The effect of an ion generator on indoor air quality in a residential room

Abstract Ion generators charge particles with a corona prior to their removal on collector plates or indoor surfaces and also emit ozone, which can react with terpenes to yield secondary organic aerosol, carbonyls, carboxylic acids, and free radicals. This study characterized the indoor air quality implications of operating an ion generator in a 27 m³ residential room, with four different test room configurations. Two room configurations had carpet overlaying the original flooring of stained/sealed concrete, and for one configuration with and without carpet, a plug-in air freshener was used as a terpene source. Measurements included airborne sampling of particulate matter (0.015–20 μ m), terpenes and C_1 - C_4 and C_6 - C_{10} aldehydes, ozone concentrations, and air exchange rates. When the heating, ventilating, and air-conditioning system was not operating (room air exchange rate = $\sim 0.5/h$), the use of the ion generator in the presence of the air freshener led to a net increase in ultrafine particles ($< 0.1 \mu m$). Also, increased concentrations of ozone were observed regardless of air freshener presence, as well as increases in formaldehyde and nonanal, albeit within measurement uncertainty in some cases. Thus, it may be prudent to limit ion generator use indoors until evidence of safety can be ascertained.

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Practical Implications

Portable ion generators are intended to clean the air of particles, but they may emit ozone as a byproduct of their operation, which has the potential to degrade indoor air quality. This study showed that under certain conditions in a residential room, the use of a portable ion generator can increase concentrations of ozone and, to a lesser degree, potentially aldehydes. Also, if operated in the presence of a plug-in air freshener that emits terpenes, its use can increase concentrations of secondary organic aerosol in the ultrafine size range.

Introduction

Exposures to ultrafine (<0.1 μ m) and fine (0.1– 2.5 μ m) particles have been associated with adverse health effects (Pekkanen et al., 2002; Pope and Dockery, 2006). Portable air cleaners are designed to remove particles from the indoor air, where a significant portion of exposure may occur because the average American spends 18 h indoors for every hour outdoors (Klepeis et al., 2001). Portable ion generators are marketed as air cleaners, and their intended purpose is to clean the air of particles by charging them with a corona before removal to oppositely charged collector plates or indoor surfaces. Portable ion generators can be set on a floor or table-top and are meant to clean a room-sized space. The particle removal capability of an ion generator can be quantified with the clean air delivery rate (CADR), which is the effective volumetric flow rate of particle-free air delivered by an air cleaner (m^3/h) (Offermann et al., 1985; Shaughnessy et al., 1994; Shaughnessy and Sextro, 2006). CADRs for portable ion generators range from 0–90 m^3/h , at least an order of magnitude less than high efficiency particulate air (HEPA) cleaners (Offermann et al., 1985; Shaughnessy et al., 1994; Niu et al., 2001a; Mullen et al., 2005; Waring et al., 2008).

The use of a corona causes ion generators to emit ozone as a byproduct of operation, at measured rates of 0.056–13.4 mg/h, and these rates are lower than dedicated ozone generators but still increase indoor ozone concentrations (Niu et al., 2001b; Mullen et al., 2005; Tung et al., 2005; Britigan et al., 2006; Waring et al., 2008). Ozone is harmful to human health (e.g.

Bell et al., 2004; Weschler, 2006), and it is also a primary driver of indoor chemistry (Weschler, 2000). The largest loss mechanism of ozone indoors is by surface reactions, which can lead to secondary emissions of carbonyls (Sabersky et al., 1973; Morrison and Nazaroff, 2002; Wang and Morrison, 2006); for instance, ozone reacts with unsaturated fatty acids in carpets to form nonanal. Ozone can also react in the gas-phase with terpenes and other unsaturated organics to form secondary organic aerosol (SOA) in the ultrafine and fine particle size ranges (e.g. Weschler and Shields, 1999, 2003; Long et al., 2000; Wainman et al., 2000; Rohr et al., 2003; Sarwar et al., 2003, 2004; Jonsson et al., 2006; Sarwar and Corsi, 2007; Zuraimi et al., 2007; Coleman et al., 2008; Langer et al., 2008; Waring et al., 2008; Chen and Hopke, 2009, 2010; Fadeyi et al., 2009), as well as carbonyls, carboxylic acids, and free radicals (Kamens et al., 1999; Leungsakul et al., 2005). Terpenes are common indoors and are emitted indoors from wood (Baumann et al., 1999) and consumer products such as air fresheners, surface cleaners, and perfumes (Nazaroff and Weschler, 2004; Singer et al., 2006; Corsi et al., 2007).

