Ozone and Limonene in Indoor Air: A Source of Submicron Particle Exposure

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Little information currently exists regarding the occurrence of secondary organic aerosol formation in indoor air. Smog chamber studies have demonstrated that high aerosol yields result from the reaction of ozone with terpenes, both of which commonly occur in indoor air. However, smog chambers are typically static systems, whereas indoor environments are dynamic. We conducted a series of experiments to investigate the potential for secondary aerosol in indoor air as a result of the reaction of ozone with *d*-limonene, a compound commonly used in air fresheners. A dynamic chamber design was used in which a smaller chamber was nested inside a larger one, with air exchange occurring between the two. The inner chamber was used to represent a model indoor environment and was operated at an air exchange rate below 1 exchange/hr, while the outer chamber was operated at a high air exchange rate of approximately 45 exchanges/hr. Limonene was introduced into the inner chamber either by the evaporation of reagent-grade *d*-limonene or by inserting a lemon-scented, solid air freshener. A series of ozone injections were made into the inner chamber during the course of each experiment, and an optical particle counter was used to measure the particle concentration. Measurable particle formation and growth occurred almost exclusively in the 0.1–0.2 μm and 0.2–0.3 μm size fractions in all of the experiments. Particle formation in the 0.1–0.2 μm size range occurred as soon as ozone was introduced, but the formation of particles in the 0.2–0.3 μm size range did not occur until at least the second ozone injection occurred. The results of this study show a clear potential for significant particle concentrations to be produced in indoor environments as a result of secondary particle formation via the ozone–limonene reaction. Because people spend the majority of their time indoors, secondary particles formed in indoor environments may make a significant contribution to overall particle exposure. This study provides data for assessing the impact of outdoor ozone on indoor particles. This is important to determine the efficacy of the mass-based particulate matter standards in protecting public health because the indoor secondary particles can vary coincidently with the variations of outdoor fine particles in summer. *Key words*: indoor air chemistry, limonene, ozone, particulate matter, secondary organic aerosol. *Environ Health Perspect* 108:1139–1145 (2000). [Online 6 November 2000]

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Over the past two decades, research focused on human exposure to air pollutants has demonstrated the dependence of exposure on individual activity patterns. A review of activity pattern data has revealed that people do not spend much time outdoors in the regulated ambient atmosphere, but instead spend most of their time indoors in either a home or work environment (*1*). While efforts will undoubtedly continue to regulate pollutant concentrations in ambient air, many people will still receive their highest exposures in indoor environments.

Assessing exposure to fine particulate matter (PM) is currently a topic of great interest due to epidemiologic evidence that small incremental changes in ambient PM_{10} (PM < 10 μm in diameter) concentrations are associated with an increase in the rates of both morbidity and mortality (*2–14*). A recent *Science* news article (*15*) states that

> death rates in the 90 largest U.S. cities rise on average 0.5% with each tiny 10 micrograms per cubic meter increase in particles less than 10 micrometers in diameter.

These studies have observed the occurrence of adverse health effects at ambient PM_{10} concentrations that commonly occur in many U.S. cities and suggest that there may be no safe threshold concentration for fine particles. Although there is debate over the results of the epidemiologic studies, the U.S. Environmental Protection Agency (U.S. EPA) found the evidence compelling enough to adopt new National Ambient Air Quality Standards for $PM_{2.5}$ (PM < 2.5 μm in diameter), in addition to the PM_{10} standard, as a means of protecting public health (*16*). The annual $PM_{2.5}$ standard was set at 15 μg/m^3 and a 24-hr standard was set at 65 μg/m^3. The existing PM_{10} standard remains at 50 μg m^3. (At the time this paper was prepared, the authority of the U.S. EPA to implement the new standard was being argued in court.)

The efficacy of the new $PM_{2.5}$ standard would depend on its success in reducing exposure to fine particles. The PM data used in the epidemiologic studies were obtained by either using area monitors, which collected ambient PM samples in proximity to the study population, or through inference from visibility measurements. Because people spend most of their time indoors, the epidemiologic findings make the assumption that indoor PM concentrations consistently track ambient PM concentrations. In a review, Wallace (*17*) examined the results of three large-scale studies that focused on particle concentrations inside homes in the United States and also briefly reviewed a number of other studies conducted in homes and buildings. Wallace estimated that 65% of $PM_{2.5}$ from outdoor sources penetrates indoors but also found that the $PM_{2.5}$ concentrations in nearly all of the homes exceeded the predicted value based on 65% penetration of outdoor particles, suggesting that most homes have sources of indoor particles. It was concluded that for a given home, there is little variation in the relationship of indoor air to outdoor air on a daily basis and that differences in fine particle concentrations between two homes in close proximity result from differences in indoor sources. A significant finding of this review is that unknown sources were found to account for approximately 25% of the PM_{10} and $PM_{2.5}$ in one of the major studies. Based on the geometric means reported, this translates to unexplained daytime concentrations of 19.5 μg/m^3 for PM_{10} and 8.7 μg/m^3 for $PM_{2.5}$. The unexplained nighttime concentrations for PM_{10} and $PM_{2.5}$ are 13.25 μg/m^3 and 6.75 μg/m^3, respectively.

