technique.

The two particle counters were located in the living room of each home, at least 5 m from an exterior door. Particles were measured near the air supply to the room in an effort to obtain data from air mixed within the entire home, i.e. as opposed to a local hot spot in the vicinity of the terpene or ozone source. Outdoor particles were measured using tubing that extended approximately 1.5 m from the exterior of the home. All samples were taken at a height of 1 m above the floor or ground. The sample tubing inlets for the two particle analyzers were within 30 cm of one another. Particle Analyzer 1 drew sample air from within the home through a 15-cm length of polyethylene tubing (3 mm OD). Particle Analyzer 2 pulled air through a 4-m length of Tygon® tubing (6 mm OD, Cole-Parmer Instrument Company, Vernon Hills, IL, USA). Outdoor sampling was accomplished with 8 m of sample tubing. Particle losses in tubing were determined in the laboratory using sample tube configurations similar to those in the field; particle number counts were then adjusted to account for deposition losses in tubing.

Ozone sampling

Ozone (indoor and outdoor) was measured using two UV-absorbance ozone analyzers (2B Technologies Inc., Golden, CO, USA, Model 202). The sample averaging time of the ozone analyzers was set to 60 s. Particle filters were included upstream of each analyzer. Both indoor and outdoor sampling air was drawn through a 2.5-m Teflon tube with the inlet placed within 30 cm of the sampling inlets for the two particle analyzers. Data collected from nearby state of Texas ozone monitoring sites were used to confirm the approximate magnitudes and trends in outdoor ozone measurements.

Determination of environmental conditions

Air exchange rates were measured by injecting a known quantity of sulfur hexafluoride (SF_6) into the return air duct of each home and monitoring its decay simultaneously in up to three rooms using a gas chromatography/electron capture detector optimized for analysis of SF_6 (Lagus Applied Technology, Inc., Escondido, CA, USA; model 101, Autotrac). Approximately 1–2 h of mixing time was allowed prior to data collection. A least squares fit was performed on the resulting data to arrive at an entire-house ACH. Indoor and outdoor temperature and relative humidity were measured hourly during each experiment using a TSI^{TM} Q-TRAK^{TM} Model 8550.

Instrument calibration

The two particle analyzers were calibrated by the manufacturers as per recommendation. Periodic zero checks were conducted on each analyzer during field experiments. The ozone analyzers were new, recently calibrated, and confirmed by comparison with other calibrated ozone analyzers at The University of Texas. Periodic zero checks were conducted during the course of the experiments.

Results

Ozone and PM_1 (particle diameters ≤ 1 μm) mass concentrations during the first experiment in apartment X are presented in Figure 1a. From 10:15 to 11:00 h (designated in the figure as points A and B, respectively) outdoor particle concentrations were measured. Outdoor ozone concentrations were not recorded at the beginning of this experiment. Indoor background conditions were measured from 11:00 to 13:00 h (point B to C). The initial indoor-to-outdoor PM_1 concentration was 0.90. During this time, the indoor ozone concentrations rose slightly as a result of outdoor ozone concentrations increasing during the same time and subsequently entering the indoor environment through infiltration. Indoor particle concentrations also increased toward the end of this period. The reason for this increase is not clear. No obvious indoor sources of particles, e.g. combustion sources, were present at the time. Outdoor sources may have included exhaust emissions from a nearby apartment parking lot.

At 13:00 h (time C) the ozone generator was switched on until the end of the experiment and indoor ozone levels increased substantially, reaching approximately 45 ppb at 14:30 h. Outdoor ozone levels were approximately 50 ppb. On average, the indoor PM_1 concentration increased by approximately 35% from 13:00 to 14:30 h with a peak concentration of nearly 18 $\mu g/m^3$ at 13:30 h. Between 14:30 to 14:45 h (points D to E), outdoor ozone and PM_1 concentrations were measured. Outdoor particle levels were the same as at the beginning of the experiment, even though indoor particles had increased significantly. This suggests that the increase in indoor particles was a result of indoor chemistry and not from infiltration of outdoor particles. Furthermore, the particle increase occurred in the absence of the experimental terpene source. The particle increase may have been the result of heterogeneous chemistry. For example, Shaughnessy et al. (1999) tested linoleum in the presence of an ozone generator and found increased particle counts after ozone exposure. Morrison and Nazaroff (2002) have also shown that ozone reactions with carpet can lead to increased emissions, particularly of C1–C13 aldehydes. Heavier aldehydes could potentially condense onto seed particles giving rise to indoor secondary organic aerosol (SOA_i).