Since ion generators are generally not very effective at removing particles and emit ozone during operation, they can operate as net producers of particles and gaseous pollutants in the presence of terpenes. Alshawa et al. (2007) operated an ion generator in an office, injected d-limonene into the air, and observed transient elevations of ultrafine particles. Other studies report the particle forming effects of dedicated ozone generators, which often emit more than 30 mg/h of ozone, in real environments with terpenes (e.g. Weschler and Shields, 1999, 2003; Hubbard et al., 2005). Also, we observed steady-state net particle and formaldehyde formation when ion generators were operated in a 14.75 m³ stainless steel chamber with terpene-emitting air fresheners (Waring et al., 2008). This work extends the chamber investigation to a residential space, since real indoor spaces have larger volumes and surface-tovolume ratios, as well as other sources and sinks of particles, ozone, and carbonyls. The goal of this study was to determine the impact of using a portable ion generator on indoor air quality in a room with varying ozone sinks and terpene concentrations.

Methods

Experimental room configurations and setup

Field experiments were performed in a 27 m³ unoccupied room, located in an approximately 475 m³ three-floor duplex townhome in Austin, Texas in 2007. The room was furnished with a futon, bookshelf with books, desk with computer and chair, television and stand, and curtains covering a sliding glass door to outdoors. The walls and ceiling were painted with flat

latex paint, and the flooring was sealed/stained concrete. A single heating, ventilating, and air-conditioning (HVAC) supply duct conditioned the room. The HVAC system was operated differently during two periods each day. The HVAC system cycled normally from 9 a.m. to 11 p.m. and was turned off overnight from 11 p.m. to 9 a.m. A ceiling fan was operated continuously throughout the testing on its lowest setting to aid in air mixing. For some experiments, carpet and padding (purchased and aired out in a laboratory approximately 1 month prior to experiments) were installed over the original flooring and/or an air freshener was used as a source of terpenes.

The room air was sampled in four different Room Configurations (RC):

- RC 1: Original flooring of sealed/stained concrete, without air freshener
- RC 2: Installed flooring of carpet with padding, without air freshener
- RC 3: Original flooring of sealed/stained concrete, with air freshener
- RC 4: Installed flooring of carpet with padding, with air freshener

Experiments were conducted for 2-day-long periods, starting and stopping at approximately 12 p.m. At least one 2-day-long experiment was conducted per room configuration without and with an ion generator operating on its highest setting, located in the center of the room. At least one full day occurred between each test in a different room configuration, and during that rest period, extra fans were used to help flush the room. A 'Hawaiian' scented plug-in liquid air freshener operated on its highest setting served as a terpene source. One liquid cartridge was used for each room configuration, and the total emission rate was 1.5 g/day, which was determined by mass difference between each experiment. The ion generator was a tower model with collector plates and no fan and was cleaned according to manufacturer instructions between each experiment. It had an ozone emission rate of 3.3 ± 0.2 mg/h, a mean CADR (±s.d.) for particles 12.6–514 nm diameter of 41 (11) m^3/h , and was IG 1 in our previous work (Waring et al., 2008).

Continuous measurements

Instruments were located within the room itself, and all samples were taken near the center of the room, 2 m from the floor. Indoor temperature and relative humidity (RH) were monitored (TSI Q-Trak 8551) as well as the temperature (Onset HOBO U12) at the supply duct register, which indicated when conditioned air was supplied to the room. Air exchange rates (h^{-1}) were measured (Lagus Autotrac ATGM) by the decay of sulfur hexafluoride (SF₆), and were calculated as the best fit slope of the negative of the natural log of

the ratio of the time-varying concentration of SF₆ to the initial concentration vs. time. The ozone monitor (2B Technologies 205) drew indoor samples through 3 m of 6 mm OD Teflon tubing, averaged over one minute. Hourly outdoor ozone concentrations were taken from a monitoring station approximately 9 km from the residence. Indoor size-resolved particle concentrations were measured in the range of 0.015– 0.533 μ m diameter with a scanning mobility particle sizer (TSI SMPS 3936L85) and in the range of 0.542–20 μ m diameter with an aerodynamic particle sizer (TSI APS 3321), both every five minutes.