The results of the analysis by Wallace (*17*) show that, although a baseline indoor PM concentration may be predicted by ambient PM concentrations and the air exchange rate, actual indoor PM concentrations will be determined by indoor sources. The increase in the baseline PM_{10} concentration by

unknown indoor sources alone may have adverse health impacts on susceptible populations, such as asthmatics and the elderly. We believe that, under appropriate conditions, at least a portion of the unknown sources is likely to be the result of indoor gas to particle transformation processes, one of which may involve the reaction of ozone (O_3) with unsaturated volatile organic compounds (VOCs) (*18,19*).

Terpenes are naturally occurring, unsaturated volatile organic compounds whose sources include vegetation and trees. In indoor settings they are emitted by wood products, are used as solvents (e.g., solvents based on pine oil), and are often used as odorants in cleaning products and air fresheners. Because of their widespread use, terpenes are commonly found in indoor air at higher concentrations than in the ambient air (*20–29*). Limonene, a terpene with a citrus/lemon fragrance, is among the terpenes most often identified in indoor settings.

Ozone is also commonly found in indoor air during warm weather. Weschler et al. (*30*) made simultaneous indoor and outdoor O_3 measurements for 150 days during the summer at three locations in a New Jersey office complex. The indoor ozone concentrations closely tracked outdoor concentrations and were dependent on the air exchange rate. At the location with the highest air exchange rate, there were 4 days in which the indoor ozone concentration exceeded 120 ppb and 17 days in which it exceeded 80 ppb. Ozone levels frequently remained elevated for 8 hr and on some occasions for 24 hr. Similar results were obtained over a 14-month monitoring period in a commercial building in Burbank, California (*31*). Zhang et al. (*32*) found that indoor ozone concentrations tracked outdoor concentrations in six New Jersey homes. Indoor ozone concentrations in excess of 120 ppb were measured on several occasions.

The formation of secondary particles through the reaction of O_3 and terpenes has been investigated in a number of smog chamber studies (*33–42*). The smog chamber studies have all used static chambers that have no air exchange with the outdoor environment. Homes and offices typically exchange air with the outdoors, which affects the lifetime of indoor air pollutants. A survey of 2,884 U.S. residences found the geometric mean air exchange rate for these residences to be 0.53 exchanges/hr (*43*). To be of any significance in terms of indoor PM, the formation of particles must occur faster than the removal of the particle precursors by ventilation. The reaction of O_3 with limonene, for example, is relatively fast, with a reaction rate constant of 5.1×10^{-6} ppb/sec (or a limonene half-life of 45 min

when the O_3 concentration is 50 ppb) (*44*), and so is likely to be important in indoor environments.

Although both terpenes and O_3 are present in indoor air, at least during a portion of the year, little information exists concerning the particle concentrations and size distributions resulting from their reaction in indoor environments. A recent study that investigated secondary particle formation caused by the infiltration of outdoor-generated O_3 into an office building found that high concentrations of fine particles were formed in offices where a source of terpenes was present (*18*). It was clearly shown that the particles were formed by the reaction of O_3 with the terpenes, demonstrating the importance of this reaction in indoor air. Here we report the results of a series of experiments designed to further investigate the potential for secondary particle formation through the reaction of O_3 and limonene in indoor environments.

Methods

The experiments were conducted in a two-stage environmental chamber, consisting of a smaller chamber nested inside a larger one. This is a dynamic system in which air exchange occurs between the two chambers. The outer chamber is the Controlled Environmental Facility (CEF) located at the Environmental and Occupational Health Sciences Institute (EOHSI) at Rutgers University Busch Campus, Piscataway, New Jersey. The CEF is a stainless-steel exposure chamber designed for human studies and was used to maintain constant temperature and humidity for each experiment and to provide an activated carbon/HEPA-filtered air supply free from volatile organic contaminants and ozone. The CEF has a volume of 25 m^3 and was operated at approximately 45 air exchanges per hour (ach) at 75°F (24°C). The inner chamber was constructed specifically for this and other indoor air quality experiments (*45*) and was operated at an air exchange rate below 1 ach. The inner dimensions of this chamber are 181 cm long by 120 cm wide by 115 cm high with a volume of 2.5 m^3, a surface area of 11.1 m^2, and a surface-to-volume ratio of 4.4 m^{-1}. The walls of the inner chamber were lined with Teflon. The premise behind using a nested chamber approach is that the CEF will serve as a model for the ambient atmosphere and the inner chamber will serve as a model indoor environment.

