

Ultra-fine and fine particle formation in a naturally ventilated office as a result of reactions between ozone and scented products

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ABSTRACT

Ultra-fine and fine particle formation as a result of chemical reactions between ozone and four different air fresheners and a typical lemon-scented domestic cleaner was studied in a fully furnished, naturally ventilated office. The study showed that under conditions representative of those occurring in such offices, air fresheners or scented cleaners may react with ozone to form secondary organic aerosols (SOA). The tested air fresheners were relatively small sources of SOA with detectable increases occurring only in the ultra-fine particle number concentration. With the cleaner, also an increase in particle mass was observed.

INDEX TERMS

Secondary organic aerosols; Air freshener; Cleaner; Terpenes

INTRODUCTION

Secondary organic aerosols (SOAs) derived from reactions between ozone and terpenes may contribute to irritation and symptoms among building occupants. Terpenes are common as odorants in cleaning agents and air fresheners, and in particular the lemon (limonene) and pinene (pinene) scents are common constituents of these products. Primarily, ozone travels from outdoors with the ventilation air, but it may also be produced indoors by electrical appliances such as photocopiers, laser printers, electrostatic air filters or commercially available ozone generators. The products of ozone/terpene reactions include low-volatility compounds that contribute to SOA formation (Weschler and Shields, 1999). Though a number of studies report on SOA formation when ozone and terpenes simultaneously are present in indoor air, these studies often have been conducted with very high ozone concentrations (>100 ppb) or with dosing of individual chemicals or mixtures of chemicals. In the current study, SOA formation as a result of chemical reactions between ozone and four different scented air fresheners as well as a typical lemon-scented domestic cleaner was studied in a naturally ventilated office under conditions that reflect standard practice.

METHODS

Experiments were performed in a fully furnished, but unoccupied, naturally ventilated office located at the Technical University of Denmark ($L \times W \times H = 4.4 \times 2.8 \times 3.0$ m³). To minimize the variability of the air exchange rate between experiments, the office window and door were kept closed during all experiments, and as a consequence the air exchange rate was rather low. The office had linoleum floor covering, painted brick walls and a suspended ceiling consisting of acoustic tiles. No renovation of the office had taken place within a period of 5 years prior to this study. General cleaning of the building includes weekly mopping of the floors. During the period when the current experiments were conducted, no mopping of the office floor took place.

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SOA formation was measured under four conditions:

1. No ozone generated or air freshener/cleaner emitted in the office. These measurements were done prior to each experiment and served as the reference condition.
2. Generation of ozone at a constant rate to yield a concentration of ~ 30 ppb; no dosing of scented products.
3. Dosing of scented products; no ozone generation.
4. Simultaneous generation of ozone at a constant rate (~ 30 ppb) and dosing of scented products.

The manufacturer characterized air freshener #1 as the smell of jasmine, geranium and rose with hints of mystical spices and rich amber woods. The remaining air fresheners were characterized by the authors as: #2 spicy with a hint of citrus; #3 spicy, sweet smell; #4 sharp, chemical smell (like glue or acetone). A commercial heated dispenser, sold for this purpose, was used to dose the four liquid air fresheners. The dispenser was adjusted to maximize the output. The cleaner was used as described on the label and the whole floor area was washed. Ozone was generated by passing air over an ultraviolet source; the generation rate was varied by changing the UV flux.

The concentration of ultra-fine particles in the size range $0.02\text{--}1\text{ }\mu\text{m}$ was monitored by an optical particle counter (P-Trak, TSI model 8525). An eight channel optical particle counter measured fine particles in eight size ranges $0.1\text{--}0.2$, $0.2\text{--}0.3$, $0.3\text{--}0.4$, $0.4\text{--}0.5$, $0.5\text{--}0.7$, $0.7\text{--}1.0$, and $>1\text{ }\mu\text{m}$ (Lasair 1002). Particle mass was estimated based on the geometrical mean diameter of each size range and an assumed density of 1.2 g/cm^3 . The ozone concentration was monitored by an ozone analyser (Seres OZ2000), which measures ozone based on the absorption of 254 nm light. Ultra-fine and fine particle concentrations as well as the ozone concentration were monitored continuously during all experiments at 15-min intervals. The outdoor ozone concentration was adopted from the website of the Danish Meteorological Institute, which has a measuring station less than 5 km from the university. Instruments for measuring SOA and ozone were located in the hall adjacent to the office. Sampling of air was made in the centre of the office at a height of circa 1 m . The length of the sampling tubes was around 2 m . Air exchange rate was measured by monitoring decay of SF_6 prior to and at the completion of an experiment, when steady-state conditions had been attained. Also, air temperature and humidity in the office were measured at these times. Mixing fans ensured full mixing of the air in the office.