Volatile organic compound sampling and analysis

Integrated gas-phase samples were taken early each morning, between 1 and 3 a.m. Light aldehydes (C_{1-} C_4) were sampled onto focus liners packed with dinitrophenylhydrazine (DNPH) coated silica gel, with a potassium iodide (KI) ozone trap (SKC 226-120). Sample flow rates were 0.5 l/min and sample volumes 30 l. The DNPH-filled focus liners were prepared based on EPA method TO-11A (US EPA, 1999) and analyzed with high pressure liquid chromatography (Waters 600). Heavy aldehydes (C_6-C_{10}) and terpenes were sampled onto Tenax-GR-filled focus liners (Atas A100094). Samples were collected without ozone scrubbers, since indoor ozone concentrations were always below 15 ppb and ozone scrubbers can degrade measurement quality. Sample flow rates were 21 ml/ min and sample volumes 1.3 l. Heavy aldehydes and terpenes were analyzed with thermal desorption followed by gas chromatography with mass spectrometry (HP5890, HP5971A), and quantified using an internal standard of 1-bromo-4-fluorobenzene, with an experimental uncertainty of 10%. The method is further outlined in our previous work (Waring et al., 2008).

Results

Test information and environmental conditions

Room information and a summary of the room environmental conditions for each experiment are listed in Table 1. Twelve experiments were completed, with four of the twelve as experimental replicates. Each 2-day-long experiment was assigned a unique test ID: the first number corresponds to the room configuration, the second letter corresponds to no ion generator (N) or ion generator (I) present, and the last number the iteration. Mean temperature and RH (\pm s.d.) while the HVAC system was cycling across all experiments were 28.0 (0.8)°C and 46 (2)%, respectively. Mean temperature and RH while the HVAC system was off across all experiments were 28.7 (0.9)°C and 49 (2)%, respectively. The predominate terpene emitted from the air freshener was d-limonene. Mean d-limonene concentrations (\pm s.d.) without and with an ion generator, respectively, for RC 1 were 10 (9.1) and 8.7 (8.1) ppb, for RC 2 were 2.6 (0.56) and 6.7 (3.7) ppb, for RC 3 were 53 (10) and 39 (4.4) ppb, and for RC 4 were 46 (5.4) and 38 (3.3) ppb.

Air exchange rates were measured while the HVAC system was cycling (λ_{cycle}) and turned off (λ_{off}), and at least one λ_{cycle} and λ_{off} was measured for each 2-daylong experiment except 1-N1, during which the HVAC system remained off. Italicized air exchange rates were calculated with <10 data points and should be regarded as approximations. The λ_{cycle} was typically measured in the afternoon between noon and 3 p.m., and the λ_{off} was typically measured at night between 10 p.m. and 1 a.m. Since air exchange rates are a function of indoor-outdoor temperature differences as well as other factors, we cannot say with certainty that the air exchange rates were constant throughout the periods when the HVAC system was cycling (9 a.m.-11 p.m.) and off (11 p.m.-9 a.m.). Thus, these rates are meant to be an indicator of the typical ranges of air exchange present in the test room at the different HVAC conditions. Over all experiments, the mean λ_{cvcle} $(\pm s.d.)$ was 1.3 (0.3)/h and λ_{off} ($\pm s.d.$) was 0.5 (0.1)/ h (when using rates calculated with 10 data points).

Typical results

As an example of typical results, Figure 1 displays the continuous particle and ozone concentrations for (a) day-one of experiment 3-N1 and (b) day-one of experiment 3-I2. These results represent typical days of testing in RC 3, which had sealed/stained concrete flooring and an air freshener. The particle concentrations are on a log-scale and on the left side of the yaxis, and the ozone concentrations are on a linear scale and on the right side of the y-axis. Particle concentrations are plotted in four bins, in the ranges of 0.015-0.05, 0.05–0.1, 0.1–0.533, and 0.542–2.5 μ m. The first three bins were measured by the SMPS and the fourth bin by the APS. The first two bins display ultrafine concentrations, which is the size range most affected by SOA formation in this study (discussed below), and the third and fourth bins display fine particle concentrations. Particles $> 2.5 \ \mu m$ typically had concentrations of 0.01–0.1 $\#/cm^3$ and are not reported. Since outdoor ozone concentrations were taken from a monitoring station 9 km away, they should be regarded as an estimate. The HVAC Off period (11 p.m.-9 a.m.) is labeled and demarcated by vertical lines on the plots.