In each set of the experiments, ozone was reacted with limonene, and particle formation was measured in real time. In the first series of experiments, we injected *d*-limonene directly into the inner chamber and reacted it with O_3 under three different conditions of relative

humidity (RH): 30%, 50%, and 70%. We conducted a second series of experiments at 50% RH using a solid, lemon-scented air freshener (Wakefern Foods, Inc., Elizabeth, NJ) as the limonene source. All of the experiments were conducted at 24°C (75°F).

An estimate of peak limonene concentrations in a home due to the use of a lemon-scented furniture polish was made by applying the product to a wooden coffee table and measuring the limonene concentration over time. A wooden coffee table, 22 inch × 40 inch, was placed inside the CEF and was sprayed for 15 sec with a lemon-scented furniture polish. The polish was wiped off using a clean, cotton cloth, and the cloth and the can of spray wax were removed from the chamber immediately after the application. Limonene measurements were made for a period of 3 hr until the concentration was no longer detectable. We determined the air exchange rate of the CEF's passive ventilation rate after the monitoring period ended. The chamber conditions were 22°C and 45%–50% RH during this experiment. A background sample was collected in the CEF before the spray wax application.

Ozone was produced using an ozone generator manufactured by Ozone Research and Equipment Corporation (Phoenix, AZ). This generator produces ozone by passing oxygen over an ultraviolet lamp. Ozone was introduced into the chamber through Teflon tubing, 0.25 inch OD, 0.125 inch ID. The ozone flow was turned off when a concentration of 60–100 ppb was reached.

We introduced limonene into the model indoor environment in two ways. In the first series of experiments, 10 mL of *d*-limonene (Aldrich Chemical, Inc., Milwaukee, WI) was injected into a heated 100-mL, three-necked flask which had zero air flowing through it at a rate of 1 L/min. The air stream flowed out of the flask through a 60-cm length of Teflon tubing (0.25 inch OD, 0.125 inch ID) and entered a port in the side of the chamber. After the injection, the flask was flushed with zero air for 5 min before the air flow was turned off. In the second series of experiments, a solid lemon-scented air freshener was placed on the floor of the inner chamber to serve as a limonene emission source. This series of experiments was conducted at 50% RH. The air freshener used was unopened before the start of the experiments. We used the same air freshener for all of the experiments and resealed it between experiments. The emission rate of limonene from the air freshener may have changed during the course of the experiments.

We determined the air exchange rate between the inner chamber and the CEF by spiking the inner chamber with methane and measuring its decay over time. Methane was

introduced into the chamber from a certified cylinder until a nominal concentration of 10 ppm was obtained. A Gow-Mac model 23–500 total hydrocarbon analyzer (Gow Mac Instrument Co., Bethlehem, PA) was used to monitor the methane concentration on a real-time basis for a period of 1–2 hr. We determined air exchange before and immediately after each set of experiments. For the experiments described in this paper, the air exchange rate varied from 0.52 to 0.76 exchanges/hr.

We measured ozone concentrations using a Thermo Environmental Model 560 ozone analyzer (Thermo Environmental Instruments, Franklin, MA). This instrument measures ozone by using the chemiluminescent reaction between O_3 and ethylene.

We measured limonene using a Varian Model 3300 gas chromatograph (Varian Inc., Walnut Creek, CA) equipped with a flame ionization detector (FID) and a 10 port gas sampling valve (Valco Instruments, Inc., Houston, TX).

Real-time particle measurements were made using a LASAIR model 1002 eight channel optical particle counter (Particle Measurement Systems, Boulder, CO). The eight channels correspond to the following particle size ranges (optical diameter): 0.1–0.2 μm, 0.2–0.3 μm, 0.3–0.4 μm, 0.4–0.5 μm, 0.5–0.7 μm, 0.7–1.0 μm, 1.0–2.0 μm, and > 2.0 μm. The instrument has a nominal sample flow rate of 50 mL/min and was operated in a continuous sampling mode using 60-sec sample intervals. We synchronized the clock on the particle counter with the clock on the data acquisition computer, which was connected to the real-time gas analyzers.

We estimated the mass concentration for each particle size range by using the particle counts and sample volume. For a given size range, we estimated the volume of a single particle using the geometric mean of the minimum and maximum diameters. The geometric mean was used instead of the arithmetic mean based on the assumption that the particles within the size range were log-normally distributed. We calculated the total particle volume for the size range by multiplying the volume of a single particle by the number of particles counted during the sample interval. An estimate of the total mass for the size interval was made by multiplying the total particle volume by the particle density. Dividing the result by the air sample volume resulted in the estimate of the mass concentration for the size range. We assumed that the particles were spherical with unit density.