Particle mass concentration tended to fluctuate. These fluctuations were likely related to the cycling of the air conditioning unit that was running during the course of the experiment. From time E to F, 14:45–15:00 h, the terpene source was opened. During this time PM_1 concentration increased substantially, with a

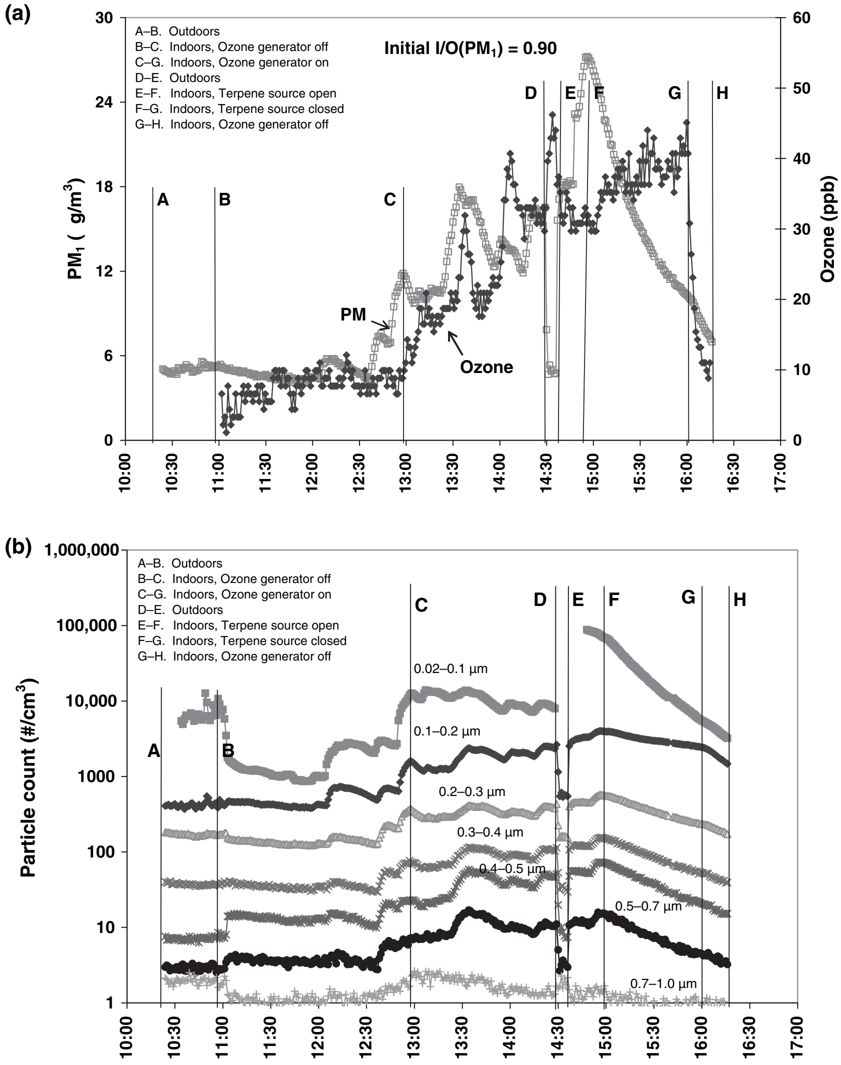

Fig. 1 Experiment 1: apartment X, air exchange rate = 1.19 h^{-1}. (a) PM$_1$ and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

peak concentration of 27 μg/m^3. At time F, 15:00 h, the terpene source was closed and particle concentration decreased rapidly, even though ozone concentrations remained elevated. This suggests that terpene emissions/indoor concentration were the limiting factor to particle mass formation.

Experiments in apartment X and subsequent homes were completed in the presence of 25–40 ppb of ozone, a reasonable value for indoor ozone concentrations during summertime conditions in some urban areas (Weschler, 2000). The terpene source was introduced via evaporation from a small container, and the 27 μg/m^3 particle concentration was achieved with this single source in apartment X.

