Rai, A.C., Guo, B., Lin, C.-H., Zhang, J., Pei, J., and Chen, Q. 2013. "Ozone reaction with clothing and its initiated particle generation in an environmental chamber," *Atmospheric Environment,* 77, 885-892.

Ozone reaction with clothing and its initiated particle generation in an environmental chamber

Aakash C. Rai[1], Bing Guo[2], Chao-Hsin Lin[3], Jianshun Zhang[2], Jingjing Pei[4,*], & Qingyan Chen[1, 4]
[1] School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA
[2] Department of Mechanical and Aerospace Engineering, Syracuse, NY 13244
[3] Environmental Control Systems, Boeing Commercial Airplanes, Everett, WA 98203, USA
[4] School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China

[*]Phone: +86-22-2740 9500, Email: jpei@tju.edu.cn

Abstract

Ozone-initiated chemistry in indoor air can produce sub-micron particles, which are potentially harmful for human health. Occupants in indoor spaces constitute potential sites for particle generation through ozone reactions with human skin and clothing. This investigation conducted chamber experiments to examine particle generation from ozone reactions with clothing (a T-shirt) under different indoor conditions. We studied the effect of various factors such as ozone concentration, relative humidity, soiling levels of T-shirt with human skin oils, and air change rate on particle generation. The results showed that ozone reactions with the T-shirt generated sub-micron particles, which were enhanced by the soiling of the T-shirt with human skin oils. In these reactions, a burst of ultrafine particles was observed about one hour after ozone injection, and then the particles grew to larger sizes. The particle generation from the ozone reactions with the soiled T-shirt was significantly affected by the different factors studied and these reactions were identified as another potential source for indoor ultrafine particles.

Keywords: Ozone; Particles; Air quality, Environmental factors; Buildings

1. Introduction

The indoor environment can be thought of as a large chemical vessel with reactions taking place continuously (Weschler and Shields, 1997). Ozone is a major driver of this indoor chemistry and reacts with various compounds in the gas phase and on surfaces to produce oxidation products (Weschler, 2011). Some of these oxidation products with low vapor pressures can also increase the indoor particle concentrations by nucleating to form new particles or condensing on existing particles (Sarwar et al., 2003; Weschler and Shields, 1999). Hence, several investigations have studied the particle generation resulting from ozone reactions with terpenes, which are common constituents of many consumer products such as cleaners, fragrances, etc. (Coleman et al., 2008b; Destaillats et al., 2006; Sarwar et al., 2004; Singer et al., 2006). These investigations concluded that ozone reactions with terpenes can be an important source of sub-micron particles in indoor air, a potential health concern. Ozone itself is a well-known health hazard for humans in various indoor settings such as buildings and airliner cabins (EPA, 2006; Weschler, 2006). The health risk from ozone is elevated in airliner cabins because of its high concentrations, especially without catalytic converters in the environmental control systems, which remove ozone from the air supply (Bhangar et al., 2008; NRC, 2002; Spengler et al., 2004). The ozone-initiated particles are also a potential health risk, but this risk is more tentative since their composition and toxicities are unknown (Carslaw et al., 2009; Weschler, 2006).

The above literature review showed that the ozone reaction with terpenes is an important source of sub-micron particles in indoor air. It is also well known that humans themselves constitute an important site for ozone reactions with their skin (Wisthaler and Weschler, 2010), clothing (Coleman et al., 2008a), and hair (Pandrangi and Morrison, 2008). These reactions are mainly attributed to squalene, which is a triterpene found in human skin oils (Wisthaler and Weschler, 2010). Hence, we can expect these ozone reactions with human skin oils to generate sub-micron particles, which was also hypothesized by Fadeyi et al. (2013). However, to our knowledge there has been no investigation of particle generation from skin oils.

Hence, this investigation was undertaken to examine particle generation due to ozone reactions with clothing with/without human skin oils under different indoor conditions. We studied the effect of various factors such as ozone concentration, relative humidity, degree of soiling of a T-shirt with skin oils, and air change rate on particle generation, and also analyzed it for a typical building condition.

2. Method

This investigation conducted experiments in an environmental chamber to simulate the desired indoor conditions. The description of the experimental setup is given in detail in Rai et al. (2013). To avoid redundant information, the following provides a summary of the experimental setup. This study used a stainless-steel chamber of dimensions 1.8 m × 1.7 m × 1.7 m as shown in Figure 1. In the center of the chamber was a steel box of 0.2 m × 0.4 m × 1.2 m. The box was used as a human simulator with a surface temperature maintained at 31±1 °C. A cotton T-shirt (area ≈ 0.9 m^2) with/without human skin oils was stretched over the human simulator, which was the primary site for ozone reactions. The T-shirt was washed in a fragrance- and dye-free detergent, and its soiling by skin oils was achieved by a male subject's (26 years old Indian) sleeping in it unless otherwise mentioned. The chamber was supplied with fresh air at an airflow of 0.5-2.7 Air Changes per Hour (ACH) and was maintained with an exhaust temperature of approximately 24 °C. The ozone was generated outside the chamber and mixed with the supply air. The ozone depleted inside the chamber and generated particles. The experiment measured the time-varying concentrations of ozone and particles at the inlet and exhaust.