Results and Discussion

An increase in the 0.1–0.2 μm particle concentration began in all of the experiments as soon as O_3 was introduced into the chamber. This is not always apparent in the data plots, especially for the initial O_3 injections, due to the scale of the ordinate. Measurable particle formation and growth occurred almost exclusively in the 0.1–0.2 μm and 0.2–0.3 μm size fractions in all of the experiments. These two size fractions combined account for 99.50% to 99.99% of the particle number ($D_p > 0.1$ μm) present at the peak concentrations. (Unfortunately, we did not have an instrument available to measure ultrafine particles with $D_p < 0.1$ μm.)

Results of the d-limonene injection experiments. The results of the experiments in which *d*-limonene was injected into the chamber at the three different conditions of relative humidity are presented in Figure 1. A significant increase in particle concentrations in the 0.1–0.2 μm size range occurred during all three experiments. The sharp decline in the particle concentration at the end of each of the three plots is due to the flushing of the chamber with fresh air at the end of the particle growth measurement period. The numerical values above the plot of the 0.1–0.2 μm particles are estimates of the particle mass concentration corresponding to the peak particle concentrations (see "Methods").

Each of the three experiments produced a large number of particles between 0.1–0.3 μm in diameter. As can be seen in Figure 1,

significant particle growth occurred over time in the 0.2–0.3 μm size range in the experiments at 50% and 70% RH. The increase in the 0.2–0.3 μm particle concentration corresponds to a decrease in the 0.1–0.2 μm particle concentration in both experiments, indicating the occurrence of particle growth processes. Figure 2 shows the mass concentration estimates resulting from the O_3 injection at 110 min for the two smallest particle size ranges at 50% RH (Figure 1B). The data at 120 min represent the mass concentrations at the time that corresponds to the peak concentration in the 0.1–0.2 μm size range. The data at 138 min represent the mass concentrations at the time that corresponds to the peak particle concentration in the 0.2–0.3 μm size range. The absolute difference between the mass concentration at 120 min and 138 min for each size range is also shown in Figure 2. The fact that the loss in mass concentration of the 0.1–0.2 μm size range is less than the gain in mass concentration of the 0.2–0.3 μm size range is consistent with continued condensation/partitioning in both size ranges.

Of the three experiments, the largest increase in the particle number concentration in the 0.2–0.3 μm size range occurred at 50% RH and the least at 30% RH. There was no increase in the particle number concentration in this size range as a result of the initial ozone injection for any of the RH conditions tested. The second ozone injection resulted in an increase in the particle number concentration in this size range at 30% and 50% RH but not at 70%. The third ozone injection resulted in an increase in concentration in this size range at both 50% and 70% RH. There was no third ozone injection at 30% RH. A comparison of Figure 1A, B, and C shows that there were differences in both the number and timing of the O_3 injections. The greatest increase in particle number concentration in the 0.2–0.3 μm size range resulted when three O_3 injections occurred over a period of approximately 80 min (Figure 1B), followed
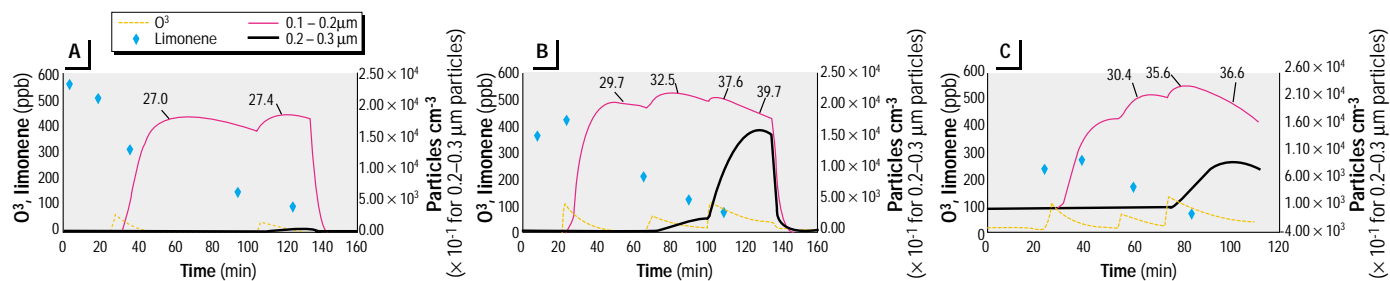
Figure 1. Particle formation resulting from reaction of ozone with *d*-limonene injected into the inner chamber at different conditions of relative humidity: (*A*) 30%, (*B*) 50%, (*C*) 70%. The numerical values appearing above the plot of the 0.1–0.2 μm particles are estimates of the particle mass concentration (0.1 μm < D_p < 0.3 μm) corresponding to the peak particle concentrations (based on unit density). The inner chamber was operated at an air exchange rate of 0.65 exchanges/hr during this experiment.

by a smaller increase when three O_3 injections occurred over 45 min (Figure 1C) and a very small increase when two O_3 injections occurred over 80 min (Figure 1A). These observations indicate that the increases in the number of 0.2–0.3 μm particles were not the direct result of the reaction of ozone with limonene but via the growth of smaller particles. Because the data are limited to particles > 0.1 μm in diameter, there is no measure of particle concentration in the ultrafine particle fraction, which is undoubtedly of great importance in explaining particle growth in the measurable size fractions.