In RC 3, the air freshener is a source of d-limonene, and Figure 1 shows particle concentrations, (a) without and (b) with the ion generator present. In Figure 1a, the highest particle concentrations occur at approximately 3 p.m. when the HVAC system was cycling. These higher particle concentrations occur concurrently with elevated outdoor and indoor ozone

Waring & Siegel

| Table | 1 | Room environmental | conditions | for | each 2-da | v test | Italicized | air | exchange | rates | were | calculated | with | ~10 | data | nnints | and | should | he | renarded | as | an eq | stimate |
|-------|---|---------------------|------------|-----|------------|----------|------------|-----|------------|-------|--------|------------|--------|-----|------|--------|-----|---------|----|----------|------|-------|---------|
| Ianic | | nooni environnentai | CONULIONS | 101 | Cauli Z-uc | ιγ ισοι. | Itancizeu | all | excitative | Iales | AAGI C | calculateu | VVILII | <1U | uala | punits | anu | SIIUUIU | ne | regarueu | as (| | sumate |

| 0 | | Ŧ | | Test ID ^b | | HVAC Cycle (9 a.m.—11 p.i | m.) | HVAC Off (11 p.m.–9 a.i | m.) | af | λ ^g _{off} (per hour) |
|------------------------|-------------------------|-------------------|-----------------|----------------------|-------------------------------|------------------------------|------------------------|----------------------------|------------------------|------------------------------------|---|
| Room configurations | Floor | lerpene source | IG ^a | | Dates of test ^c | T ^d (s.d.) (°C) | RH ^e (s.d.) | T ^d (s.d.) (°C) | RH ^e (s.d.) | , r _{cycle} (per hour) | |
| RC 1 | Stained/sealed concrete | None | No | 1-N1 | May 22–24 | _ | _ | 27.9 (0.8) | 55 (2) | _ | 0.62, 0.65 |
| | | | | 1-N2 | June 14–16 | 27.4 (0.6) | 47 (3) | 28.0 (0.4) | 51 (3) | 1.5 | 0.55, <i>0.58</i> |
| | | | Yes | 1-11 | June 5–7 | 27.4 (0.7) | 51 (3) | 27.7 (0.2) | 48 (1) | 1.2 | 0.75 |
| | | | | 1-12 | June 18–20 | 27.9 (0.5) | 47 (3) | 28.7 (0.3) | 48 (2) | 1.4 | 0.51, <i>0.55</i> |
| RC 2 | Carpet | None | No | 2-N1 | June 27–29 | 27.6 (0.7) | 48 (2) | 28.6 (0.5) | 52 (2) | 1.1 | 0.52 |
| | | | Yes | 2-11 | July 1–3 | 28.4 (0.6) | 47 (2) | 29.2 (0.2) | 49 (1) | 1.3 | 0.51 |
| RC 3 | Stained/sealed concrete | Air freshener | No | 3-N1 | July 31–August 2 | 27.2 (0.5) | 47 (2) | 28.1 (0.4) | 50 (2) | 0.7 | 0.18 |
| | | | | 3-N2 | August 9–11 | 27.7 (0.5) | 44 (1) | 28.7 (0.3) | 47 (2) | 1.2 | 0.32, <i>0.68</i> |
| | | | Yes | 3-11 | August 4–6 | 27.5 (0.6) | 46 (2) | 28.4 (0.5) | 49 (2) | 1.2 | 0.40, <i>0.66</i> |
| | | | | 3-12 | August 6–8 | 28.0 (0.4) | 44 (1) | 28.8 (0.4) | 47 (1) | 1.5 | 0.51, 0.66 |
| RC 4 | Carpet | Air freshener | No | 4-N1 | July 7–9 | 29.3 (0.6) | 46 (2) | 30.1 (0.4) | 48 (2) | 1.4 | 0.69 |
| | | | Yes | 4-N2 | July 10–12 | 29.5 (0.5) | 42 (1) | 30.6 (0.5) | 45 (1) | 1.9 | 0.44, <i>0.63</i> |

^alon generator; ^bTest ID: the first number = Room Configuration, the second letter = ion generator (N) or ion generator (I), and the last number = experimental iteration; ^cExperiments started and stopped at approximately 12 p.m.; ^dTemperature; ^eRelative humidity; ^fAir exchange rate during HVAC Cycle period; ^gAir exchange rate during HVAC Off period. HVAC, heating, ventilating, and air-conditioning; RC, Room Configurations; RH, relative humidity.



Fig. 1 Typical indoor particle number and indoor and outdoor ozone concentrations (a) without and (b) with an ozone-emitting ion generator operating. The test room had a sealed/stained concrete floor and an air freshener present (Room Configuration 3)

concentrations, and their source is likely both SOA formation and infiltration of outdoor particles. The lowest particle concentrations are at night while the HVAC system was off. However, Figure 1b shows that with the ozone-emitting ion generator present, the trend is reversed. At approximately 6 p.m., particle concentrations for particles of $< 0.1 \mu$ m began to rise. Then right after 11 p.m., near the start of the HVAC Off period, concentrations rose more sharply and continued to climb, not reaching steady-state by the time the HVAC system switched on at 9 a.m.