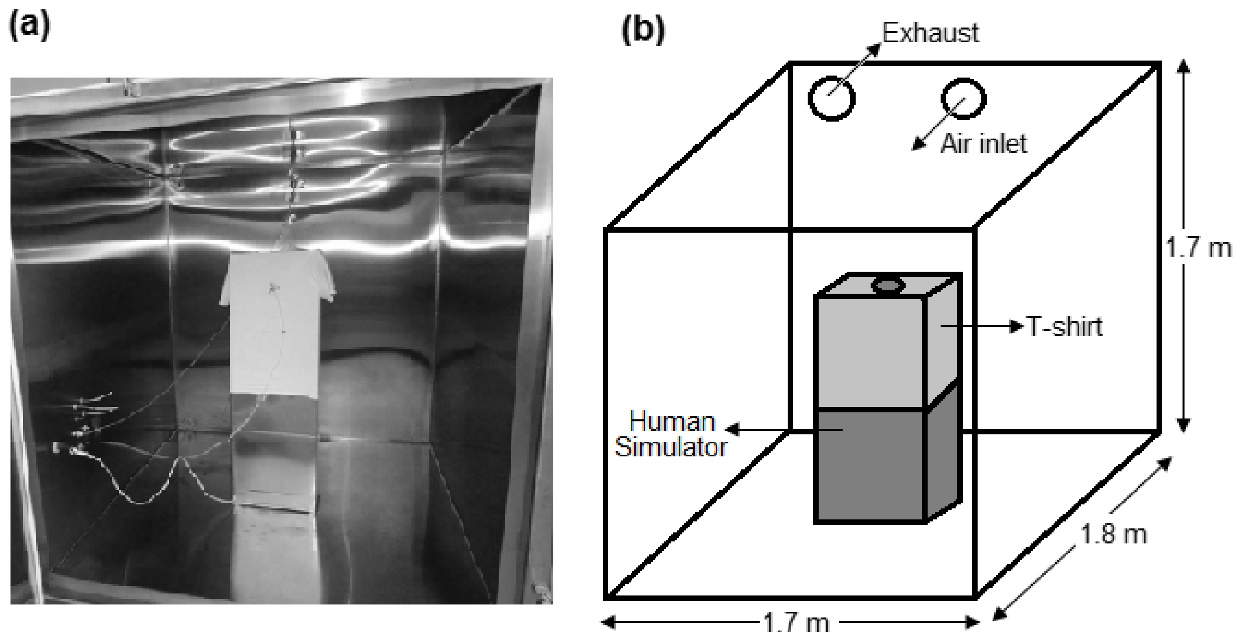

Fig. 1. Schematic of the environmental chamber used to study particle generation from ozone reactions with a T-shirt on a human simulator

The ozone concentration was measured with a photometric ozone analyzer (Model 202 by 2B Technology). The particle size distributions were monitored by a Scanning Mobility Particle Sizer (SMPS) (Model 3936 by TSI), which measured the number concentrations of particles between 9.65 and 421.7 nm in diameter and separated them into 105 bins (or 64 bins per decade of particle diameter). The SMPS software also calculated the particle mass concentrations by:

$$M = \rho \frac{\pi}{6} D_p^3 N \qquad (1)$$

where ρ is the particle density; D_p the geometric midpoint diameter of the particle size bin; N the particle number concentration; and M the particle mass concentration. The particle density was taken as 1.2 g/cm^3 as suggested by Turpin and Lim (2001), who derived their results by using the data of Rogge et al. (1993) for atmospheric organic aerosols. Note that the particle number concentrations are approximate values since the SMPS was not calibrated before making the measurements, and the existing factory settings were used. Hence, the mass concentrations also bear large uncertainties since it was derived from the number concentrations by using Eq. (1).

In order to examine the particle generations due to ozone reactions with clothing and identify the effect of different factors on these generations, this investigation designed 12 experimental cases. Table 1 summarizes the chamber conditions in these cases. The first three cases (Cases 1-3) studied the effect of different surfaces on particle generation. These were the chamber surfaces, a laundered T-shirt surface, and a T-shirt surface soiled with human skin oils. Next, Cases 4-11 were used to investigate the effects of different factors such as ozone concentration, relative humidity, degree of T-shirt soiling, and air change rate on particle generations. Finally, particle generation for a typical building condition was studied in Case 12.

Table 1

Details of the experimental conditions in the chamber used for studying particle generation from ozone reactions with human clothing

Case	Ozone concentration (ppb)	Relative humidity (%)	Hours the T-shirt was worn (h)	Air change rate (ACH)
1	42	15	No T-shirt	0.5
2	46	17	Laundered T-shirt	0.5
3	40	12	6	0.5
4	148	20	6	0.5
5	54	44	6	0.5
6	70	23	2	0.5
7	57	24	12	0.5
8	53	27	6 hours by a different human subject	0.5
9	75	12	No T-shirt	2.7
10	51	11	6	2.7
11	133	11	6	2.7
12	22	28	6	0.5

In all the above cases, we measured the background ozone and particle concentrations from t = 0 - 2.5 h. The background levels were typically low and the ozone and particle number concentrations were about 5 ppb and 200 $\#/cm^3$, respectively. From t = 2.5 h, ozone was continuously injected in the chamber and we measured the time varying ozone and particle concentrations until t = 12.5 h, when the experiment was completed.

3. Results

This section first presents the results from Cases 1, 2, and 3, which were used to identify the effects of different surfaces on ozone-initiated particle generations. Next, the results of Cases 4 - 12 were used to analyze the influence of different factors on these particle generations and also to study them for a typical building condition. Table 2 summarizes the key results.

Table 2

Key results from the study of particle generation from ozone reactions with human clothing

Case	$N_{max, exhaust}$ (#/cm^3)	Time at $N_{max, exhaust}$ (hours)	GMD at $N_{max, exhaust}$ (nm)	GSD at $N_{max, exhaust}$	Particle number concentrations at the end of experiment (#/cm^3)		Particle mass concentrations at the end of experiment (µg/m^3)	
					Inlet	Exhaust	Inlet	Exhaust
1	1212	8.2	20	2.2	271	509	0.15	0.30
2	2180	5.2	28	1.8	512	1235	0.28	0.49
3	8034	4.2	31	1.4	138	1408	0.08	0.79
4	23326	3.7	31	1.4	134	2212	0.07	1.10
5	8639	4.0	35	1.5	102	1819	0.07	1.86
6	3762	4.7	34	2.3	878	1404	0.62	2.09
7	8929	4.2	32	1.5	240	1886	0.14	1.29
8	5527	4.5	36	1.6	200	1293	0.15	1.32
9	323	6.0	19	2.3	217	208	0.17	0.16
10	781	1.7	19	2.2	159	192	0.05	0.17
11	714	0.5	20	2.2	140	171	0.08	0.11
12	1185	6.5	36	1.7	62	591	0.04	0.18

$N_{max, exhaust}$ is the peak particle number concentration at exhaust; GMD and GSD are the geometric mean diameter and standard deviation of particle size distributions, respectively.

3.1. Effect of different surfaces on the ozone initiated particle generation

This subsection discusses particle generation due to ozone reactions with the steel chamber, laundered T-shirt, and soiled T-shirt surfaces. Figure 2 shows that the exhaust particle concentrations were very low in Cases 2 and 3 without ozone injection ($t < 2.5$ h). The particle concentrations were not measured without ozone in Case 1 because of a malfunction of the SMPS. After ozone injection ($t > 2.5$ h), the exhaust particle concentration did not show a significant increase without the T-shirt (Case 1) if can be assumed that the conditions for Cases 2 and 3 for $t < 2.5$ h applied to Case 1. However, the particle concentration increased significantly when the T-shirt was present (Cases 2 and 3). Compared with the laundered T-shirt (Case 2), the particle concentration was much higher with the soiled T-shirt (Case 3) after ozone injection. These results show that the ozone reactions with the T-shirt generated particles, which were enhanced by the soiling of the T-shirt, probably due to the ozone reactions with human skin oils as suggested by Fadeyi et al. (2013).