Figure 1b shows the particle number concentration on a logarithmic scale vs. time for each of the six smallest size ranges measured during the first experiment in apartment X. The most noticeable increase in particle counts occurred after the terpene source had been opened in the presence of ozone. It is interesting to note that the initial increase in particle numbers, which corresponds to the increase in particle concentration in Figure 1a, is largely a result of an increase in particles in the smallest size range. There appears to be some lag in the increase in numbers of particles for each size range, as particles effectively grow because of indoor chemistry; this phenomenon was more evident in other experiments. The particle growth wave may have only extended to the smallest size ranges for two reasons: the terpene source may not have been present long enough for the growth wave to progress further and/or the relatively high air exchange rate (1.19 h^{-1}) may have decreased the amount of time available for ozone/terpene chemistry and particle formation/growth to occur. Previous work by Weschler and Shields (2000) showed that the products of ozone–terpene reactions decrease by approximately an order of magnitude when the air exchange rate is increased from 0.1 ACH to 1 ACH, under conditions similar to those achieved in these experiments.

The results of the second experiment performed in apartment X are presented in Figure 2a,b. During this experiment, the initial indoor PM_1 concentration was approximately 4.5 times greater than the outdoor concentration. The reason for the relatively elevated indoor PM_1 at the start of this experiment was not ascertained; no obvious indoor sources were observed. However, as this experiment was completed in an apartment complex, it is conceivable that activities in adjoining apartment units, e.g. cooking or smoking, could have lead to elevated particle levels in apartment X.

As in the first experiment, PM_1 concentration increased even before the ozone generator was activated. At time C, 12:00 h, when the ozone generator was activated, particle growth did not occur immediately. However, at time D, 13:00 h, when the terpene source was opened, the PM_1 concentration increased to 36 $\mu g/m^3$. As in the first experiment, increases in particle concentration tended to be cyclical and related to the cycling of the HVAC system. At time E, 14:00 h, when both the terpene source was removed and the ozone generator was switched off, both PM_1 and ozone concentrations decreased rapidly. The more rapid decay in ozone is attributed to greater interactions between ozone and indoor surfaces relative to particle deposition onto indoor surfaces. Furthermore, continued condensation of by-products onto particle surfaces, even after termination of ozone and terpene emissions, would tend toward reduction of the natural decay rate of secondary organic aerosol mass concentration.

Figure 2b shows particle counts in seven size ranges, plotted on a logarithmic scale, for the second experiment in apartment X. At 13:00 h (time D) when both the ozone generator and the terpene source were present, the particles in the smallest size range increased and then decreased rapidly, followed by an increase and subsequent decrease in the second smallest size range.

The results of the third experiment, completed in house Y, are shown in Figure 3a,b. The initial ratio of indoor-to-outdoor PM_1 was 0.58. Outdoor concentra-

