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Ultrafine particle removal and generation by portable air cleaners

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Abstract

Portable air cleaners can both remove and generate pollutants indoors. To investigate these phenomena, we conducted a two-phase investigation in a 14.75 m^3 stainless steel chamber. In the first phase, particle size-resolved (12.6–514 nm diameter) clean air delivery rates (CADR) and efficiencies were determined, as were ozone emission rates, for two high-efficiency particle arresting (HEPA) filters, one electrostatic precipitator with a fan, and two ion generators without fans. The two HEPA air cleaners had count average CADR (standard deviation) of 188 (30) and 324 (44) $m^3 h^{-1}$; the electrostatic precipitator 284 (62) $m^3 h^{-1}$; and the two ion generators 41 (11) and 35 (13) $m^3 h^{-1}$. The electrostatic precipitator emitted ozone at a rate of $3.8 \pm 0.2\,mg\,h^{-1}$, and the two ion generators 3.3 ± 0.2 and $4.3 \pm 0.2\,mg\,h^{-1}$. Ozone initiates reactions with certain unsaturated organic compounds that produce ultrafine and fine particles, carbonyls, other oxidized products, and free radicals. During the second phase, five different ion generators were operated separately in the presence of a plug-in liquid or solid air freshener, representing a strong terpene source. For air exchange rates of between 0.49 and 0.96 h^{-1}, three ion generators acted as steady-state net particle generators in the entire measured range of 4.61–157 nm, and two generated particles in the range of approximately 10 to 39–55 nm. Terpene and aldehyde concentrations were also sampled for one ion generator, and concentrations of terpenes decreased and formaldehyde increased. Given these results, the pollutant removal benefits of ozone-generating air cleaners may be outweighed by the generation of indoor pollution.

Keywords: Indoor air quality; Portable ion generators; Secondary organic aerosol (SOA); Ozone reactions; Terpenes

1. Introduction

As more Americans realize the importance of indoor air quality, there is increased interest in air cleaning devices. Shaughnessy and Sextro (2006) report that 3 of 10 American households own one type of air cleaning device. The California Air Resources Board (2007) reports that 14% of California households own an air cleaner, and 10% own an air cleaner that produces ozone intentionally or as a byproduct. Common portable air cleaners designed to remove indoor airborne particles include: (1) high-efficiency particle arresting (HEPA) filters, which force air with a fan through filter media, and (2) ionizers, which charge incoming particles with a corona, removing them to

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oppositely charged collector plates and/or building surfaces. One type of ionizer, electrostatic precipitators (ESP), have a fan and collection plates, and tend to have higher flow rates than smaller ion generators, which often do not have a fan and may or may not have collection plates.

Researchers have developed performance metrics to uniformly evaluate portable air cleaners so that direct performance comparisons are possible. One such metric is the clean air delivery rate (CADR), which is the effective volumetric flow rate of clean (i.e., particle free) air delivered by the air cleaners. The CADR is a function of particle diameter, and it is the best available metric to compare portable air cleaners because it takes into account (and is the product of) the flow rate through the air cleaner and the particle removal efficiency (Shaughnessy et al., 1994; Offermann et al., 1985; Shaughnessy and Sextro, 2006). Additionally, the CADR is more independent of the testing environment than other metrics that have been used to evaluate air cleaners, such as the air cleaning factor (ACF) (e.g., Lee et al., 2004), which is dependent on the volume and air exchange rate of the experimental chamber. Typical measured CADRs for particles associated with environmental tobacco smoke (ETS) range from 277–407 $m^3 h^{-1}$ for HEPA air cleaners, 197–499 $m^3 h^{-1}$ for ESP, and 2–51 $m^3 h^{-1}$ for ion generators (Shaughnessy et al., 1994; Offermann et al., 1985). Most reported CADRs are not size-resolved and were determined with fine (100 nm–2.5 μm diameter) or larger particles, rather than the ultrafine (<100 nm) particle size range.

Size-resolved ultrafine particle removal by portable air cleaners is important to quantify because elevated exposure to ultrafine particles is associated with effects on human health, including cardiopulmonary diseases (Pekkanen et al., 2002). Further, indoor peak concentrations of ultrafine particles can be several times outdoor concentrations (Wallace, 2006), and the typical American spends 18 h indoors for every hour outdoors (Robinson and Nelson, 1995), so most exposure to ultrafine particles is likely indoors. Typical indoor sources of ultrafine particles are gas stoves (Wallace et al., 2004), vented gas clothes dryers (Wallace, 2005), electric ovens (Dennekamp et al., 2001), and candles (Wallace, 2000). Additionally, chemical reactions between ozone and unsaturated organic compounds, such as the terpenes d-limonene or α-pinene (both commonly found indoors), can result in significant formation of oxygenated gases (e.g., aldehydes) and secondary organic aerosol (SOA) in the ultrafine and fine range due to nucleation or partitioning of semi-volatile reaction products to smaller seed particles (e.g., Weschler and Shields, 1999). Studies on mice suggest that the health effects due to SOA may be different and more deleterious than those from primary aerosols (e.g., Rohr et al., 2002).

The potential to generate particles indoors due to reactions between ozone and terpenes is of particular concern with respect to ionizers because they influence indoor ozone concentrations. Measured ozone emission rates from portable ion generators range from 0.056–2.757 $mg h^{-1}$ (Niu et al., 2001), 0.95–13.42 $mg h^{-1}$ (Tung et al., 2005), 0.74–4.04 $mg h^{-1}$ (Mullen et al., 2005), and 0.16–2.2 $mg h^{-1}$ (Britigan et al., 2006). In typical indoor environments with a significant terpene source (such as an air freshener), an ozone emission rate of this magnitude might lead to increases in ultrafine and fine particles. It follows that if an ion generator had a low CADR for ultrafine and fine particles, it might operate as a net particle emission source, rather than a removal device, in certain size ranges. For instance, Alshawa et al. (2007) showed that injections of 15 and 45 mg of d-limonene into an office with an energized ion generator led to a transient elevation in ultrafine particle concentrations. It is clear that more research is necessary to understand the total impact of portable air cleaners on ultrafine and fine particle concentrations.