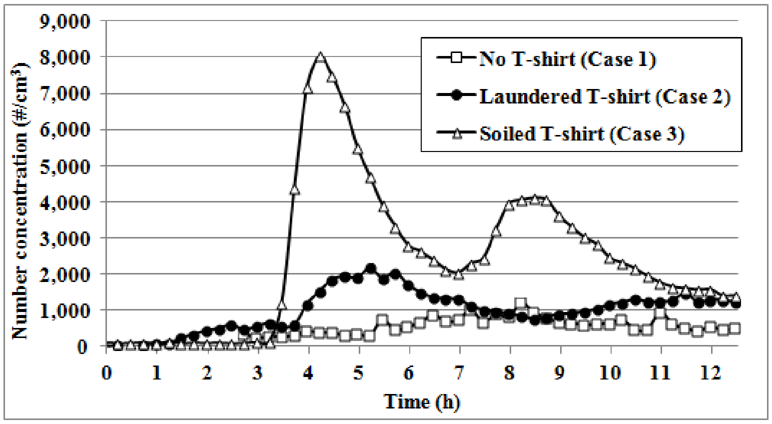

Fig. 2. Effect of chamber, laundered T-shirt, and soiled T-shirt surfaces on the ozone-initiated particles measured at the exhaust

We further analyzed particle generation due to ozone reactions with the soiled T-shirt (Case 3) since it was the most significant. Figure 3 shows the temporal variations of particle number and mass concentrations at the inlet and exhaust for Case 3. The corresponding particle size distributions at the exhaust are shown in Figure 4 for some important points in time. The exhaust particle concentrations were low from t = 0 - 2.5 h as shown in Figures 3 and 4(a) due to the low inlet concentrations. From t = 2.5 h, ozone was continuously injected in the chamber, but the particle concentrations were still low even after 40 minutes (t = 3.2 h) as shown in Figure 4(b). At t = 3.4 h, a primary burst of ultrafine particles with a geometric mean diameter of approximately 18 nm was measured as shown in Figure 4(c). This one-hour delay after the ozone injection was probably due to the time required for the generation of sufficient precursors from the ozone reactions (low-vapor-pressure oxidation products), which can form particles.

The primary burst could be attributed to nucleation (which forms new particles) or condensation (which leads to particle growth) on smaller existing particles, which grew to sizes measurable by SMPS. However, nucleation seems more likely, since condensation on existing particles should also produce particle bursts in higher sizes as suggested by Sarwar et al. (2003). After the primary burst, the number and mass concentrations increased for about 45 minutes (until t = 4.2 h), and the particles sizes also grew as shown in Figures 3 and 4(d). Hence, nucleation, condensation, and coagulation mechanisms seemed to prevail. The number concentrations then decayed (until t = 7.0 h), which means that new particles formed at a slower rate as compared to the removal of existing particles by ventilation and deposition. However, the mass concentrations and particle sizes continued to increase, indicating that particle generation by condensation was dominant, as shown in Figures 3, 4(e) and (f). Coagulation of particles could also be responsible for some of the particle growth, but it cannot account for the increasing mass concentrations, suggesting that growth by condensation was more significant.

A secondary burst of ultrafine particles was observed at t = 7.2 h as shown in Figures 3 and 4(g). Hence, it seems that new particles were formed by nucleation, since insufficient particles were left in the chamber, which reduced the surface area available for condensation as shown in Figure S1. A similar phenomenon was also observed by Coleman et al. (2008b) during ozone initiated particle generations from terpene-rich household products. The particle concentrations and sizes continued to increase until t = 8.5 h, probably as a result of nucleation, condensation, and coagulation mechanisms as shown in Figures

3 and 4(h). Finally, the particle number concentrations decayed until the end of the experiment because of ventilation and deposition. The mass concentrations also decayed, probably because of a decrease in particle generation rate or particle growth beyond the measuring range. Figures 4(i) and (j) illustrate the particle size distributions towards the end of the experiment. We did not observe another burst of particles toward the end of the experiment despite the number concentrations (and surface area) being lower than that at which the secondary burst was observed. Hence, it seems that the particle generation rate declined towards the end, probably as a result of depletion of skin oils from the T-shirt surface.

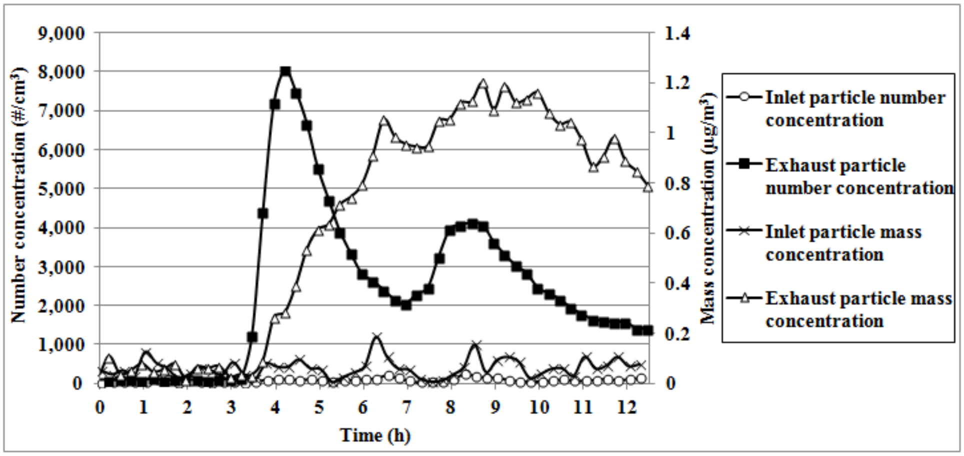

Fig. 3. Temporal variations of particle number and mass concentrations at the inlet and exhaust for the ozone reactions with the soiled T-shirt in Case 3.