The majority of these particle increases are most likely due to SOA formation from ozone emitted by the ion generator reacting with d-limonene, since outdoor ozone concentrations approached zero during the HVAC Off period. The measured concentrations of d-limonene for (i) day-one of experiment 3-N1 was 49 ppb and (ii) day-one of experiment 3-I2 was 36 ppb. Since the air exchange rate was higher for 3-I2 than 3NI, the difference of 13 ppb is due to a combination of the loss mechanisms of ozone reactions and air exchange. Detectable SOA formation occurred while the HVAC system was off because the air exchange rate decreased from λ_{cycle} to λ_{off} , increasing the residence time of ozone, terpenes, and their reaction products (see below for more discussion of this). After the air exchange rate decreased, the SOA formation rate was high enough relative to the particle loss rate (removal by air exchange, deposition, and the ion generator) to cause an increase in particle concentrations.

Summary of all results

Figure 2 displays a summary of the effects of operating an ion generator in each room configuration. The solid lines separate the results into the four room configurations, and within those, the dashed lines separate the results into no operation (N) and opera-



Fig. 2 Summary particle, ozone, formaldehyde (HCHO), and nonanal concentrations in the four Room Configurations, for tests without (N) and with (IG) an operating ion generator. Absolute and percent differences are on the plot, and positive differences indicate the ion generator increased concentrations. For particles, absolute and percent differences are for ultrafine size range only

tion (IG) of an ion generator. Figure 2 shows the means for each room configuration $(\pm s.d.)$ for particle, ozone, formaldehyde, and nonanal room concentrations, for results during periods when the HVAC system was turned off. The ion generator had a negligible effect on concentrations of other sampled compounds. It is most appropriate to compare the effect of the ion generator while the HVAC was off as this coincided with the periods of lowest outdoor ozone concentrations, lowest air exchange rates, and least occupant activity in the home. For an operating HVAC system, accumulation of deposited materials and high mass transfer rates associated with these systems would likely lead to ozone reactions with HVAC system surfaces and associated byproduct formation. Displayed particle concentrations are the mean of all results from 4 to 6 a.m., which was chosen to be as near the end of the HVAC Off period as possible before particles associated with the morning rush hour may have influenced concentrations on some test days. Ozone concentrations are the mean of results with the HVAC system off, since ozone reached steadystate within about an hour of the change from λ_{cycle} to λ_{off} . Formaldehyde and nonanal concentrations are the integrated results from the sample times (1–3 a.m.) averaged across all measurements for a given room configuration.

The data presented in Figure 2 were refined as follows. For all pollutants, the second day of the 1-N1 experiment was discarded because the HVAC system was not shut off as intended. For particle samples, the first day of the 1-N2 experiment was discarded because a car was pulled into the attached garage right before the HVAC system was turned off, which coincided in time with a large increase of particles that persisted throughout the averaging time. To establish meaningful background concentrations with which to evaluate the ion generator effect on pollutant concentrations, Chauvenet's criterion (Holman and Gajda, 1989) was applied to each day of testing without the ion generator. Two outliers were discarded, one high unexplained particle concentration for the second day of the 2-N1 experiment and one low unexplained formaldehyde concentration for the first day of the 1-N1 experiment. Also listed on Figure 2 are absolute and % differences of the pollutants that are associated with operating the ion generator in RC 1-4, calculated with the mean concentrations as (ion generator-no ion generator) and (ion generator-no ion generator)/(no ion generator) \times 100, respectively. Positive differences indicate that the ion generator increased the concentration in that room configuration.

Generally, Figure 2 shows that particle number concentrations decreased with the operation of the ion generator in RC 1 and 2 but increased with the operation of the ion generator in RC 3 and 4. The majority of the particle number increase was in the ultrafine range, and the % increases on Figure 2 are for ultrafine particles only, providing evidence that ozone reactions were responsible for this rise. There was a decrease in d-limonene mean concentrations in RC 3 of 14 ppb and in RC 4 of 8 ppb, indicating that the particle number increases were likely SOA formed from ozone/d-limonene reactions. The particle formation due to the ion generator operation in RC 3 and 4, with the d-limonene source was larger in magnitude than its removal by the ion generator in RC 1 and 2. The summary results in Figure 2 show that particles larger than the ultrafine range are either decreased or unaffected by the use of the ion generator.