2. Methodology

A two-phase investigation was performed. During the first phase, five different portable air cleaners were characterized according to their power draw, airflow rate, particle size-resolved (12.6–514 nm diameter) CADR and single pass efficiency, and ozone emission rate. During the second phase, a set of screening experiments were conducted in which five portable ion generators were operated in the presence of a terpene source (either a plug-in or solid air freshener) to determine the impact of SOA formation on steady-state particle concentrations (in the range of 4.61–157 nm diameter). All tests were conducted in a 14.75 m^3 stainless steel chamber. Nylon sampling lines were installed approximately 1.5 m from the floor in the center of the chamber to measure particles and ozone. The 6 mm OD tube lengths were approximately 3.5 m for the particle measurements and 3 m for the ozone measurements. Three oscillating fans were operated in the chamber to ensure that the air was well-mixed. The chamber air exchange rate (h^{-1}) during all of the tests was measured by releasing approximately 3 L of CO_2 into the chamber and monitoring its continuous decay with a TSI model 8551 Q-Trak.

2.1. Phase 1: characterization of portable air cleaners

During the first phase, five different portable air cleaners were tested: two different HEPA air cleaners (HEPA 1 and 2), one ESP, and two different ion generators (IG 1 and 2). The ESP had collector plates, a high-flow fan, a pre-filter for removal of large diameter particles, and an activated carbon post-filter for removal of generated ozone. Neither IG 1 nor IG 2 used a fan, and IG 1 was a common tower model and IG 2 a common table-top model. The air cleaners were cleaned as per the manufacturers' instructions before all testing. The electrical power draw, airflow rate, particle size-resolved (12.6–514 nm diameter) CADR and single-pass removal efficiency, and ozone emission rate were determined for each air cleaner.

The electrical power drawn by the highest setting of each air cleaner was monitored with a Brand Custom Power Meter. The airflow rate through each of the air cleaners at their highest setting was determined by attaching to the inlet of the air cleaner an airtight capture hood that was also connected to an Energy Conservatory Duct Blaster calibrated fan (uncertainty 3% of volumetric flow). When the air cleaner was energized and the flow rate of the fan was such that the pressure difference was zero between the air inside and outside of the capture hood, the flow rate of the air cleaner equaled that of the fan (Offermann et al., 1985).

For the CADR tests, the chamber was operated so that the inlet air was as free of particles, ozone, and organic compounds as possible. To this end, all chamber openings were closed and/or taped and inlet air was filtered through HEPA and activated carbon filters. The inlet chamber fan also positively pressurized the chamber (at ~1 Pa pressure difference from the laboratory) and prevented unfiltered air from entering the chamber due to infiltration. Additionally, since the ozone emitted by the ionizers could react with any remaining terpenes in the chamber air to produce particles, 4 m^2 of activated carbon strips were hung on chamber surfaces during the CADR tests to remove the ozone emitted, thus removing this potential particle source from the CADR test environment.

Particles were generated in the chamber by burning three sticks of incense for approximately 15 min. Once the incense was extinguished, the size-resolved natural decay constant of particles, k_n (h^{-1}), due to air exchange and deposition on the chamber walls and activated carbon was measured using a TSI model 3936 scanning mobility particle sizer (SMPS) with a TSI model 3080 electrostatic classifier (EC) and a TSI model 3785 water-based condensation particle counter (WCPC). The SMPS was equipped with a TSI model 3081 long-differential mobility analyzer (long-DMA) and was set to measure particles in the range of 12.6–514 nm over 104 particle size bins, every 3 min. Then, three more sticks of incense were burned for 15 min, and the size-resolved particle decay was measured with the air cleaner energized at its highest setting, k_{ac} (h^{-1}). The size-resolved decay constants (k_n and k_{ac}) were calculated by fitting a linear regression line to the slope of $-\ln(C(t)/C_0)$, which is the negative of the natural log of the time-varying concentration ($C(t)$) normalized by the initial concentration at the time the incense was extinguished (C_0), versus time (h). The particle size-resolved CADR ($m^3\,h^{-1}$) was calculated by applying a mass balance to the chamber and subtracting the background decay of particles from the decay when the air cleaner was energized: $\text{CADR} = V(k_{ac}-k_n)$ where V is the volume of the chamber (m^3) (Shaughnessy et al., 1994). It should be noted that this equation may not be valid for air cleaners that generate ozone, because of the potential source term associated with SOA formation. Thus, the use of activated carbon strips or other removal of ozone and unsaturated compounds are required to use this expression for calculating the CADR of an ozone-generating air cleaner.

The CADR for each of the 104 size bins was based on the maximum number of data points to calculate the decay slopes without (k_n) and with (k_{ac}) the air cleaner in operation for which the R^2 value for that decay slope remained above 0.975, with a minimum of four data points (12 min of decay). In addition, calculated CADR values were discarded if they did not meet the following quality control criteria: (1) the first data points during the natural and air cleaner decay periods both had a number concentration of at least 100 cm^{-3}, and the first four data points during each of the two decay periods were (2) non-zero and (3) decreasing in number as time increased. These quality control criteria were necessary because the incense burning did not always generate enough particles in a particular size bin to yield meaningful results. The CADR uncertainty was calculated as the quadratic sum of the standard error of each decay slope. The ESP was tested twice and IG 1 three times, and their CADRs are the averages of those single-test CADRs that met the three criteria.