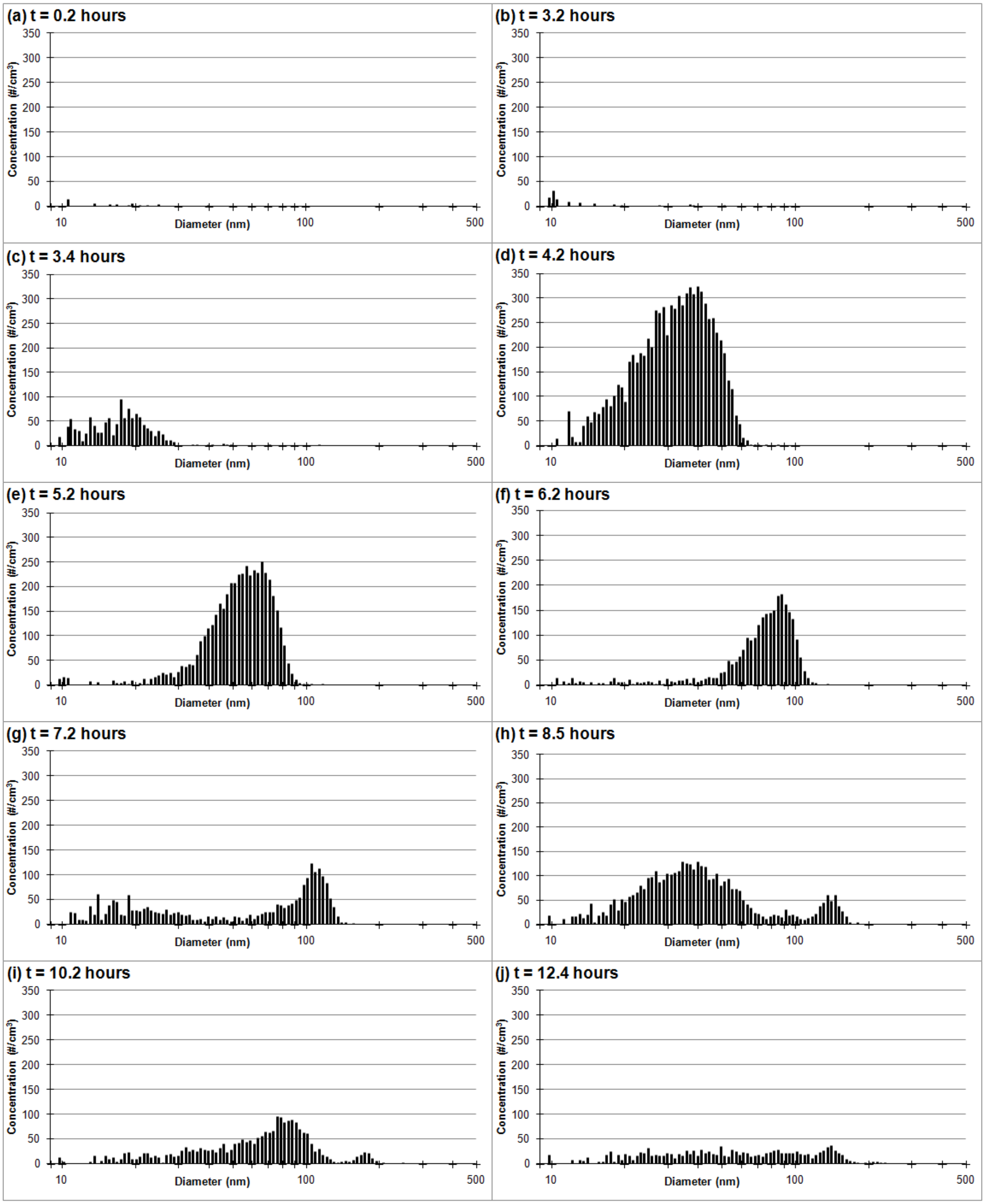

Fig. 4. Evolution of particle size distributions at the exhaust for the ozone reactions with the soiled T-shirt in Case 3

3.2 Effect of different factors on the ozone initiated particle generation

This investigation used Cases 4 to 11, given in Table 1, to identify the effect of different factors on particle generation resulting from ozone reactions with a soiled T-shirt. These cases were originally designed by keeping Case 3 as the reference and varying one factor at a time to isolate its effect on particle generation. However, it was difficult to control the chamber conditions precisely, and sometimes more than one factor varied from the reference case, which made the reference case unsuitable for comparison. Hence, we compared those cases which had roughly identical conditions except for the factor to be examined. The factors examined were ozone concentration, relative humidity, soiling degree of the T-shirt, and air change rate.

Effect of ozone concentration

This investigation compared Cases 3 and 4, given in Table 1, which had 40 ppb and 148 ppb ozone, respectively, in order to identify the effect of ozone on particle generation. The other conditions were similar between the two cases.

Figures 5(a) and (b) compare the particle number and mass generation, respectively, from the ozone reaction with the soiled T-shirt in Cases 3 and 4. In both the cases, the inlet particle concentrations were very low throughout the experiment. A primary and secondary burst of ultrafine particles was measured at exhaust after ozone was injected at t = 2.5 h and the particle generation mechanisms were also similar. However, the primary burst occurred earlier in Case 4 (148 ppb ozone), and the particle number and mass concentrations were also generally higher as shown in Figures 5(a) and (b). Hence, it seems that the high ozone concentration in Case 4 increased the production of particle-forming precursors from its reactions with the soiled T-shirt. The secondary burst of particles happened later in Case 4 than that in Case 3 since the high particle concentrations (and high surface areas) in Case 4 probably sustained condensation for a longer period of time.