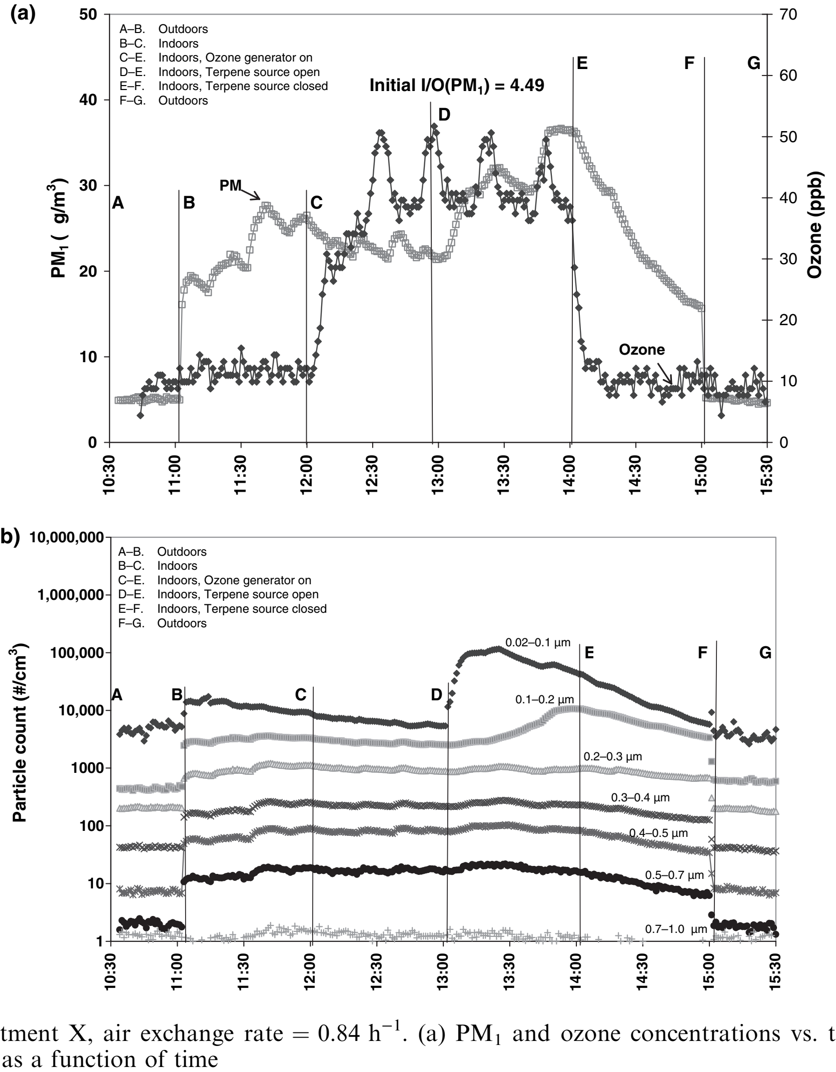

Fig. 2 Experiment 2: apartment X, air exchange rate = 0.84 h^{-1}. (a) PM_1 and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

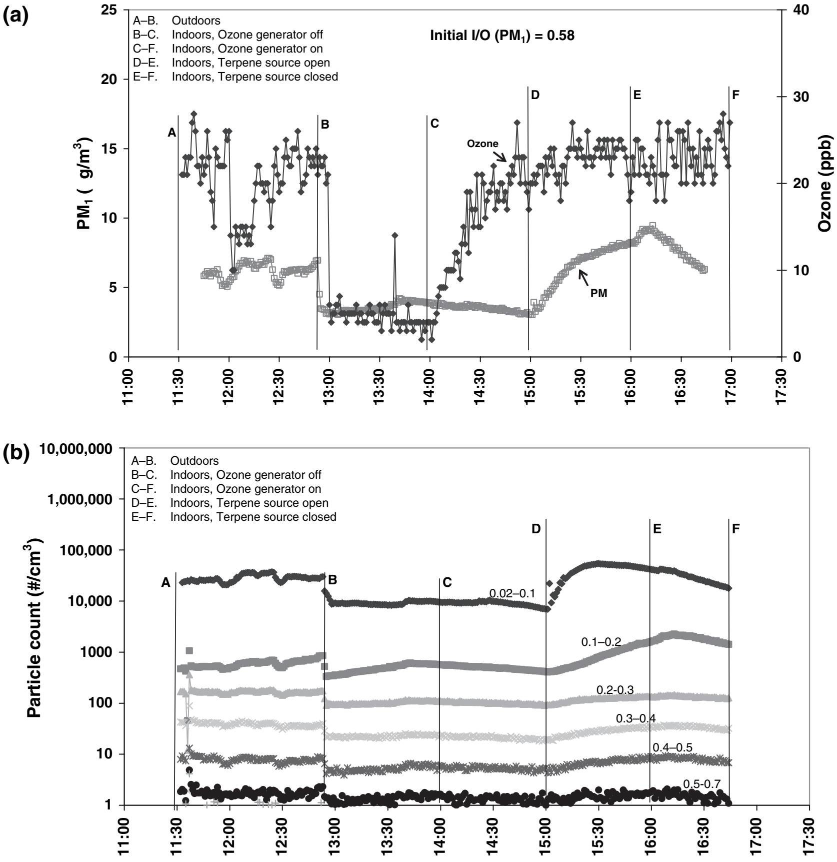

Fig. 3 Experiment 3: house Y, air exchange rate = 0.9 h^{-1}. (a) PM_1 and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

tions of ozone and PM_1 from times 11:30 to 13:00 h (points A–B) and background indoor concentrations from 13:00 to 14:00 h (points B–C) are shown. At 14:00 h (point C) the ozone generator was switched on and ozone concentrations increased steadily, up to approximately 25 ppb. However, there was little growth in particle concentration until time D, when the terpene source was opened. At time D (15:00 h), the particle concentration increased steadily until 16:00 h, after which time the terpene source was closed and the particle concentration began to decrease.