The CADR equals the product of the flow rate through the air cleaner and the single-pass removal efficiency. The size-resolved single pass removal efficiency, η (–), for each air cleaner was calculated as the ratio of CADR to air flow rate.

To measure the ozone emission rates for each of the air cleaners, all ozone from the incoming air into the chamber was removed with an activated carbon filter, and the ozone concentrations inside the chamber were measured every minute with a calibrated 2B Technologies model 205 dual beam ozone monitor (± 1 ppb or 2%). The air cleaner was placed in the chamber and energized, and the increase in chamber ozone concentrations over time was measured. Once a steady state was reached for 10 min, the air cleaner was switched off, and the ozone decay with time was measured. Then a mass balance was used to determine the ozone emission rate for each air cleaner, using the decay period to determine the deposition loss of ozone to the chamber surfaces, following the work of Niu et al. (2001). To avoid artificially inflating both the loss rate during the decay period and thus the ozone emission rate for the ESP, the activated carbon filter on the outlet of the ESP was removed during the decay period.

2.2. *Phase 2: ion generators in the presence of a terpene source*

During the second phase, five different tower-variety ion generators from two popular manufacturers were tested in the chamber. Three units of different models of one brand were tested: IG 1, 3, and 4. Two units of the same model of a different brand were also tested: IG 5A and 5B. IG 4 was operated with a UV lamp intended to neutralize bioaerosols. All five ion generators were brand new units and were cleaned according to the instructions of the manufacturer before testing. Screening chamber experiments were performed to determine the change in steady-state particle concentrations (4.61–157 nm diameter) resulting from the operation of an ion generator in an environment with high terpene concentrations (due to a plug-in or liquid air freshener).

The chamber was cleaned with tap water (i.e., no terpene containing cleanser) and allowed to dry overnight initially before testing and once again halfway through testing. It was treated to remove ozone reaction sites by operating two ion generators in it overnight before each test. Each test took place over an approximate 1-day period. During each test, continuous measurements of ozone and particle concentrations of the air in the chamber were taken. The ozone concentrations were measured every minute with a calibrated UV absorbance ozone analyzer (2B Technologies model 205). The particle concentrations were measured with the same SMPS used in the first-phase. However, during the second phase it was equipped with a TSI model 3085 nano-differential mobility analyzer (nano-DMA) and configured to measure particles in the diameter range of 4.61–157 nm over 99 particle size bins, with a scan-time of 3 min for all tests except IG 5B, which had a scan-time of 5 min.

The test for IG 1 had four distinct periods of testing: the Background (BG) period, the Air Cleaner (AC) only period, the Air Cleaner/Air Freshener (AC/AF) period, and the Air Freshener (AF) only period. The tests for IG 3, 4, 5A, and 5B did not include the AF period as no particle formation was seen during this phase. During the BG period, the ion generator was not energized and there was no terpene source. During the AC period, the ion generator was energized but there was also no terpene source. During the AC/AF period, the ion generator was energized and a new plug-in air freshener for IG 1 or solid air freshener for IG 3, 4, 5A, and 5B was located approximately 1.5 m from the floor in the center of the chamber. The plug-in air freshener was “Hawaiian” scented and emitted a total mass of 1.5 g day^{-1}, and the solid air fresheners were made to be hung (e.g., in an automobile) and were “country fresh” and “pine” scented. During the AF period, the ion generator was not energized and the air freshener was in the chamber. Each period of the test was conducted for at least 4 h to ensure that a steady-state condition was obtained. Additionally, for the IG 1 test, the chamber was operated under the positively pressurized conditions described above for the CADR and ozone emission tests.

For each of the five tests, the resulting steady-state particle concentrations during each period were compared. The steady-state concentrations were calculated as the mean concentrations for the last 20 scans (1 h) during each of the test periods for all but IG 5B, for which the last 12 scans were used. Due to the small sample size and non-equal variance, a modified *t*-test (Hines and Montgomery, 1990) was used to evaluate if there were statistically significant changes ($\alpha < 0.05$) in steady-state concentrations among the different periods.

Additionally, for the IG 1 experiment, terpene and light aldehyde samples were taken during the last hour of the steady-state periods. Terpenes were sampled onto two Atas glass focus liners packed with Tenax-GR 60/80 mesh sorbent connected in series, at flow rates of between 21.9 and 23.1 $\mathrm{cm^3\,min^{-1}}$ for between 33 and 43 min. The terpenes were analyzed by thermal desorption, gas chromatography, with mass spectrometry (HP5890 GC equipped with Atas Optic 2 thermal desorber and HP5971A mass selective detector), for a total run time of 21 min. The focus liners were thermally desorbed by ramping at 10 $^\circ\mathrm{C\,s^{-1}}$ from an initial temperature of 45 °C up to a holding temperature of 280 °C. The split ratio for the thermal desorber was 10:1, and a sample transfer pressure of 15 psi was held for 3 min before dropping to 7 psi and linearly increasing to 25 psi over the remainder of the run time. A Restek Rtx 5SilMS capillary column was used (30 m length, 0.25 mm internal diameter, 0.5 μm film thickness). The GC oven was held at the initial temperature of 40 °C for 2.5 min, after which it was ramped at 10 $^\circ\mathrm{C\,min^{-1}}$ up to 150 °C and then 25 $^\circ\mathrm{C\,min^{-1}}$ from 150 to 310 °C, at which it was held for 1.1 min until the end of the run time. The terpenes were quantified with an internal standard of 1-bromo-4-fluorobenzene. The measurement uncertainty was calculated as the percentage ratio of one standard deviation over the mean of the internal standard variation and was 12%. The light aldehydes were sampled onto dinitrophenylhydrazone (DNPH)-coated silica cartridges preceded by a KI ozone scrubber, at flow rates of between 488 and 503 $\mathrm{cm^3\,min^{-1}}$ for between 60 and 65 min. Batches of DNPH-coated cartridges were prepared based on EPA method TO-11A (U.S. Environmental Protection Agency, 1999). Analytes were identified and quantified using DNPH standards.