As shown in Figure 1, the initial concentrations of limonene during the first (30% RH) and the second (50% RH) experiments were up to two times higher than those for the third experiment (70% RH). However, the highest particle (0.1–0.2 μm) number concentrations were measured in the third experiment. This result suggests that relative humidity may play a role in the formation of particles via the ozone–limonene reaction. However, this interpretation must be made with caution because the experimental conditions (i.e., the timing and number of ozone injections) were slightly different for the three humidities examined.

We have quantitatively examined the effect of relative humidity on particle growth during that portion of the experiment that is directly comparable for each of the humidities examined—namely, the first 29 min after the initial ozone injection. (Direct comparisons are not valid beyond this point because of differences in the timing of subsequent ozone injections.) For this period, the limonene data points have been fitted with a continuous curve. The ozone concentrations at 1-min intervals were then multiplied by the corresponding fitted limonene concentrations. These values were summed and the resulting value, $\Sigma[O_3][\text{limonene}]$, is directly proportional to the amount of reaction that has occurred during this 29-min period. The particle counts in the 0.1–0.2 μm diameter size-range were also summed for the same 29-min period, $\Sigma[0.1$ μm particles$]$, and this sum was divided by $\Sigma[O_3][\text{limonene}]$. The results are presented in Table 1. The indicated ratio is similar for the experiments conducted at 30% and 50% (1.04 vs. 1.03), but is somewhat larger for the experiment conducted at 70% RH (1.21). That is, the results in Table 1 are consistent with a modest relative humidity effect on the growth of 0.1–0.2 μm particles. Such a result is expected for a mechanism in which Criegee biradicals can react with water to form low-volatility oxidized organics, including organic acids (46). These results are also consistent with the recent findings by

Tobias et al. (47) regarding the effect of relative humidity on the chemical composition of secondary organic aerosol formed from reactions of 1-tetradecene and ozone.

Results of the lemon-scented air freshener experiments. The results of the two particle formation experiments using the solid air freshener are presented in Figures 3 and 4. The limonene concentrations in the chamber resulting from the air freshener were lower than the concentrations achieved by the direct injections of *d*-limonene and resulted in lower particle concentrations. There are no limonene data in Figure 4 due to an equipment failure. The estimated mass concentrations are shown at the peaks in the plot of the 0.1–0.2 μm particles.

Although particles were formed immediately upon the first ozone injection, there was a time lag of approximately 30 min before an appreciable growth occurred in the 0.1–0.2 μm size range. There was no time lag for particle growth for subsequent ozone injections. There were no measurable particles formed in the 0.2–0.3 μm size range during the experiment shown in Figure 3. The experiment presented in Figure 4 shows significant particle growth in the 0.2–0.3 μm size range resulting from the fourth ozone injection. The estimated particulate mass concentration at the peak of the 0.2–0.3 μm particle concentration is 23.5 μg/m³. As in the case of the direct limonene injections, the increase in the 0.2–0.3 μm particle concentration corresponds to a decrease in the 0.1–0.2 μm particle concentration, indicating the occurrence of particle growth.
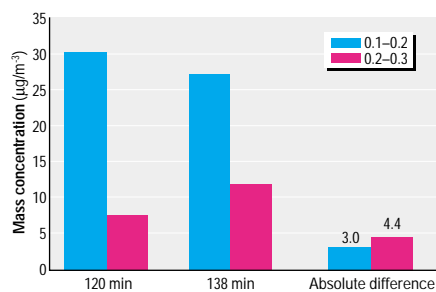
Figure 2. Growth in the mass of 0.2–0.3 μm particles resulting from condensation onto and/or partitioning into 0.1–0.2 μm particles at 50% RH (Figure 1B).

Table 1. The sum of particle concentrations (0.1–0.2 μm size range) at 1-min intervals divided by the sum of [O_3][limonene] at corresponding 1-min intervals.[a]

Relative humidity (%)	$\dfrac{\Sigma[0.1 \text{ μm particles}]}{\Sigma[O_3][\text{limonene}]}$
30	1.04
50	1.03
70	1.21

[a]The resulting quotient is for the first 29 min of each experiment following the initial injection of ozone.

The major difference between the experiment shown in Figure 3 and the one shown in Figure 4 is the duration. The third O_3 injection in the second experiment occurred 453 min after the air freshener was placed in the chamber (Figure 4), compared to 218 min in the first air freshener experiment (Figure 3), and produced more than twice the particle concentration in the 0.1–0.2 μm size range than the first experiment. The fourth O_3 injection was made 586 min after the air freshener was placed in the chamber, 460 min after the first O_3 injection, and resulted in the production of a significant particle concentration in the 0.2–0.3 μm size range (Figure 4). The above results are consistent with the theory that aerosol yield in a given ozone/terpene system is not constant but varies with the existing particle surface area/unit volume. The greater the existing surface area of airborne particles, the greater the yield (48).