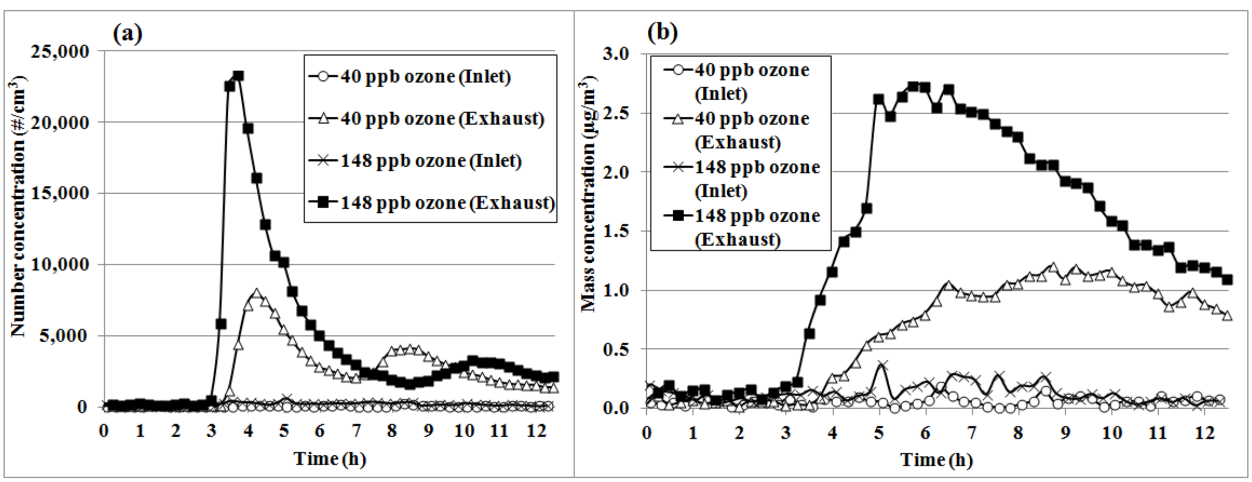

Fig. 5. Effect of ozone concentration on (a) particle number generation and (b) particle mass generation when the ozone reacted with the soiled T-shirt

Effect of relative humidity

This study used Case 5 with a relative humidity of 44% to study the impact of relative humidity on particle formation, by comparing it with Case 3 with a relative humidity of 12%. The other conditions were roughly similar for the two cases.

The inlet and exhaust particle number concentrations over time were approximately the same in Cases 3 and 5 as shown in Figure 6(a), except that the secondary burst was less pronounced in Case 5. The secondary burst was less significant in Case 5 because condensation was dominant over nucleation due to the large surface area of existing particles as shown in Figure S2. The particle mass concentrations were also significantly higher in Case 5 (44% RH), as shown in Figure 6(b), because of larger particle sizes. Such an increase in sizes was reported by Dua and Hopke (1996) for some indoor particles at high relative humidity conditions, and was attributed to hygroscopic growth. Hence, it seems that the particles generated by ozone reactions with the soiled T-shirt were hygroscopic in nature, and their sizes increased at high relative humidity, which also increased their masses.

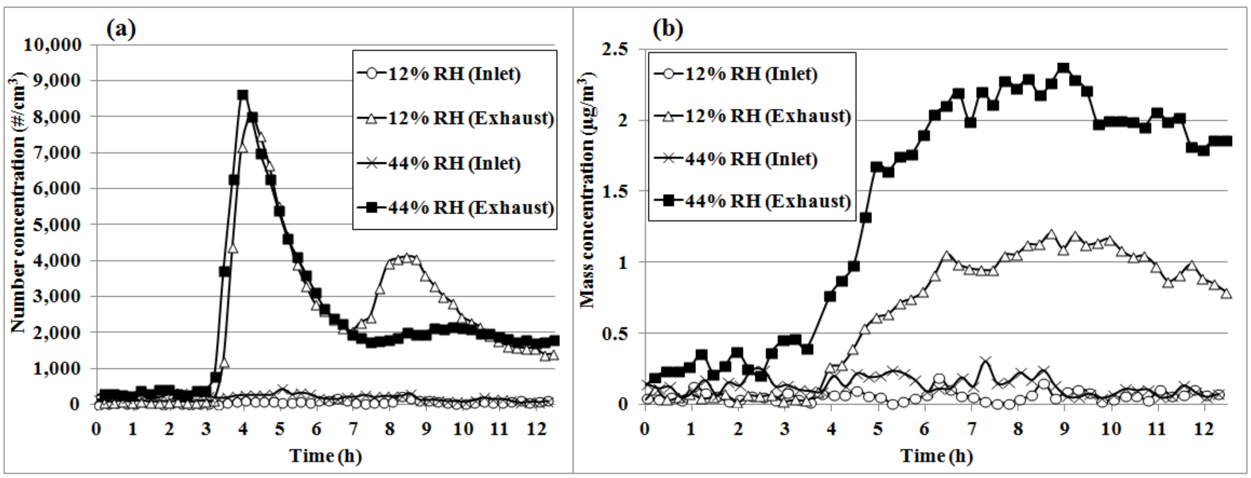

Fig. 6. Effect of relative humidity on (a) ozone-initiated particle number generation and (b) ozone-initiated particle mass generation with the soiled T-shirt

Effect of T-shirt soiling

This investigation used Cases 6 and 7 given in Table 1, which had different soiling levels of the T-shirt but otherwise similar conditions, to identify the effect of soiling level on particle generation. The different soiling levels of the T-shirt were achieved by the male subject's sleeping in it for 2 hours and 12 hours in Cases 6 and 7, respectively.

The generation of new particles from ozone reactions were very low in Case 6 compared with that in Case 7 as shown in Figure S3(a) because of the high initial particle concentrations in Case 6. Such a phenomenon was also reported by Sarwar et al. (2003), who found that low initial particle concentrations (and low surface areas) supported nucleation of new particles, whereas high initial concentrations (and high surface areas) favored condensation on existing ones. The particle mass generation was higher in Case 6 than that in Case 7 as given in Table 2 and shown in Figure S3(b), probably because the 2-hour soiling level was sufficiently high for the reaction and the reaction was already saturated.

In order to characterize the effect of skin oils from different human subjects on particle generation, this investigation used a T-shirt soiled by a female subject (middle-aged American) in Case 8. The results were compared with those of Case 7 under similar conditions. The particle number generation was lower in Case 8 than that in Case 7 due to high initial concentrations as shown in Figure S4(a), which was discussed when comparing Cases 6 and 7. The particle mass generation was approximately equal in Cases 7 and 8 as given in Table 2 and shown in S4(b), which indicates that it was unaffected by the different human subjects in these cases.

Effect of air change rate

Cases 9 to 11, given in Table 1, were at a higher air change rate of 2.7 ACH. Case 9 was without a T-shirt; Case 10 with a soiled T-shirt at 51 ppb ozone; and Case 11 with a soiled T-shirt at 133 ppb ozone. In all of these cases, particle generation due to ozone reactions was not observed because the exhaust and inlet particle concentrations were approximately the same, as illustrated in Table 2. It seems that there was insufficient time for particle formation at the high air change rate, since the high ventilation could quickly remove the particle-forming precursors from the chamber. These results are in qualitative agreement with a previous study by Weschler and Shields (2003), who measured particle generation from gas phase ozone reactions with d-limonene (a terpene) under different air change rates. They found that ozone-initiated particle generations decreased when the air change rate was increased, and finally that no excess particles were detected at air change rates exceeding 12.0 ACH.