3. Results and discussion

3.1. Phase 1: characterization of portable air cleaners

The electrical power draw (W), air flow rates ($\mathrm{m^3\,h^{-1}}$), and a summary of CADR ($\mathrm{m^3\,h^{-1}}$) for the five portable air cleaners tested during the first experimental phase are listed in Table 1. The flow rate for IG 2 was not determined because it was below the detection limit of the Duct Blaster calibrated fan (30 $\mathrm{m^3\,h^{-1}}$). The ESP had the highest tested flow rate of 850 $\mathrm{m^3\,h^{-1}}$, and IG 1 the lowest measurable value of 51 $\mathrm{m^3\,h^{-1}}$. The ESP and HEPA 1 and 2 each had flow rates an order of magnitude higher than IG 1, which is expected since they all employ a fan to move air through the unit. These electrical power draw and air flow results are on the same order as others reported in the literature for similar portable air cleaners (Shaughnessy et al., 1994; Offermann et al., 1985; Mullen et al., 2005).

The reported CADRs, including the minimum, maximum, count average (standard deviation), and median values, are summarized in Table 1. Reported CADRs for the particle diameter range of 12.6–514 nm are displayed in Fig. 1. Both axes of Fig. 1 are plotted on a logarithmic scale, and the

Table 1
Electrical power draw, air flow rates, and summary of size-resolved (12.6–514 nm diameter) reported particle number CADR values

Air cleaner	Electrical power draw (W)	Air flow rate ($\mathrm{m^3\,h^{-1}}$)	Summary of CADR ($\mathrm{m^3\,h^{-1}}$)				
			Min	Max	Mean (s.d.)	Median	*N*
ESP	102.2	850 ± 26	112	455	284 (62)	283	83
HEPA 1	205.6	309 ± 9.3	92	259	188 (30)	188	76
HEPA 2	102.6	571 ± 17	203	481	324 (44)	340	75
IG 1	8.4	51 ± 1.5	16	76	41 (11)	39	85
IG 2	4.9	< 30	17	74	35 (13)	31	71

N is the number of 104 size bins that met the three CADR reporting criteria described in Section 2.

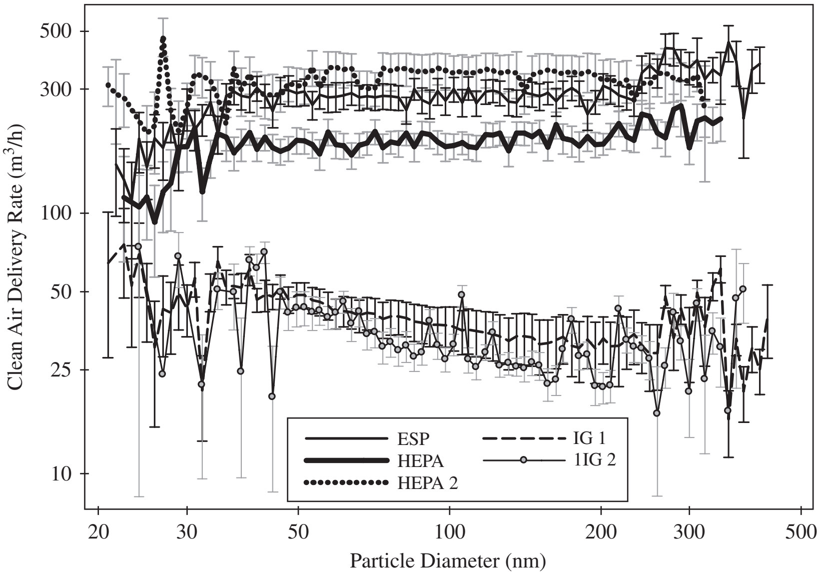

Fig. 1. CADR as a function of particle diameter.

whiskers represent the calculated uncertainty of the CADR for each size bin.

The ESP or HEPA 2 had the highest CADR, depending on the particle size. Overall, HEPA 2 exhibited the largest count average CADR (± 1 standard deviation) of 324 (44) $\mathrm{m^3\,h^{-1}}$. The ESP followed with a count average CADR of 284 (62) $\mathrm{m^3\,h^{-1}}$, and the ESP also exhibited the largest range of CADR from 112 $\mathrm{m^3\,h^{-1}}$ for 23.3 nm particles to 455 $\mathrm{m^3\,h^{-1}}$ for 359 nm particles. HEPA 1 had higher CADR than both IG 1 and 2, and it exhibited a count average CADR of 188 (30) $\mathrm{m^3\,h^{-1}}$, which is approximately 100–150 $\mathrm{m^3\,h^{-1}}$ lower than both the ESP and HEPA 2, commensurate with its lower flow rate than the ESP and HEPA 2. IG 1 and 2 both generally had a CADR an order of magnitude lower than the other tested air cleaners, and IG 1 had a count average CADR of 41 (11) $\mathrm{m^3\,h^{-1}}$ and IG 2 had 35 (13) $\mathrm{m^3\,h^{-1}}$.