Data are presented as particle number concentration on a logarithmic scale vs. time in Figure 3b. During the time of particle growth, D–E, the particle growth wave is clear between the two smallest particle sizes.

The results of the second experiment in house Y are presented in Figure 4a,b. The initial ratio of indoor-to-outdoor PM concentration for this experiment was 0.76. Outdoor ozone concentrations increased from 5 to 50 ppb during the course of this experiment. The indoor ozone concentration was much lower than the outdoor concentration until the ozone generator was switched on at time C. From C to E the level of indoor ozone increased to an approximately steady-state concentration of 30 ppb, where it remained until the ozone generator was switched off at time H.

For this experiment, the terpene source was opened for 1 h, closed for 1 h, and then reopened for an additional hour. As in the first experiment in house Y, there was no significant increase in particle mass concentration until the terpene source was opened. Upon the introduction of the terpene source in the presence of ozone, a significant increase in particle concentration occurred (starting at time D). When the terpene source was removed, approximately 1 h later at E, the PM_1 decayed slightly, before increasing dramatically at the second introduction of the terpene source (at time F). The peak particle concentration (near time G) was 14.5 $\mu g/m^3$. The fact that the increase in PM_1 mass concentration was greater after the terpene source was opened for a second time may have been due to the increase in surface area associated with particle mass generated between D and E, i.e. during the first activation of the terpene source.

Figure 4b shows a slight increase in particle number concentration after the ozone generator was switched on, but before the terpene source was opened. The majority of this increase occurred in the smallest size range and did not affect overall particle mass concentration. However, at time D, when the terpene source was opened, the particle growth wave is obvious. This phenomenon was repeated at time F, when the terpene

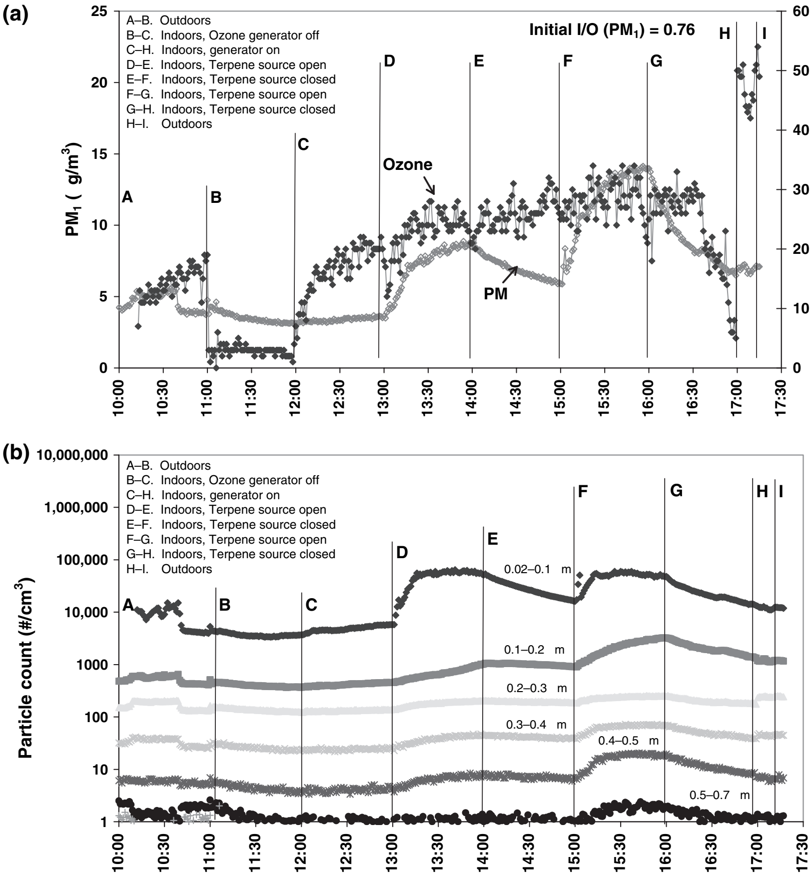

Fig. 4 Experiment 4: house Y, air exchange rate = 1.0 h^{-1}. (a) PM_1 and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

source was reopened, and particle growth occurred up to and including 0.5–0.7 microns.