Results of the spray wax experiment. The limonene concentrations measured over time after the spray wax application are presented in Figure 5. The highest limonene concentration measured was 175 ppb (975 μg/m³). This concentration is higher than most indoor limonene concentrations reported in the literature (20–29); however, the data reported in the literature are typically derived from integrated samples, which do not reflect information about short-term peak concentrations.

We determined the decay rate of the limonene in the chamber after the injection by plotting the natural log of the limonene concentration against time. The slope of the regression line yields a decay rate of 0.52/hr. The air exchange rate in the chamber was determined to be 0.76 exchanges/hr. This indicates the continued limonene emission (net rate = 0.24/hr) from the coffee table after the peak limonene concentration was reached. The data collected suggest that peak
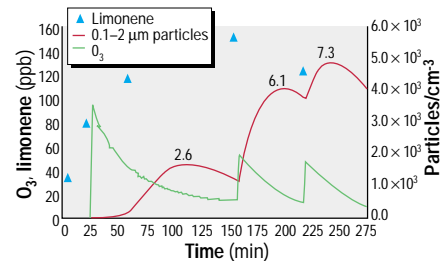
Figure 3. Particle formation resulting from injecting ozone into the chamber containing a lemon-scented, solid air freshener: multiple particle formation events. The numerical values above the solid line are estimates of the particle mass concentration (D_p < 0.3 μm) corresponding to the peak particle concentrations (based on unit density). The inner chamber was operated at an air exchange rate of 0.65 exchanges/hr during this experiment.

limonene concentrations in homes and offices may easily exceed 100 ppb through the use of lemon-scented furniture polish and that the waxed surfaces may emit limonene for a period of time after the wax is applied. If the time at which this product is used were to correspond with a period of elevated O_3 in the home or office, significant particle formation and exposure is likely to result.

Comparison to previous study. The overall results of the present research are in agreement with the results of a study investigating particle formation in an office building resulting from O_3/terpene reactions (*18*). In that investigation, a terpene source was placed in one of two adjacent offices. Ozone and particle concentrations were continuously monitored in both offices. Ozone was introduced either by the use of an O_3 generator or by the natural outdoor to indoor transport of O_3 into the office building. The results show up to an order of magnitude increase in the 0.1–0.2 µm particle concentration in the office containing the terpene source when O_3 was present. The results also show significant particle growth in the larger size ranges over time periods of 12–14 hr as a result of condensation and coagulation. For the experiments in which O_3 was introduced by natural outdoor to indoor transport, concentrations of 0.1–0.2 µm particles were found to track the O_3 concentrations and the additional contribution to the fine particle mass concentrations was estimated to exceed 20 µg/m^3.

Nature of the condensed phase products. The products of the ozone–limonene reaction that are expected to contribute to particle growth include highly oxidized, low-volatility species produced by both primary and secondary processes. In 1992, Grosjean

et al. (*34*) tentatively identified limonaldehyde [4-methyl-3-(3-oxobutyl)pent-4-enal] as a product in the ozone/*d*-limonene system. In a mechanistic diagram they also showed limononic acid [4-methyl-3-(3-oxobutyl)pent-4-enoic acid] as a logical primary reaction product (*34*). In 1993, Grosjean et al. (*35*) reported that aerosol products accounted for 22% of the reacted *d*-limonene in their ozone/*d*-limonene experiments, suggesting that these aerosols contained a number of low volatility C_9 and C_{10} polyfunctional oxygenated products. Based on mechanistic considerations, Weschler and Shields (*18*) suggested that possible secondary products in the ozone/*d*-limonene system included keto-limononaldehyde (3-acetyl-6-oxoheptanal) and keto-limononic acid (3-acetyl-6-oxoheptanoic acid). Glasius et al. (*42*) have used GC-MS and HPLC-MS to identify at least 10 different oxidized organics in the secondary aerosols produced by the ozone–limonene reaction. Among these the most abundant constituents were limonic acid, limononic acid, limonaldehyde and 7-hydroxylimononic acid.

Influence of air exchange rate. The air exchange rate determines the residence time of indoor air. As the air exchange rate increases, less time is available for the ozone–limonene reaction to proceed, for semivolatile products to condense/partition onto existing aerosols, and for existing aerosols to coagulate. The experiments shown in Figures 1–5 were conducted at air exchange rates between 0.52 and 0.65 exchanges/hr. At higher air exchange rates the contribution of the ozone–limonene reaction to secondary particle formation is less. A recent study by Weschler and Shields

(*49*) examined the contribution of the ozone–limonene reaction to indoor particle growth under conditions of low and high ventilation rates. The authors found that the concentrations of 0.1–0.2 µm particles were much larger at the lower air exchange rates even though the ozone concentrations were higher at the higher air exchange rates, [see Figure 6 of Weschler and Shields (*49*)]. The potential for indoor ozone–terpene reactions to contribute to submicron particle exposures is an additional reason to maintain adequate ventilation in indoor environments because a higher ventilation rate will reduce the residence time of reactants indoors.