The single-pass efficiency, η (–), of the air cleaners is plotted in Fig. 2. These efficiency curves are the efficiencies of the air cleaners, not the filtration media. The HEPA air cleaners and ESP each have efficiencies of approximately <0.6 (60%) for particle sizes of <200 nm and start to increase slightly above 200 nm. These low efficiencies are perhaps unexpected for the HEPA air cleaners, which have filter efficiencies of at least 99.97% for all particle sizes. This reduced air cleaner efficiency is likely due to bypass of air around the filter media or the unit itself. It could also be due to short-circuiting of air flow in the chamber (i.e., it is not well-mixed), but we attempted to reduce this effect by operating three fans on their highest setting in the chamber. IG 1 exhibited efficiencies of greater than one for some particle sizes, potentially because ions emitted into the space can lead to particle reductions greater than the air flow capacity of the device. However, the CADRs, one of two

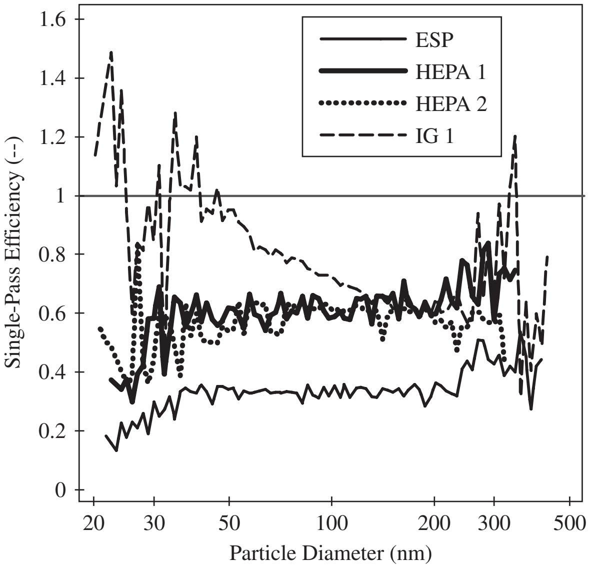

Fig. 2. Air cleaner efficiency, η (–), as a function of particle diameter. Efficiency for IG 2 was not determined because its flow rate was below detectable limit (30 $\mathrm{m^3\,h^{-1}}$).

components in the efficiency calculation, have large uncertainty in the upper and particularly lower size bins of the measured range (Fig. 1). The efficiency for IG 2 was not determined since its flow rate could not be measured.

The influence of a particular air cleaner on particle concentrations in a given space may be quantified by the air cleaner effectiveness. Miller-Leiden et al. (1996) defined the air cleaner effectiveness, H (–), as one minus the ratio of the indoor particle concentration with an operating air cleaner (C_{AC}) to the indoor concentration with no air cleaner operating ($C_{\mathrm{No\ AC}}$), as

$$H = 1 - \frac{C_{\mathrm{AC}}}{C_{\mathrm{No\ AC}}} = 1 - \frac{\lambda + \beta_{\mathrm{P}}}{\lambda + \beta_{\mathrm{P}} + \mathrm{CADR}/V} \qquad (1)$$

where λ is the air exchange rate of the space (h^{-1}), and β_{P} is the size-resolved particle deposition loss rate (h^{-1}). The air cleaner effectiveness is bounded by zero and one, with zero indicating a completely ineffective air cleaner (0% of the particles are removed) and one indicating a perfectly effective air cleaner (100% of the particles are removed). The air cleaner effectiveness assumes steady-state and a well-mixed space, neglects removal by the HVAC system, is independent of indoor sources (so long as they are the same for both C_{AC} and $C_{\mathrm{No\ AC}}$), and is highly dependent on the volume of the space. For Eq. (1), we assumed an air exchange rate of $0.5\,\mathrm{h}^{-1}$, which is the median air exchange rate of 2844 residences reported in Murray and Burmaster (1995), and used the predicted fit to experimental values for β_{P} as summarized by Riley et al. (2002). Fig. 3 displays the air cleaner effectiveness of each of the five tested air cleaners as a function of particle diameter, for a typical (a) $50\,\mathrm{m}^3$ room and (b) $392\,\mathrm{m}^3$ residential house. The room volume of $50\,\mathrm{m}^3$ was assumed, and the residential house volume of $392\,\mathrm{m}^3$ is the median floor area from the U.S. Bureau of the Census (2005) of $163.3\,\mathrm{m}^2$ multiplied by an assumed ceiling height of 2.4 m.

The HEPA air cleaners and the ESP are more effective at removing particles in the tested range than either IG 1 or 2, as indicated in Fig. 3. In the typical $50\,\mathrm{m}^3$ room, the HEPA air cleaners and the ESP remove approximately 80–90% of particles with diameters above 50 nm. The IG 1 and 2 only remove 40–60% of the same size particles. In the $392\,\mathrm{m}^3$ residential home, the HEPA air cleaners and the ESP remove approximately 40–60% of particles with diameters above 50 nm. However, the IG 1 and 2 have little effect on particle concentrations in the median-sized home, removing only 10–20% of particles in the same size range.