Each experiment commenced with the measurement of air exchange rate, air temperature and humidity as well as initial SOA and ozone concentrations (condition 1). In experiments evaluating air fresheners, either ozone (condition 2) or the air freshener (condition 3) or the combination of these (condition 4) were supplied to the room. After $6\text{--}8\text{ h}$ when steady-state conditions were attained, measurement of air exchange rate, air temperature and humidity were repeated and the room was ventilated for at least one night prior to the next round of experiments. In the experiment with ozone and a cleaner, a steady-state ozone concentration was first attained and then the floor was washed with the cleaner.

RESULTS

During all experiments, the air exchange rate varied in the range $0.2\text{--}0.8\text{ h}^{-1}$ (mean 0.4 h^{-1} , s.d. 0.2 h^{-1}). Under conditions (1) and (3) the ozone concentration in the office was close to zero as a result of the low air exchange rate and surface removal. The average outdoor ozone concentration was 34 ppb (s.d. 12.5 ppb).

Figure 1 shows that the concentration of ultra-fine particles initially increased when ozone was generated in the room (condition 2) but no scented product was present. This may reflect reactions between ozone and low levels of unsaturated hydrocarbons naturally present in the

room air or heterogeneous reactions between ozone and compounds on the surfaces in the office. The air exchange rate was 0.7 h^{-1} at the beginning of the experiment (10:30 h) and 0.3 h^{-1} during the final measurements (17:00 h). The ozone concentration fluctuated slightly around 35 ppb after the build-up period. Measurement of fine particles ($>0.1 \mu\text{m}$ diameter) was performed only at the beginning and end of this experiment when the number concentration (sum of all ranges) was around $700 \text{ particles/cm}^3$.

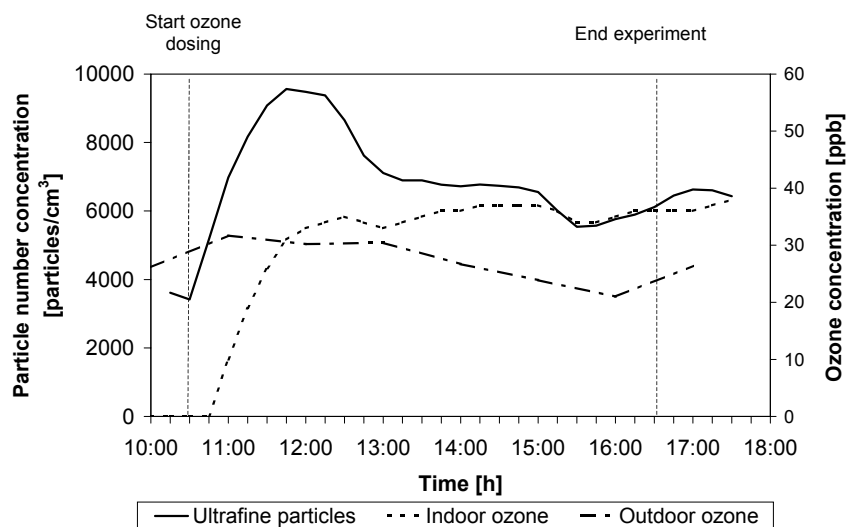


Figure 1 Ultra-fine particle concentration, indoor and outdoor ozone concentration with dosing of only ozone.

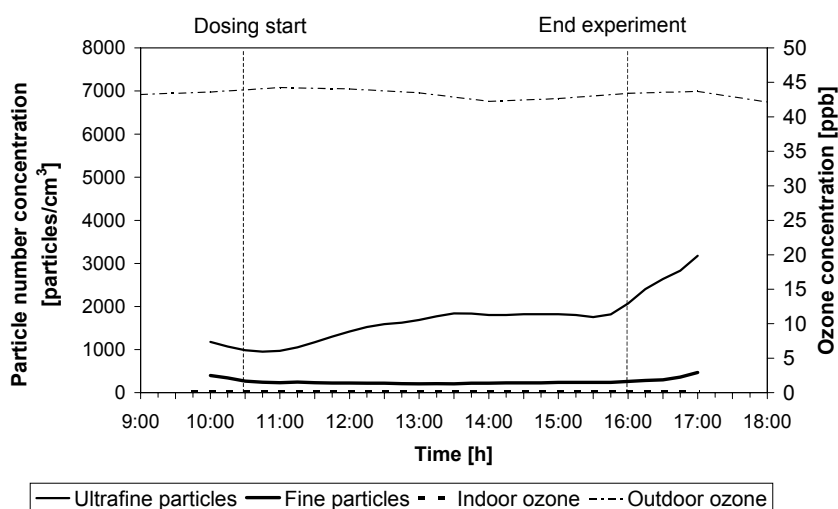


Figure 2 SOA concentration, indoor and outdoor ozone concentrations during dosing of fragrance #1.