3.3 Ozone initiated particle generations under typical building conditions

Most of the cases studied (Cases 1 to 8) were with an air change rate of 0.5 ACH, which corresponded to typical ventilation conditions in buildings. However, these cases had high ozone concentrations when compared with about 10 ppb as typically found in buildings. The high concentration, in fact, helps us accurately characterize the effect of different factors on the ozone reactions, since a low ozone concentration would considerably increase the experimental uncertainties.

To study particle generations for a typical building condition, we conducted Case 12 as a low-ozone case with only 22 ppb concentration, which can be found in buildings on a poor air quality day. In this case, a primary burst of ultrafine particles was observed about one hour after ozone injection, which was followed by growth in particle sizes as shown in Figure S5. Finally, the particle number concentration attained a steady value of about 600 #/cm^3 with most particles lying in the ultrafine region (diameters < 100nm). Hence, it seems that the ozone reactions with human clothing can become a possible source for indoor ultrafine particles, which is further discussed in the next section.

4. Discussion

Ultrafine particles are presumably responsible for the association between the exposure to particulate matter and morbidity and mortality (Donaldson et al., 1998; Seaton et al., 1995; Sioutas et al., 2005). Wallace and Ott (2011) estimated the indoors exposure to ultrafine particles as 2373 #/cm^3 when no sources were present, and the total daily intake was estimated to be 172000 #-h/cm^3 for typical suburban locations. We calculated that the ozone reactions with human surfaces can contribute between 80-160 #/cm^3 ultrafine particles for typical building conditions on a poor air quality day (See the Supporting Information for details), which corresponds to a daily intake of 1760 – 3520 #-h/cm^3 ultrafine particles for 22 hours spend indoors. Hence, such ozone reactions can account for approximately 5% of the indoor ultrafine particles and 2% of the total daily intake. Note that the above calculations had some simplifying assumptions and only provide a very rough estimate of exposure to ozone-initiated ultrafine particles from human surfaces.

The ozone-initiated particle generations from human surfaces seem quite small when compared with those from ozone reactions with common consumer products such as fragrances and cleaners. For example, Long et al. (2000) observed a peak increase of 7-100 times in particle number concentrations in Boston-area homes due to the ozone reactions with a commercial cleaning agent. However, other human surfaces such as skin and hair could potentially react with ozone and generate particles at much higher rates compared to that by clothing, since human skin oil seems to be an important ingredient for the particle generations. Such particle generations could become significant in indoor settings with high occupancy and ozone levels such as airliner cabins. However, it should be noted that airliner cabins typically have very high air change rates, which can offset the effects of high occupant density and ozone concentration.

5. Conclusions

This investigation experimentally studied the particle generation due to ozone reactions with clothing (a T-shirt) in an environmental chamber under typical indoor conditions. The study identified the effect of some important factors such as ozone concentration, relative humidity, degree of soiling of the T-shirt with human skin oils, and air change rate on the particle generation. The study led to the following conclusions:

The ozone reactions with T-shirt with/without human skin oils led to generation of sub-micron particles. Particle generation was significantly higher when the T-shirt was soiled with skin oils. Those particles were initially generated in the ultrafine region and then grew to larger sizes.

The particle generation increased with increasing ozone concentrations. A higher relative humidity did not increase the particle number generation, but led to hygroscopic growth of particles to larger sizes, which increased their masses. The particle generation was relatively unaffected by an increase in soiling level of T-shirt from 2 hours to 12 hours or by different human subjects. At a higher air change rate, few particles were formed due to short residence time of the air. The ozone reactions with clothing in typical building conditions were identified as another potential source of ultrafine particles.

Acknowledgements

This study was partially supported by the National Basic Research Program of China (The 973 Program) through Grant No. 2012CB720100 and the Center for Cabin Air Reformative Environment (CARE) at Tianjin University, China. This investigation was also partially funded by the U.S. Federal Aviation Administration (FAA) Office of Aerospace Medicine through the National Air Transportation Center of Excellence for Research in the Intermodal Transport Environment at Purdue University under Cooperative Agreement 10-C-RITE-PU. Although FAA sponsored this project, it neither endorses nor rejects the findings of the research. This information is presented in the interest of invoking comments from the technical community about the results and conclusions of the research.

References:

Bhangar, S., Cowlin, S.C., Singer, B.C., Sextro, R.G., Nazaroff, W.W., 2008. Ozone levels in passenger cabins of commercial aircraft on North American and transoceanic routes. Environmental Science & Technology 42, 3938–3943.

Carslaw, N., Langer, S., Wolkoff, P., 2009. New Directions: Where is the link between reactive indoor air chemistry and health effects? Atmospheric Environment 43, 3808–3809.

Coleman, B.K., Destaillats, H., Hodgson, A.T., Nazaroff, W.W., 2008a. Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics. Atmospheric Environment 42, 642–654.

Coleman, B.K., Lunden, M.M., Destaillats, H., Nazaroff, W.W., 2008b. Secondary organic aerosol from ozone-initiated reactions with terpene-rich household products. Atmospheric Environment 42, 8234–8245.

Destaillats, H., Lunden, M.M., Singer, B.C., Coleman, B.K., Hodgson, A.T., Weschler, C.J., Nazaroff, W.W., 2006. Indoor secondary pollutants from household product emissions in the presence of ozone: a bench-scale chamber study. Environmental Science & Technology 40, 4421–4428.

Donaldson, K., Li, X.Y., MacNee, W., 1998. Ultrafine (nanometre) particle mediated lung injury. Journal of Aerosol Science 29, 553–560.

Dua, S.K., Hopke, P.K., 1996. Hygroscopic growth of assorted indoor aerosols. Aerosol Science and Technology 24, 151–160.

EPA (U.S. Environmental Protection Agency), 2006. Air quality criteria for ozone and related photochemical oxidants (final). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-05/004aF-cF.

Fadeyi, M.O., Weschler, C.J., Tham, K.W., Wu, W.Y., Sultan, Z.M., 2013. Impact of human presence on secondary organic aerosols derived from ozone-initiated chemistry in a simulated office Environment. Environmental Science & Technology 47, 3933–3941.

Long, C.M., Suh, H.H., Koutrakis, P., 2000. Characterization of indoor particle sources using continuous mass and size monitors. Journal of the Air & Waste Management Association 50, 1236–1250.