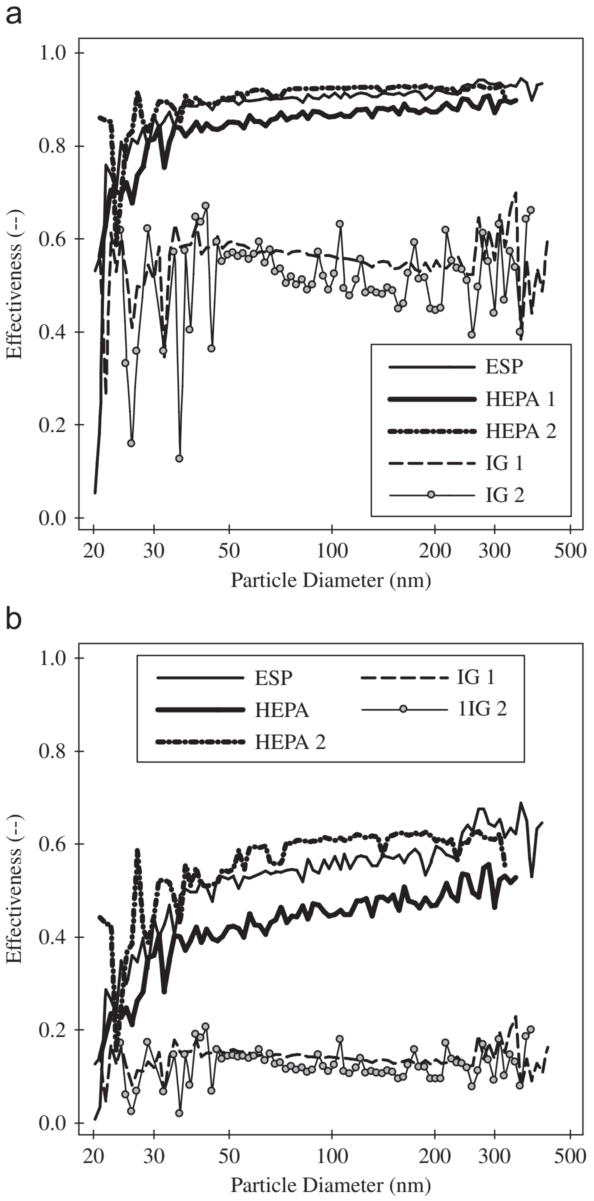

Fig. 3. Air cleaner effectiveness, H (–), as a function of particle diameter for a hypothetical: (a) $50\,\mathrm{m}^3$ room and (b) $392\,\mathrm{m}^3$ residential building.

Results from the ozone emission tests for the three portable air cleaners found to emit ozone, the ESP and IG 1 and 2, are listed in Table 2. The ozone emission rates ranged from 3.3 to $4.3\,\mathrm{mg\,h}^{-1}$. This range is comparable to the emission rates reported by Niu et al. (2001) and Tung et al. (2005) for portable ionizers. Overall, no clear relationship between CADR and ozone emission was observed,

Table 2
Ozone emission rates for ionizers tested in the first phase, as well as predicted ozone concentration increases, C^*, and equivalent outdoor ozone increases, ΔC_{out}, for a hypothetical residential 50 m^3 room and 392 m^3 home

Air cleaner	Ozone emission rate (mg h^{-1})	$V = 50\,\text{m}^3$		$V = 392\,\text{m}^3$	
		C^* (ppb)	ΔC_{out} (ppb)	C^* (ppb)	ΔC_{out} (ppb)
ESP	3.8±0.2	8.6	77	1.1	9.9
IG 1	3.3±0.2	7.5	67	1.0	8.6
IG 2	4.3±0.2	9.7	88	1.2	11

as IG 2 emitted the most ozone but had the lowest CADR, and the ESP emitted nearly the same amount and had the highest CADR. However, the ESP also utilized an activated carbon filter, which removed some of the ozone it generated.

One way to quantify the impact of these ozone emissions, E, on the previously discussed hypothetical spaces with volumes, V, of 50 and 392 m^3, respectively, is with the predicted indoor ozone concentration increase due to the device, C^* (ppb), as

$$C^* = \frac{E/V}{\lambda + \beta_{O_3}} \tag{2}$$

where the air exchange rate, λ, was again assumed as 0.5 h^{-1} (Murray and Burmaster, 1995), and the ozone deposition loss rate, β_{O_3}, was assumed as 4.0 h^{-1}, which is an experimentally determined value for offices and bedrooms (Weschler, 2000). The indoor ozone concentration increases for each volume are also listed in Table 2. These predicted increases are significant, particularly for the smaller room, given that a recent epidemiological study found that a 10 ppb increase in the outdoor ozone concentration of the previous week was associated with a 0.52% increase in daily mortality (Bell et al., 2004). Moreover, 89% of the ozone removal ($\lambda + \beta_{O_3}$) is due to surface reactions (β_{O_3}), which may yield byproducts more harmful than the ozone itself (Weschler, 2004).

The equivalent outdoor ozone concentration increase, ΔC_{out} (ppb), is the amount the outdoor concentration of ozone would need to increase to equal the predicted indoor ozone concentration increase due to the ozone emitting device, as

$$\Delta C_{\text{out}} = \frac{E/V}{p\lambda} \tag{3}$$

where p, the ozone penetration factor (dimensionless), was assumed as unity due to the lack of values for this parameter in the literature. The equivalent outdoor ozone increases for the two hypothetical spaces are also listed in Table 2. Caution must be used in interpreting C^* and ΔC_{out} for the 50 m^3 volume, since a volume of this size would likely be connected to other parts of the building.

3.2. Phase 2: ion generators in the presence of a terpene source

A summary of chamber conditions and results from the second phase are listed in Table 3. The air exchange rates were 0.49–0.96 h^{-1}. The mean steady-state ozone concentration for IG 1 during the BG period of 0.1 ppb is near zero since ozone was intentionally removed from the chamber supply air by activated carbon. The five energized ion generators during the AC period elevated the ozone concentrations significantly ($\alpha < 0.05$) over the corresponding BG period concentration. The reactions between the ozone and the terpenes during the AC/AF period each resulted in a significant ($\alpha < 0.05$) reduction from the corresponding AC period ozone concentration. During the AF period for IG 1, the ozone-emitting ion generator was not energized, so the chamber returned to a low ozone concentration. The concentration during the AF period did not return completely to the BG period concentration likely due to interference between compounds emitted by the air freshener and the ozone monitor. Because of this effect, there is likely a small bias in the AC/AF period ozone concentration results as well.