The results of the first experiment in house Z are presented in Figure 5a,b. This house had a relatively low initial indoor-to-outdoor PM_1 ratio of 0.31, which is as expected for a house with a low air exchange rate (0.24 h^{-1}) due to increased time for deposition of fine particles to surfaces inside the house. Additionally, the lower air exchange rate increased the amount of time available for ozone/terpene chemistry and particle formation/growth to occur. As shown, initial indoor ozone concentrations (measured from B to C) were much lower than outdoor concentrations (measure from A to B and again from F to G) until the ozone generator was switched on. In house Z there was little increase in particle mass concentration until the terpene source was opened at 13:00 h (point D). At this time there was a rapid increase in PM_1 concentration that appeared to happen in two cycles, consistent with cycling of the air conditioning system during the experiment.

Figure 5b shows two interesting phenomena. First, after the ozone generator was switched on, there was an increase in particle number concentration in the smallest size range, even though corresponding particle mass concentration did not increase measurably during the same time, as shown in Figure 5a. Secondly, a well-defined particle growth wave was present in house Z, presumably due to the low air exchange rate and time available for homogenous chemistry and gas–particle interactions. A large 'burst' in particles from 0.02 to 0.1 μm in diameter occurred at time D. There was then a decrease in that size range while particle counts in the next largest size range, 0.1–0.2 μm in diameter, increased simultaneously. Near 15:30 h, when the particle counts for the 0.1–0.2 μm size range were no longer increasing, particles in the 0.2–0.3 μm size range began to increase. A similar phenomenon was observed by Sarwar et al. (2003) when ozone and terpenes were introduced to a large (11 m^3) stainless steel chamber. For experiments with similar air exchange rates and initial ozone concentrations, the particle growth wave reached the 0.2–0.3 μm particles at approximately 3 h and did not extend to the 0.3–0.4 μm particles until nearly 6 h after the terpene source was introduced.

The results of the final experiment in house Z are presented in Figure 6a,b. The initial ratio of indoor-to-outdoor PM_1 was 0.34, a value very similar to that observed during experiment 5. As in experiment 5, a low air exchange rate (0.30 h^{-1}) was observed. Unlike the first experiment at house Z, there was an increase in

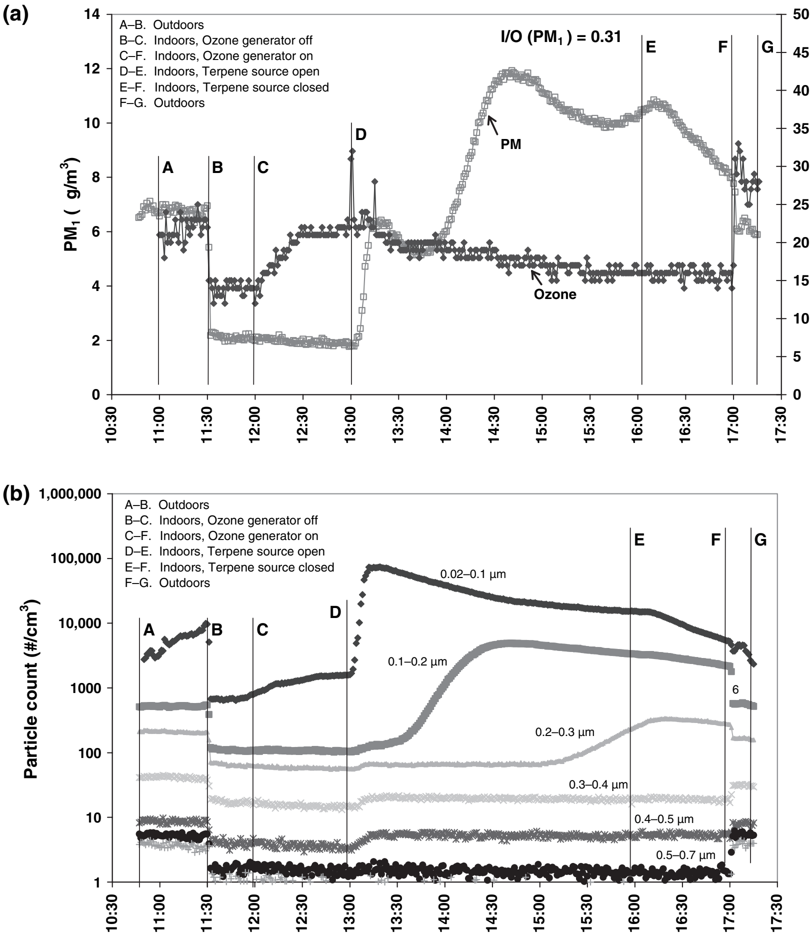

Fig. 5 Experiment 5: house Z, air exchange rate = 0.24 h^{-1}. (a) PM$_1$ and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

particle mass concentration after the ozone generator was switched on, but before the terpene source was opened (points C–D). This may have been because of ozone reactions with terpenes or unsaturated by-products of ozone–terpene reactions that were formed in house Z during the first field event the day before. As house Z had a low air exchange rate relative to apartment X or house Y, the persistence of terpenes or reaction products may have been enhanced through sorptive interactions with indoor materials and continuous desorption on the day of the second experiment.