Exposure implications. Secondary aerosol formation in indoor environments and the resulting exposure has been overlooked in assessing total particle exposure, including the interaction of outdoor-generated pollutants with indoor-emitted pollutants. A number of studies investigating organic aerosols in ambient air have shown that secondary organic aerosols are correlated with O_3 and make up a significant fraction of the total organic aerosol. Pratsinis et al. (*50*) found a strong correlation between secondary aerosol formation and O_3 and estimated that as much as 30% of the organic aerosol in the Los Angeles Basin is due to gas to particle conversion processes. Turpin and Huntzicker (*48*) also found that secondary particle formation correlated well with O_3 concentrations and was responsible for up to 70% of organic aerosol during peak aerosol episodes in the Los Angeles Basin. Schauer et al. (*51*) placed an upper estimate of the total organic aerosol attributable to secondary sources in the South Coast Air Basin in California at 31%. Investigations by Kavouras et al. (*52,53*) have shown that the reaction of O_3 with monoterpenes plays a significant role in secondary particle formation over forested areas. The common occurrence of O_3 in indoor air coupled with the common use of terpene-based products is likely to produce secondary aerosols in indoor air as well. When the findings of the ambient air investigations into secondary particle formation are considered in conjunction with the findings
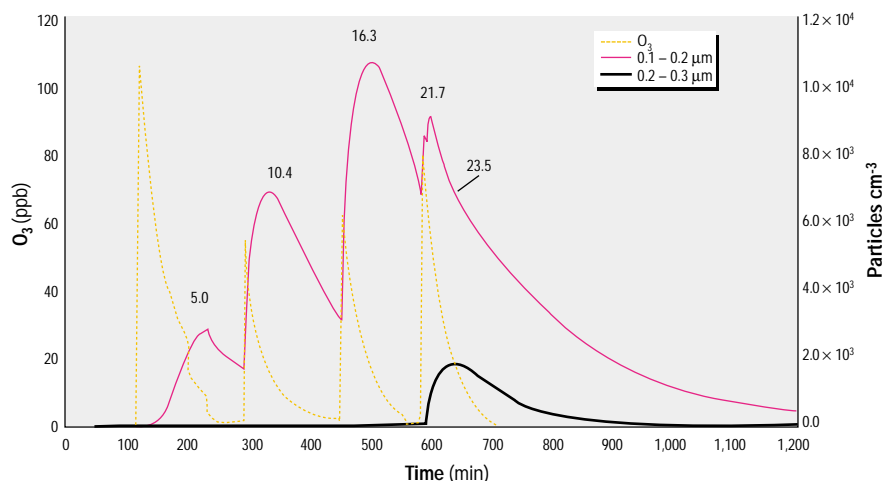
Figure 4. Particle formation resulting from injecting ozone into the chamber containing a lemon-scented, solid air freshener: multiple particle formation events over an extended time period. The numerical values above the plot of the 0.1–0.2 µm particles are estimates of the particle mass concentration corresponding to the peak particle concentrations (based on unit density). The inner chamber was operated at an air exchange rate of 0.52 exchanges/hr during this experiment.
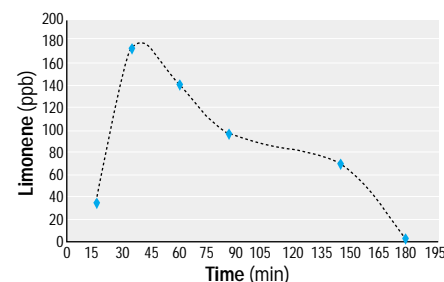
Figure 5. Limonene concentration measured after spray wax was applied to a coffee table.

of this research and the work by Weschler and Shields (*18*), it is clear that the impact of elevated ambient O_3 concentrations on indoor particle concentrations is 2-fold. First, the baseline indoor particle concentration increases due to the penetration of elevated ambient concentrations of fine particles into indoor air (provided sufficient concentrations of VOCs with particle-forming potential are present in ambient air). Second, the indoor particle concentration increases due to the secondary particles formed by the reaction of O_3 (present by outdoor to indoor transport) with indoor sources of unsaturated volatile organic compounds, such as limonene. Exposure assessments based on ambient air monitoring data alone are likely to underestimate indoor particle exposures in buildings where the precursors for secondary particle formation are present.

Conclusions and Recommendations

The experiments conducted in this study produced significant number and mass concentrations of submicron particles as a result of the ozone–limonene reaction. The common occurrence in indoor air of both outdoor-generated O_3 and indoor-generated limonene, their fast rate of reaction, and particle-forming potential is well documented. This study shows a clear potential for secondary particle formation in indoor environments through the ozone–limonene reaction.