The resulting particle total (4.61–157 nm diameter) number concentrations measured during the steady-state periods for all five ion generator tests are listed in Table 3. For every test but IG 1, the steady-state particle concentrations were higher during the BG period than the AC period when the ion generator was energized. Steady-state particle concentrations during the AC/AF period were much higher than either the BG or AC period for

Table 3
Summary of chamber (volume = 14.75 m^3) air exchange rates (λ), mean ($\pm$1 standard deviation) temperature and relative humidity (RH) over all periods, as well as steady-state ozone and total (measured range of 4.61–157 nm diameter) particle number concentrations

Air cleaner	λ (h^{-1})	Temp. (s.d.) (°C)	RH (s.d.) (%)	Ozone (O_3) and total particle (PM) steady-state concentrations					Size range with net formation (nm)
					BG	AC	AC/AF	AF	
IG 1 *Liquid plug-in, "Hawaiian" scent*	0.87	25.9 (0.5)	46.4 (1.7)	O_3 (ppb) PM (cm^{-3})	0.1[a] 114.5	92.3 145.4	16.6 1135	4.8 140.4	21.7–157
IG 3[b] *Solid hanging, "pine" scent*	0.91	26.2 (0.2)	54.3 (1.5)	O_3 (ppb) PM (cm^{-3})	22.7 213.0	46.2 136.7	9.9 2545	n/a n/a	4.6–157
IG 4 *Solid hanging, "country fresh" scent*	0.96	27.3 (0.3)	52.1 (1.3)	O_3 (ppb) PM (cm^{-3})	10.5 305.2	44.8 130.5	11.7 650.3	n/a n/a	20.9–157
IG 5A *Solid hanging, "pine" scent*	0.54	26.9 (2.6)	49.1 (1.6)	O_3 (ppb) PM (cm^{-3})	10.7 501.8	117.7 152.3	19.2 1569	n/a n/a	9.5–55.2
IG 5B[a] *Solid hanging, "pine" scent*	0.49	27.0 (0.40)	47.1 (2.0)	O_3 (ppb) PM (cm^{-3})	10.0 250.8	115.7 200.1	18.2 886.6	n/a n/a	9.47–38.5

BG is Background period, AC is Air Cleaner only period, AC/AF is Air Cleaner/Air Freshener period, AF is Air Freshener only period."Size range with net formation" is the range of particles over which there was a statistically significant ($\alpha < 0.05$) increase in concentrations of AC/AF period over BG period.

[a] Ozone monitor uncertainty was the greater of 1 ppb or 2%.

[b] Temperature and RH were measured during BG period only.

all five ion generators, higher than the BG period by a factor of 2–12 and the AC period by a factor of 4–19. For IG 1, the steady-state particle concentration during the AF period was much lower than the AC/AF period by a factor of eight and on the same order as those during the BG and AC periods. Thus, our screening experiments demonstrate a *net increase* in steady-state particle concentrations due to the use of an ion generator in the presence of a terpene source.

Additionally, the particle size range with net formation, which is the range of measured particle size bins for which there was a statistically significant ($\alpha < 0.05$) increase in the particle number concentration of the AC/AF period over the BG period, is presented in Table 3. IG 1, 3, and 4 showed significant increases in nearly the entire range of investigated particles, and IG 5A and 5B showed significant increases in the range of approximately 10 nm to between 39 and 55 nm.

The steady-state particle number concentrations as a function of particle diameter during the BG, AC, AC/AF, and AF periods for the IG 1 test are displayed in Fig. 4a. Results for IG 3 and 4 exhibit similar trends, but results for IG 5A and 5B display elevated concentrations during the AC/AF period for the narrower particle size range.

The change in concentrations for five particle size bins as a function of time is displayed in Fig. 4b. After the air freshener was introduced to the chamber (the vertical line on the plot), the particle concentrations initially increased sharply and then declined to their steady-state values. Similar growth patterns were also seen for the other experiments, as well as those of other researchers (e.g., Weschler and Shields, 1999). The final steady-state concentrations are controlled principally by the competition between the source of particles due to ozone/terpene reactions and the loss of particles due to removal by the ion generator and air exchange.

The resulting steady-state concentrations of terpenes and light aldehydes during the steady-state periods for the IG 1 test are listed in Table 4. The d-limonene measured during the BG period was likely reduced to below the detection limit during the AC period because it reacted with the ozone emitted by IG 1. This SOA forming reaction may be why for IG 1 the total number of particles for the AC period was elevated over the BG period (see Table 3). The chief terpene emitted by the plug-in liquid air freshener was also d-limonene, and its concentration was elevated during the AC/AF period and then further increased during the AF period. β-Myrcene was also emitted by the air