Since the ion generator emitted ozone at a rate of 3.3 ± 0.2 mg/h, it increased ozone concentrations in all room configurations. Ozone concentration increases were largest in RC 1, the second largest in RC 2, the third largest in RC 3, and were the smallest in RC 4. The successive decreases in the ozone concentration increases likely reflect the increasing reactivity of each

room configuration with ozone. With the sealed/ stained concrete flooring and no terpene source, RC 1 likely results in the fewest reactions of ozone with surfaces and gas-phase compounds. With the addition of the carpet in RC 2 the surface reactivity of the room with ozone increased (Cano-Ruiz et al., 1993; Morrison and Nazaroff, 2000), and the air freshener in RC 3 increased the gas-phase reactivity of the room with ozone (Singer et al., 2006). Finally, the combination of the carpet and air freshener in RC 4 likely yielded the most reactive room configuration, and the associated ozone concentration difference in RC 4 without and with the ion generator was small. The fact that the ozone concentration difference is smaller for RC 3 than RC 2 implies that the addition of the air freshener may have increased the reactivity of the room more than the addition of the carpet.

Concentrations of two aldehvdes, formaldehvde and nonanal, also increased due to the operation of the ion generator in every room configuration, and these aldehydes are products of reactions initiated by ozone (Reiss et al., 1995; Morrison and Nazaroff, 2002; Singer et al., 2006). Though we measured C_1 - C_4 and C₆-C₁₀ aldehydes, only formaldehyde and nonanal were affected by the use of the ion generator. In RC 1 and 2, most aldehyde increases are likely due to ozone interactions with surfaces in the room since there was not a source of gas-phase unsaturated organics in the room. In RC 3 and 4, however, ozone also likely reacted with emissions from the air freshener, leading to formaldehyde production as well (Singer et al., 2006). Nonanal production is associated with ozone reactions with interior residential surfaces such as carpets, walls, floors, and countertops (Morrison and Nazaroff, 2002; Wang and Morrison, 2006). The largest nonanal increase is in RC 1, even though it was expected that the addition of carpet would lead to higher nonanal concentrations. However, Wang and Morrison (2006) observed that some carpets do not produce secondary emissions of nonanal.

It is important to point out that in most cases formaldehyde and nonanal increases are within measurement uncertainty or may be influenced by factors outside of those considered in the experiment. Because our experiments were performed in a real indoor environment, the summary results shown in Figure 2 exhibit both the net effect of the ion generator in each room configuration and fluctuations in background conditions, which included fluctuations in background concentrations of all measured pollutants and air exchange rates. The exclusion of the one particle and one formaldehyde data point from the background results using Chauvenet's criterion was in an effort to deemphasize background fluctuations and/or experimental error. Air exchange rates are a function of both the house geometry and outdoor weather conditions, and measured λ_{off} were similar but fluctuated among

experiments over a range of 0.32-0.65/h. Fluctuations in the air exchange rate would affect pollutants with already high total loss rates (e.g. ozone, SOA) the least and those with low total loss rates (e.g. formaldehyde and nonanal) the most. We have not attempted to correct for variations in air exchange rates since the measured rates did not exactly coincide with averaging times. Also, since we are comparing a small number of 2-day tests, statistical significance tests are not meaningful and were not performed. However, in spite of any background concentration and air exchange rate fluctuations that may be represented in the data, the emergent trend is that the ion generator can increase concentrations of ozone and, to a lesser extent, formaldehyde and nonanal, as well as ultrafine particles if operated in the presence of a terpene source.

Discussion

Impact of the different flooring on ozone reactions

One goal of this research was to explore the impact of adding the carpet, an ozone sink. The addition of another ozone sink, the air freshener, increased gasphase reactions of ozone with d-limonene, which are apparent in the SOA formation in RC 3 and 4 vs. the lack of formation in RC 1 and 2. However, by varying the flooring surface in the room, we were also able to observe the impact of adding carpeting by comparing RC 1 and 2.

The ozone surface decay rates, β_{O3} (h⁻¹), for RC 1 and 2 were calculated. β_{O3} is defined as $v_d \cdot A/V$ (Sabersky et al., 1973; Weschler, 2000a,b), where v_d (m/h) is the ozone deposition velocity to all room surfaces, A (m²) is the total surface area of all room surfaces, and V (m³) is the room volume. There was a constant ozone emission source with the operating ion generator. When outdoor-to-indoor transport of ozone is negligible, β_{O3} can be determined with Equation 1, which assumes steady-state, well-mixed conditions, and that gas-phase ozone reactions are negligible:

$$\beta_{\rm O3} = \frac{E_{\rm O3}/V}{C_{\rm O3}} - \lambda_{\rm off} \tag{1}$$

where C_{O3} (mg/m³) is the mean ozone concentration in the room during 4–6 a.m. (when outdoor ozone was at its lowest concentration), and E_{O3} (mg/h) is the ozone emission rate of the ion generator (3.3 ± 0.2 mg/h). The ozone decay rates were calculated with the mean λ_{off} during tests in RC 1 and 2. Ozone decay rates were only calculated for RC 1 and 2 because Equation 1 neglects gas-phase reactions of ozone, and the air freshener in RC 3 and 4 renders this assumption invalid. The calculated ozone decay rates were $4.0 \pm 0.65/h$ for RC 1 and $5.3 \pm 0.48/h$ for RC 2, which are comparable to other reported ozone decay rates (Lee et al., 1999; Weschler, 2000a,b). The larger decay in RC 2 over RC 1 likely reflects increased ozone deposition to the added carpet. Please note that if there are pollutants present at concentrations leading to meaningful gas-phase reactions with ozone, β_{O3} actually includes their effects on ozone decay as well. However, this effect is likely to be minimal. For instance, d-limonene is very reactive with ozone and the highest average d-limonene concentration in RC 1 and 2 was 10 ppb, which is associated with an ozone decay rate of 0.18/h, or 4.5% of the calculated β_{O3} for RC 1.

Knowing the decay rates for RC 1 and 2 allows the estimation of their whole-room formaldehyde and nonanal yields. Thus, if β_{O3} includes decay due to d-limonene reactions, the formaldehyde yield will reflect that ozone loss as well, since ozone/d-limonene reactions yield formaldehyde (Grosjean et al., 1993). The molar yield, Y(-), is defined as the ratio of the molar increase in the aldehyde to the molar reduction of ozone and is represented by Equation 2, which makes the same assumptions as Equation 1:

$$Y = \frac{\lambda_{\rm off} \Delta C_{\rm aldehyde}}{\beta_{\rm O3} \Delta C_{\rm O3}} \tag{2}$$

where $\Delta C_{\text{aldehyde}}$ and ΔC_{O3} are the concentration differences (in ppb) of the aldehyde and ozone for that particular room configuration due to the use of the ion generator. For ΔC_{O3} , mean values between 1 and 3 a.m. were used, which coincides with the aldehyde sampling times. The whole-room yields for formaldehyde are 0.061 ± 0.25 for RC 1 and 0.12 ± 0.055 for RC 2, with the higher yield likely due to the presence of carpet. The whole-room yields for nonanal are 0.018 ± 0.0075 for RC 1 and 0.0091 ± 0.0087 for RC 2. We are not aware of any other whole-room yields in the literature.

Impact of air exchange rate

We also varied the air exchange rate in each room configuration. Assuming comparable outdoor concentrations of a pollutant, indoor emissions cause higher room concentrations as the air exchange rate decreases. Thus, after the change from the HVAC Cycle to the HVAC Off period, concentrations of ozone from the ion generator and d-limonene from the air freshener increase as the air exchange rate in the room decreases from λ_{cycle} to λ_{off} . SOA formation also increased with decreasing air exchange rate, which is consistent with the literature (Weschler and Shields, 2000, 2003). The resulting concentrations of d-limonene in the room and values of λ_{cycle} to λ_{off} provided an opportunity to see the importance of the air exchange rate on SOA formation. For a reaction to be important indoors, it must proceed at a fast enough rate to compete with air exchange loss (Weschler and Shields, 2000). For the reaction of d-limonene and ozone, the pseudo firstorder loss rate for ozone, k_p (h⁻¹), can be approximated as the product of the second order reaction rate constant of ozone and d-limonene (0.018 ppb/h) and the d-limonene concentration (ppb). When influential SOA formation occurred in our study, k_p during that time period should be greater than the associated air exchange rate.