NRC (National Research Council), 2002. The airliner cabin environment and the health of passengers and crew. National Academies Press.

Pandrangi, L.S., Morrison, G.C., 2008. Ozone interactions with human hair: ozone uptake rates and product formation. Atmospheric Environment 42, 5079–5089.

Rai, A.C., Guo, B., Lin, C.-H., Zhang, J., Chen, Q., 2013. Ozone reaction with clothing and its initiated VOC emissions in an environmental chamber. Submitted to Indoor Air.

Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T., 1993. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. Atmospheric Environment. Part A. General Topics 27, 1309–1330.

Sarwar, G., Corsi, R., Allen, D., Weschler, C., 2003. The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence. Atmospheric Environment 37, 1365–1381.

Sarwar, G., Olson, D.A., Corsi, R.L., Weschler, C.J., 2004. Indoor fine particles: the role of terpene emissions from consumer products. Journal of the Air & Waste Management Association 54, 367–377.

Seaton, A., Godden, D., MacNee, W., Donaldson, K., 1995. Particulate air pollution and acute health effects. The Lancet 345, 176–178.

Singer, B.C., Coleman, B.K., Destaillats, H., Hodgson, A.T., Lunden, M.M., Weschler, C.J., Nazaroff, W.W., 2006. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. Atmospheric Environment 40, 6696–6710.

Sioutas, C., Delfino, R.J., Singh, M., 2005. Exposure assessment for atmospheric ultrafine particles (UFPs) and implications in epidemiologic research. Environmental Health Perspectives 113, 947–955.

Spengler, J.D., Ludwig, S., Weker, R.A., 2004. Ozone exposures during trans-continental and trans-pacific flights. Indoor Air 14, 67–73.
Turpin, B.J., Lim, H.-J., 2001. Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Science and Technology 35, 602–610.
Wallace, L., Ott, W., 2011. Personal exposure to ultrafine particles. Journal of Exposure Science and Environmental Epidemiology 21, 20–30.
Weschler, C.J., 2006. Ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-initiated chemistry. Environmental Health Perspectives 114, 1489–1496.
Weschler, C.J., 2011. Chemistry in indoor environments: 20 years of research. Indoor Air 21, 205–218.
Weschler, C.J., Shields, H.C., 1997. Potential reactions among indoor pollutants. Atmospheric Environment 31, 3487–3495.
Weschler, C.J., Shields, H.C., 1999. Indoor ozone/terpene reactions as a source of indoor particles. Atmospheric Environment 33, 2301–2312.
Weschler, C.J., Shields, H.C., 2003. Experiments probing the influence of air exchange rates on secondary organic aerosols derived from indoor chemistry. Atmospheric Environment 37, 5621–5631.
Wisthaler, A., Weschler, C.J., 2010. Reactions of ozone with human skin lipids: sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. Proceedings of the National Academy of Sciences 107, 6568–6575.

Supporting Information

Particle generation and growth

The generation of new particles by nucleation versus particle growth by condensation depends on the surface area of existing particles. A low particle surface area concentration in the chamber favored generation of new particles (by nucleation), whereas a high surface area concentration favored particle growth (by condensation). To illustrate this, the variations of particle number and surface area concentrations with time are shown in Figure S1 for Case 3. As shown in the figure, initially the particle surface area concentration was very low and facilitated a huge primary burst (t = 3.4 h) of ultrafine particles from the ozone reactions. The surface area concentration then increased until about t = 6.0 h due to particle generation and growth. Then, from t = 6.0 h to t = 7.5 h, the surface area concentration decreased, which probably led to the secondary burst of particles by nucleation at t = 7.2 h since insufficient surface area was available for particle growth by condensation. Finally the particle number and area concentrations decayed till the end of the experiment, probably due to a reduction in ozone-initiated particle generations because of depletion of skin oils from the T-shirt.

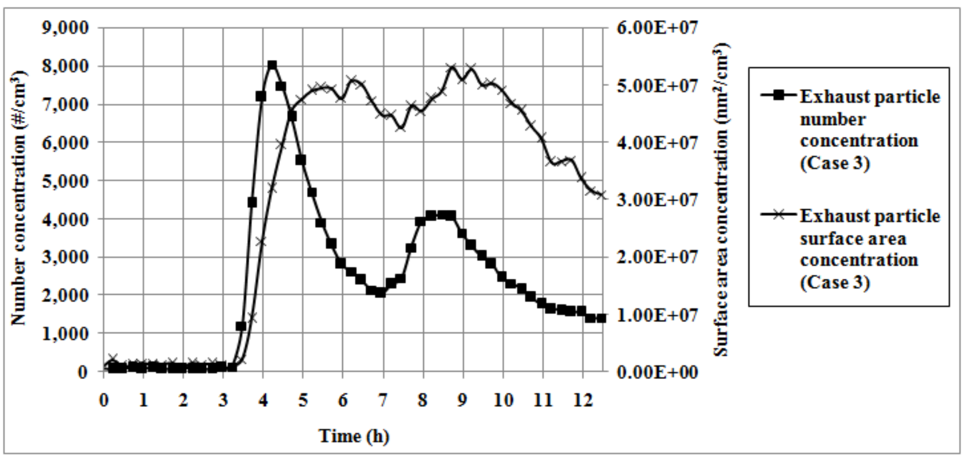

Fig. S1. Particle number and surface area concentrations in Case 3

Figure S2 compares the surface area concentrations in Cases 3 (12% RH) with that in Case 5 (44% RH). The particle surface areas were much higher in Case 5 probably due to hygroscopic growth of particles at high humidity conditions. The high surface areas in Case 5 favored condensation over nucleation and reduced the secondary burst of particles in Case 5 compared to that in Case 3 as shown in Figure 6(a).