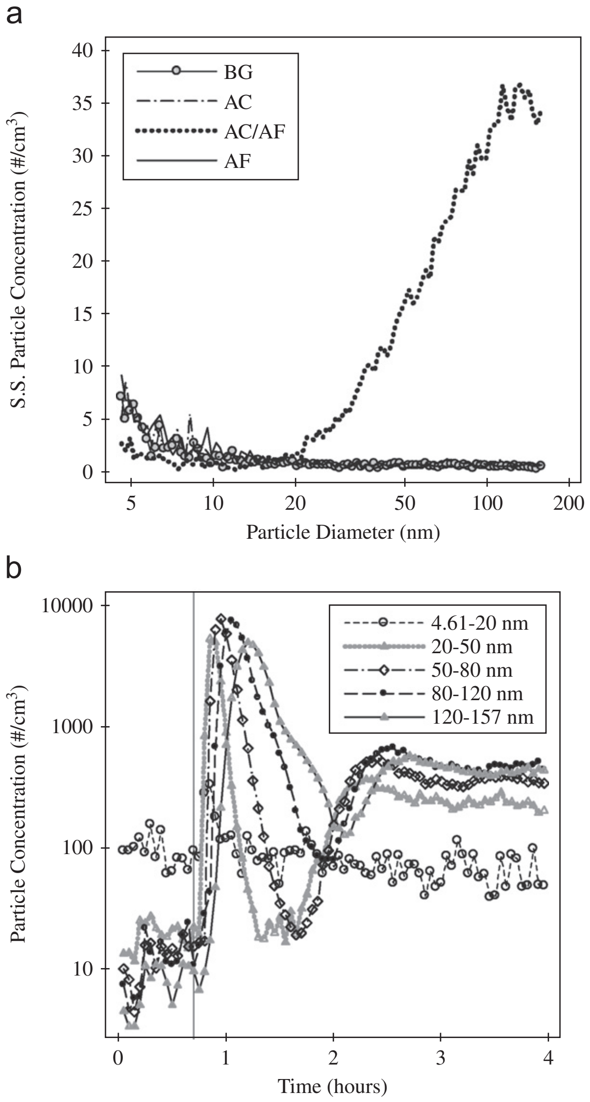

Fig. 4. For IG 1 during second phase: (a) steady-state particle concentrations as a function of particle diameter (*x*-axis on a log-scale), and (b) particle concentrations as a function of time (*y*-axis on a log-scale) after plug-in liquid air freshener was energized (represented by vertical line on plot). BG is Background period, AC is Air Cleaner only period, AC/AF is Air Cleaner/Air Freshener period, AF is Air Freshener only period.

freshener, though at a much lower rate, and this terpene was only detectable during the AF period. The ozone/d-limonene reaction is likely primarily responsible for particle formation observed during the IG 1 test. d-Limonene is a common terpene found indoors (Brown et al., 1994), is a citrus scent in commercial products and an active ingredient in some organic solvents, and readily reacts with ozone to yield particles (Weschler and Shields, 1999).

Table 4
Steady-state light aldehyde and terpene concentrations during the IG 1 test

Compound	Steady-state concentrations (μg m^{-3})			
	BG	AC	AC/AF	AF
Terpenes				
d-Limonene	1.4±0.2	b.d	81.9±9.8	94.6±11.4
β-Myrcene	b.d.	b.d	b.d.	2.7±0.3
Light aldehydes				
Formaldehyde	17.6±2.8	19.3±2.8	49.3±3.9	45.9±2.7
Acetaldehyde	14.4±0.5	22.4±0.4	14.6±0.4	9.4±0.5

BG is Background period, AC is Air Cleaner only period, AC/AF is Air Cleaner/Air Freshener period, AF is Air Freshener only period.
b.d. represents below the detectable limit of the GC/MS.

Without the air freshener, the use of the ion generator increased the formaldehyde concentration during the AC period. In the presence of the air freshener, the use of the ion generator during the AC/AF period increased formaldehyde concentrations slightly over that during the AF period. The high formaldehyde concentration observed during the AF period could be the result of ozone or formaldehyde diffusion into the liquid air freshener during the AC/AF period. No clear trend was observed for acetaldehyde, as observed by others conducting research on the products of ozone and air fresheners (Singer et al., 2006).

One limitation regarding the second phase screening experiments is that the application of these results to real indoor environments is dependent on there being similar ozone and terpene concentrations, which might differ for the following reasons. Indoor volumes are typically larger, diluting the influence of the ozone and terpene emissions. There is a much larger surface-to-volume ratio (S/V) indoors than in the chamber, and the multitude of indoor surfaces, including carpeting and other furnishings, compete with terpenes as ozone reaction sites (e.g., Weschler et al., 1992). Additionally, there may be indoor particle sources that compete in magnitude with the secondary emissions due to the use of an ion generator, diminishing the effect of the SOA formation. Large indoor sources of formaldehyde might have the same effect. Additional tests are being conducted in real indoor settings to address these concerns. However, these results do demonstrate that ozone-emitting ion generators can generate ultrafine and fine particles, as well as gas-phase byproducts, when operated in the presence of a terpene source.

4. Conclusions

A two-phase investigation was performed to assess the magnitude of indoor pollutant removal and generation due to the use of a portable air cleaner. The tested HEPA filters and ESP remove particles much more effectively than the ion generators. For the measured particle diameter range of 12.6–514 nm, the two HEPA air cleaners had count average CADR (standard deviation) of 188 (30) and 324 (44) $m^3 h^{-1}$; the electrostatic precipitator 284 (62) $m^3 h^{-1}$; and the two ion generators 41 (11) and 35 (13) $m^3 h^{-1}$. The three tested ionizers, the ESP and the two ion generators, emitted ozone at rates of 3.3–4.3 $mg h^{-1}$.

Ozone emitted by ion generators can react with terpenes to produce secondary organic aerosol (SOA) in the ultrafine and fine size ranges. The five tested ion generators acted as *steady-state net particle generators* under the experimental conditions in the test chamber. The measured range of particle diameters was 4.61–157 nm, and three of the five ion generators acted as steady-state net particle generators in nearly the entire measured range, and two ion generators in the range of approximately 10 to 39–55 nm. The benefits of using an ozone-emitting ion generator indoors may be outweighed by its particle, ozone, and aldehyde generation.

In summary, this investigation suggests caution in the use of ozone-emitting ion generators in indoor environments. Furthermore, technologies do exist, such as the portable HEPA filters tested here, that are effective at particle removal and do not generate ozone or other harmful byproducts.

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