After the terpene source was opened (from D to E), the PM$_1$ mass concentration increased from approximately 3 to 12 μg/m^3, and then decayed slightly. The reason for the PM$_1$ decrease after 13:00 h was not obvious. Ozone concentrations were approximately constant.

Two burners on a gas stove in a kitchen adjacent to the living room of house Z were switched on for 15 min at E and H in Figure 6a. The burners were located approximately 7–10 m from all indoor sampling instruments. Ultra-fine particle concentrations associated with combustion of natural gas increased rapidly upon activation of the burners, and decreased rapidly following de-activation. The indoor ozone concentration dropped rapidly, presumably because of titration by nitric oxide released by the burners. Interestingly, after the burners were switched off, the PM$_1$ concentration continued to drop to levels lower than those observed before activating the gas burners. This was likely because of significant reductions in the indoor ozone concentration because of titration by nitric oxide (NO). This reaction produces nitrogen dioxide (NO_2), which in turn can react with ozone to produce the nitrate radical ($NO_3^\bullet$). The nitrate radical is highly reactive and can spur additional reactions culminating in nitric acid, as well as SOA$_i$ (Weschler and Shields, 1997). These results underscore the complex nature of indoor air chemistry in the presence of sources that can affect indoor ozone concentrations.

Figure 6b shows the particle number concentrations on a logarithmic scale vs. time for each of the six smallest size ranges measured during the noted experiment in house Z. It is apparent that the increase in particle mass when the ozone generator was switched on was primarily the result of an increase in the smallest size range of particles. The particle growth

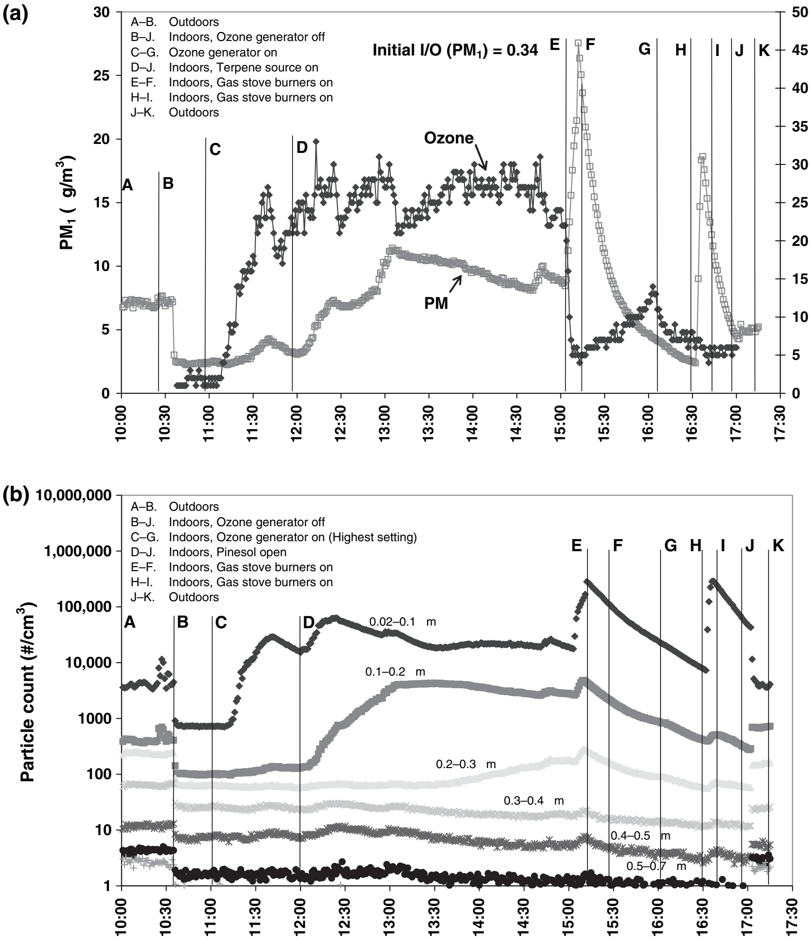

Fig. 6 Experiment 6: house Z, air exchange rate = 0.24 h^{-1}. (a) PM_1 and ozone concentrations vs. time; (b) particle number concentration and growth as a function of time