Measured d-limonene concentrations for RC 3 and RC 4 during the HVAC Off period with the operating ion generator were 39 and 38 ppb, respectively. Concentrations during the HVAC Cycle period were not measured, but they were estimated for RC 3 and RC 4 as 18 and 17 ppb, respectively, with measured HVAC Off values (sampled from 1 to 3 a.m.) and associated HVAC Cycle air exchange rates and ozone concentrations. Using these concentrations, the pseudo firstorder loss rate for ozone in RC 3 for the HVAC Cycle period was $k_{p,cycle,RC3} = 0.32/h$ and for the HVAC Off period was $k_{p,off,RC3} = 0.70/h$. Pseudo first-order loss rates for ozone in RC 4 for the HVAC Cycle period was $k_{p,cycle,RC4} = 0.31/h$ and for the HVAC Off period was $k_{p,off,RC4} = 0.68/h$. For RC 3 and RC 4, $k_{p,cycle,RC3}$ and $k_{p,cycle,RC4}$ were less than the mean $\lambda_{\text{cycle}} = 1.3/\text{h}$, but $k_{\text{p,off,RC3}}$ and $k_{\text{p,off,RC4}}$ were greater than the mean $\lambda_{\text{off}} = 0.5/\text{h}$. Thus, it was not until the HVAC system was turned off and the mean room air exchange rate lowered from $\lambda_{\text{cycle}} = 1.3/\text{h}$ to $\lambda_{\rm off} = 0.5/h$ that the reaction loss rate could effectively compete with the air exchange loss rate. During the HVAC Off period, the SOA from this reaction was formed at a high enough rate relative to particle loss rates in the room to yield detectable particle concentration increases.

Impact of indoor temperature

The average room temperature approached 30°C at all conditions because of the heat from the instrumentation. However, typical room temperatures in the US are often between 18 to 27°C, depending on the season and thermostat operation. The total mass of SOA formed from ozone and d-limonene reactions increases as temperature decreases (Sarwar and Corsi, 2007; Leungsakul et al., 2005). Though the reaction rate of ozone and terpenes decreases as temperature diminishes, this decrease is surpassed by the increase in gas-to-particle partitioning that occurs as the vapor pressures of condensing products decrease. For reactions between ozone and d-limonene, Leungsakul et al. (2005) report that the mass of SOA formed changes at a rate of -0.016/°C, and Sarwar and Corsi (2007) report a rate of $-0.04/^{\circ}$ C. However, for gas-phase ozone reaction products, such as formaldehyde or nonanal, lowering the ambient temperature would likely decrease concentrations because of reduced homogeneous reaction rates. These effects indicate that our results may underestimate SOA formation and overestimate aldehyde byproducts when compared to a similar indoor environment at a lower temperature.

Impact of ion generators on indoor air quality

The ion generator used in this investigation increased concentrations of ultrafine particles, ozone, and, to a lesser extent, formaldehyde and nonanal. It also slightly decreased concentrations of fine particles. Portable ion generators are common in the US (Piazza et al., 2007; Shaughnessy and Sextro, 2006), and other brands and models may lead to different results. For instance, IG 2 in our previous work had a CADR $(\pm s.d.)$ of 35 (13) m³/h and an ozone emission rate of 4.3 ± 0.2 mg/h (Waring et al., 2008). The lower CADR and higher ozone emission rate would likely lead to increased concentrations of particles, ozone, formaldehvde, and nonanal over what we observed here. However, the electrostatic precipitator (ESP) in our previous work had a much higher CADR $(\pm s.d.)$ of 284 (62) m^3/h and a slightly higher ozone emission rate of 3.8 \pm 0.2 mg/h (Waring et al., 2008). Thus, the ESP would likely lead to decreased particle concentrations in all RC because the CADR is approximately an order of magnitude greater than the other loss mechanisms. The ESP would, however, still likely increase concentrations of ozone, formaldehyde, and nonanal. Also, our study was conducted in an unoccupied room, but ion generators are often used in occupied spaces. Ozone can react with human skin and hair, and produce considerable levels of acetone, nonanal, decanal, 6-MHO and 4-OPA (Wisthaler et al., 2005; Tamás et al., 2006; Weschler et al., 2007).

The pollutants increased by the ion generator have consequences for human exposure and health. An

outdoor ozone increase of 10 ppb in the previous week's ambient concentration has been associated with a 0.52% increase in mortality (Bell et al., 2004). Reaction products of ozone and d-limonene have been shown to increase respiratory burden in mice (Rohr et al., 2002). However, newer research has shown that not the SOA from ozone/terpene reactions but gasphase products, such as formaldehyde, more complex aldehydes, carboxylic acids, and free radicals, may be responsible for acute effects (Wolkoff et al., 2008). We know of no investigation into the chronic effects of SOA exposure. Formaldehyde is a human carcinogen, having been associated with nasopharyngeal cancer (Cogliano et al., 2005), and nonanal is an odorous and irritating compound (Morrison and Nazaroff, 2002). Thus, given the results in this investigation as well as previous research on ion generators (Alshawa et al., 2007: Waring et al., 2008), the operation of ion generators have the potential to degrade indoor air quality, and it may be prudent to limit their use indoors until evidence of safety can be ascertained.

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Waring & Siegel

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