Similarly, Figure 2 shows SOA concentration and indoor and outdoor ozone concentrations when fragrance #1 was dosed in the office (condition 3). During the experimental period, the ozone concentration was almost zero, and a very slight increase in SOA formation was observed. The air exchange rate increased from 0.2 h^{-1} at the beginning to 0.8 h^{-1} at the end of the experiment. It is assumed that the increase of the ultra-fine particle concentration at the end of the experiment can be ascribed increased transport of traffic-generated particles from outdoors.

Shortly after the start of simultaneous dosing of ozone and fragrance #1 at 11:15 h (condition 4), the ultra-fine particle concentration started to increase (Figure 3). The increase continued for approximately 1.5 h after which time the concentration remained constant during the rest of the experimental period. Slightly different evolution of the ultra-fine particle concentration was observed with two of the other three fragrances tested. For fragrances 2 and 3 a peak was observed after 1.5 h and then the concentration decreased steadily until the experiment ended. With fragrance #4 the concentration of ultra-fine particles decreased to the pre-dosing level within 4 h. Peak ultra-fine particle concentrations with the four fragrances were 12 000, 27 000 (Figure 3), 35 000, and 40 000 particles/cm³. In all experiments, the initial concentration of ultra-fine particles was less than 5000 particles/cm³ prior to the simultaneous dosing of ozone and air freshener. Figure 3 also shows that the fine particle concentration was negligibly affected by the dosing. The air exchange rate decreased from 0.8 to 0.5 h⁻¹ during the experiment shown in the figure.

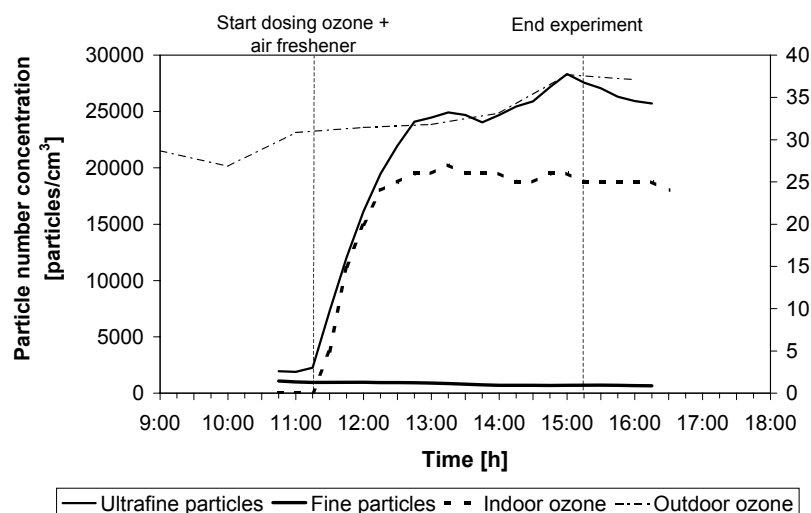


Figure 3 SOA concentration, indoor and outdoor ozone concentration with simultaneous dosing of ozone and fragrance #1.

Figure 4 shows SOA formation when the floor was washed in the lemon-scented cleaner. The ozone generator was turned on at 10:30 h, but had to be adjusted twice during the day to reach the desired concentration of 30 ppb. Between 16:15 and 16:25 h, the floor was washed in the cleaner. As a result, the ozone concentration decreased and the concentration of ultra-fine particles increased during a 30 min period while the floor was wet. Also, a modest increase in the concentration of fine particles in the three smallest size ranges (0.1–0.2, 0.2–0.3 and 0.3–0.4 µm) was seen during this period, although this is only indicated in Figure 4 by the sum of all size ranges of fine particles. The air exchange rate was the same at the beginning and end of this experiment, 0.3 h⁻¹.

During experiments with the air fresheners, particle mass (sum of all size ranges) remained nearly constant or even decreased slightly. With the cleaner, particle mass increased from 6.5 µg/m³ prior to beginning the cleaning event to 9.5 µg/m³ approximately 40 min after cessation of the event.