The results of the present research, along with the results of the study conducted by Weschler and Shields (*18*) show that the potential exists for the accumulation of $PM_{2.5}$ in excess of 20 μg/m³ in indoor air as a result of using terpene-based products in the presence of elevated outdoor-generated O_3 concentrations. When the increase in the baseline particle concentration infiltrating from ambient air is considered in addition to the particle concentration resulting from indoor air chemistry, the impact of outdoor O_3 on total particle concentrations in indoor air is significant. In view of the epidemiologic evidence of adverse health effects of fine PM and the fact that indoor sources of particles contribute a significant fraction of the total particle exposure, it is important to obtain an understanding of the physicochemical properties and concentrations of the particles formed by gas-to-particle conversion processes occurring in both ambient and indoor air. Determining the contribution of secondary aerosols to overall particle exposure is necessary to determine the efficacy of the mass-based $PM_{2.5}$ standards in protecting human health because the indoor particles generated from ozone–terpene reactions can vary coincidently with the variations of outdoor summertime fine particles. Studies are needed that track indoor, outdoor, and personal particle concentrations as well as indoor O_3 and indoor/outdoor particle counts and size distributions. Such studies will also provide information as to how much of the unexplained fraction of indoor particles, as presented by Wallace (*17*), is the result of secondary particle formation. Because the ultrafine particle fraction (< 0.1 μm) is undoubtedly of great importance in explaining particle growth in the size fractions commonly measured, it is important to include measurements of ultrafine particles in future studies.

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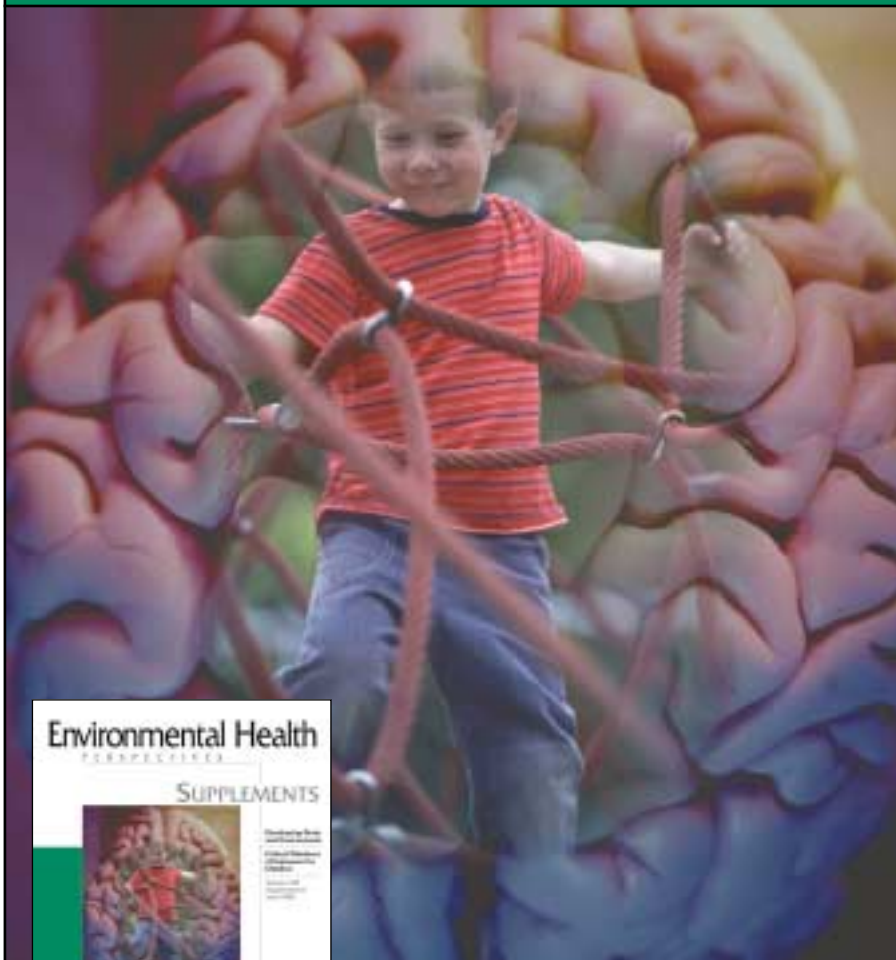
Environmental Health Perspectives (*EHP*) publishes monographs on important environmental health topics and an annual review issue as supplements to the monthly journal. The June supplement (Volume 108, Supplement 3) consists of two monographs focusing on children's environmental health issues. The theme of the first monograph is the association between exposure to toxic chemicals and various neurodevelopmental disorders such as learning disabilities, intellectual retardation, dyslexia, attention deficit/hyperactivity disorder, autism, and propensity to violence. The theme of the second monograph is the effect of the timing of the exposure on the development of various childhood disorders.