wave that resulted after the terpene source was opened was more obvious in house Z than in apartment X or house Y, but seemed to only be relevant for the lowest three particle sizes ($<0.3\ \mu$m) even with an air exchange rate of only 0.3 h^{-1}. A substantial increase in the number of ultra-fine particles was evident when the burners were activated.

One clear trend was observed in this study: indoor particle concentrations were maximized when terpene concentrations were increased due to the opening of a pine oil-based cleaner simultaneous with the activation of an ozone generator. The increase in PM_1 under such conditions varied from 6 to 22 $\mu g/m^3$, with an arithmetic mean increase of 11.5 $\mu g/m^3$.

Table 1 includes a summary of the conditions and results of the six sampling events, and underscores the complexity of indoor chemistry in real living spaces. The total mass of particles generated for each experiment was determined using the following equation:

$$M = \sum (C\Delta tQ + V\Delta C), \tag{3}$$

where M = mass generation (μg), C = particle mass concentration ($\mu g/m^3$), Δt = change in time (h), Q = airflow rate through the house (m^3/h), V = volume of the home (m^3), and ΔC = change in concentration over time interval ($\mu g/m^3$).

The mass of particles generated for each experiment was normalized by the number of terpene sources and the amount of time the terpene sources were open (last row of Table 1). Apartment X had the largest increases in PM_1 and the largest normalized PM_1 mass generation rate, despite its relatively high air exchange rate. However, apartment X had the highest indoor ozone levels and the lowest indoor temperatures, both of which are conducive to SOA_i formation (Sarwar et al., 2003). In addition, because of its connectivity to adjacent apartment units, there is somewhat less certainty that all of the changes in particle mass concentration observed in apartment X were because of ozone-initiated chemistry.

House Y had a similar air exchange rate and relative humidity to apartment X. However, the temperature was higher and the indoor ozone concentration was lower, which previous work suggests would lead to lower indoor particle concentrations (Sarwar, 2003). This is countered by the greater number of terpene sources in house Y vs. apartment X, and the mass generation for experiment 4 in house Y was comparable with experiment 2 in apartment X.

In addition to having the lowest air exchange rate, house Z also had the greatest volume and a lower HVAC cycling frequency than apartment X. It is conceivable that the longer mixing time for house Z affected indoor chemistry by yielding less uniform ozone and terpene concentrations than in the other dwellings. House Z was also characterized by a lower relative humidity than either apartment X or house Y. Overall, house Z exhibited a lower source-normalized mass generation rate than apartment X or house Y.

Firm conclusions cannot be drawn from these experiments in relation to the effects of environmental parameters on SOA_i formation in real homes. However, these results do show that as chemical reactors real homes are significantly more complex systems than are controlled laboratory chambers.

Conclusions

It is apparent that indoor secondary organic aerosols do form from ozone/terpene reactions in residential environments, and can contribute to human exposure to such particles when ozone generators are used indoors. In this study, the use of an ozone generator led to significant increases in particle levels in each of three homes as a result of ozone/terpene interactions when a terpene source was present. While use of the ozone generator appeared to facilitate particle mass increases under some conditions in the absence of the terpene source, these increases were immeasurable in most cases and, when present, much smaller than when a terpene source was applied.

When the ozone generator was used while a terpene source was present, particles increased from smaller to larger diameters, although the extent of this growth was limited to particles less than approximately 0.7 μm in diameter. As this process occurred, the number of particles in each size range increased initially, beginning with the smallest size range, and then decreased as the number of particles in the next size range increased.

Explicit ozone generators should be a concern with respect to elevated inhalation exposure of building occupants to ozone. The results of this study suggest that the occupants of residential dwellings may also be exposed to elevated levels of fine and ultra-fine particles when an ozone generator is employed in a residential setting, particularly during periods of relatively high terpene concentrations, e.g. during use of pine oil-based cleaners or scented deodorizers.

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