DISCUSSION

The tested fragrances of air fresheners as well as the lemon scented cleaner resulted in SOA formation when ozone was present in the air, although the air fresheners were relatively small sources of SOA with detectable increases occurring only in the ultra-fine particle number concentration. The number concentration of ultra-fine particles was lower than in previous

experiments conducted with higher ozone concentrations (>100 ppb) or dosing of chemicals rather than scented consumer products (e.g. Fan *et al.*, 2003; Rohr *et al.*, 2003). Also, Sarwar *et al.* (2003), when spraying liquid air freshener or a lemon-scented cleaner into a chamber, measured higher fine particle concentrations, although the ozone concentration varied between experiments in the range 3–15 ppb. Fan *et al.* (2003) studied reactions between ozone at 40 ppb and mixtures of VOCs commonly found in indoor air, both with and without α -pinene and D-limonene. The major chemical transformations that occurred were driven by ozone/ α -pinene and ozone/D-limonene reactions. The current results corresponded to a study performed by Long *et al.* (2000), who in nine homes recorded generation of $PM_{2.5}$ and ultra-fine particles after cleaning events with a cleaner containing α -pinene. In their study, however, the indoor ozone concentration was not manipulated.

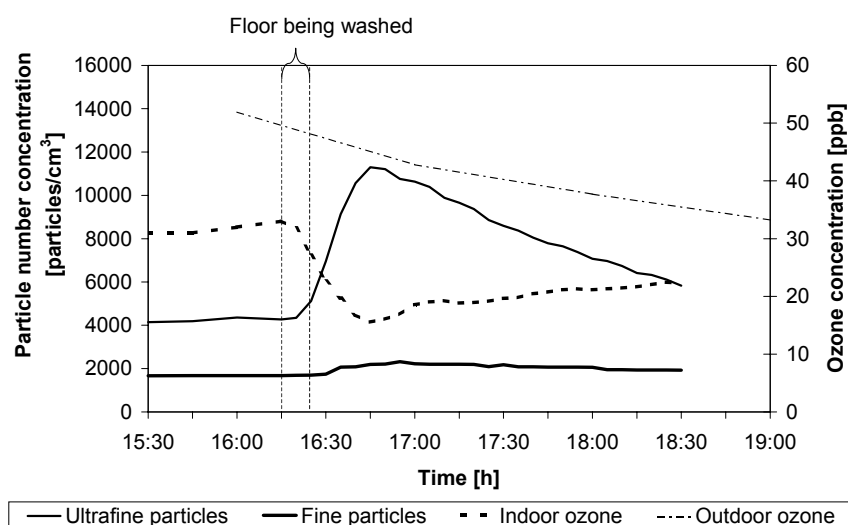


Figure 4 SOA concentration, indoor and outdoor ozone concentration with simultaneous dosing of ozone and the lemon-scented cleaner.

Weschler and Shields (2003) observed a shift in particle size distribution during the course of their experiments. Number concentration peaks occurred in larger size ranges as time progressed, and the size range with an observable peak decreased with increasing air exchange rate. Only with the lemon-scented cleaner did the results of this study indicate such a shift, even though the air exchange rate was approximately half that reported by Weschler and Shields. Air exchange rate determines not only the amount of time available for homogeneous atmospheric chemical reactions, but also the supply rate of outdoor ozone and the rate at which pollutants generated indoors are removed (Weschler and Shields, 2003). The current experiments utilized constant dosing of the air freshener at the highest possible rate resulting in a clearly perceptible scenting of the air. The concentration of the chemicals emitted by air fresheners may therefore have been somewhat above the level that commonly will be preferred by occupants of buildings or which is possible with higher air exchange rates. Despite the presumed high concentration of chemicals, however, no increase of particle mass was detected in these experiments.

The products of ozone/terpene reactions are a source of SOA in indoor environments (Weschler, 2003 and references therein). Bioassay experiments indicate that the products of these reactions are irritating to mice at elevated concentrations (Wolkoff *et al.*, 1999; Rohr *et al.*, 2002). However, the impact on humans of ozone/terpene products, including SOA, remains ambiguous (Fiedler *et al.*, 2002; Klenø *et al.*, 2002).

CONCLUSIONS AND IMPLICATIONS

Under conditions representative of those occurring in naturally ventilated buildings, air fresheners or scented cleaners may react with ozone to form SOA. The tested air fresheners were relatively small sources of SOA with detectable increases occurring only in the ultra-fine particle number concentration. The implications of SOA formation for occupants of buildings are as yet unclear, although the literature indicates some irritation effects of ozone/terpene reaction products.

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