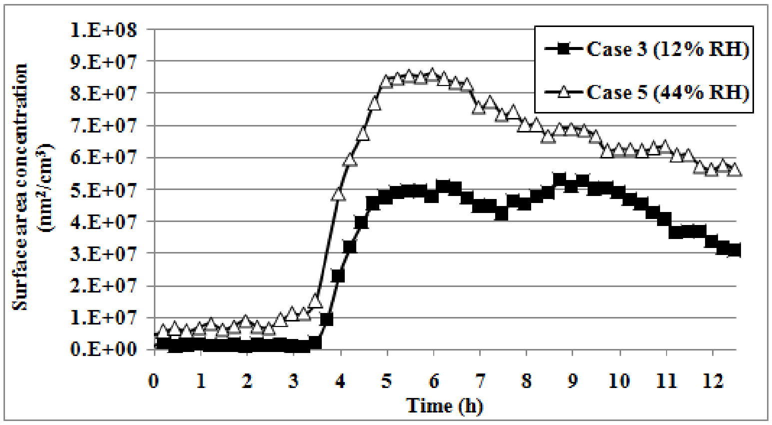

Fig. S2. Effect of relative humidity on the particle surface area concentration

Effect of T-shirt soiling

Initially, the exhaust particle number and mass concentrations with the 2-hour soiled T-shirt in Case 6 were higher than those with the 12-hour soiled T-shirt in Case 7 because of the high inlet concentrations as shown in Figures S3(a) and (b). From t = 2.0 - 3.5 h, the exhaust concentrations in Case 6 further increased because of an increase in the inlet particle concentrations. For t > 3.5 h the exhaust concentrations continued to increase, but not the inlet concentrations. This indicates that the particles were generated from the ozone reactions in Case 6 because the ozone was injected at t = 2.5 h. Since the inlet particle concentrations for Case 7 were relatively stable and small, it is much easier to see particle generation from the ozone reaction after the ozone was injected at t > 2.5 h.

After ozone injection, the particle number concentration in Case 7 was significantly higher than that in Case 6 because of low background particle concentrations as shown in Figure S3(a). However, the particle mass generation in Case 7 was lower than that in Case 6 as shown in Figure S3(b), probably because the 2-hour soiling level was sufficiently high for the reaction.

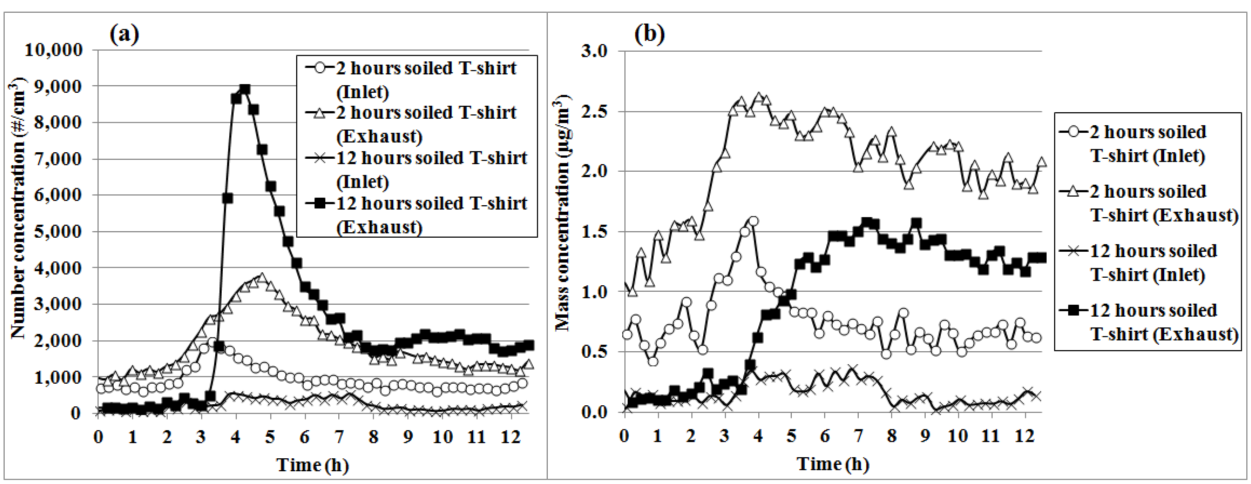

Fig. S3. Effect of the soiling level of the T-shirt by skin oils on (a) ozone-initiated particle number generation and (b) ozone-initiated particle mass generation

Figures S4(a) and (b) show the particle number and mass concentrations, respectively, at the inlet and exhaust for the two cases with different human subjects. The particle number generation was higher in Case 7 (male subject) than that in Case 8 (female subject), but the particle mass generations were approximately equal. Those results were previously discussed in the paper.

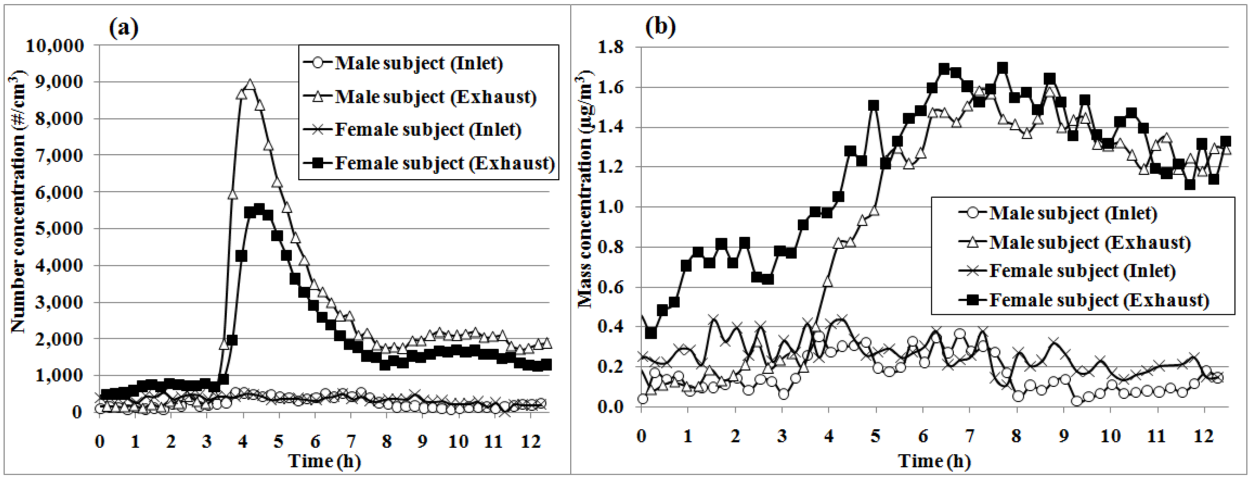

Fig. S4. Effect of T-shirt wearing by different human subjects on (a) ozone-initiated particle number generation and (b) ozone-initiated particle mass generation

Ozone-initiated particle generations under typical building conditions

Figure S5 shows the ozone-initiated particle generations under typical building conditions on a poor air quality day. It is clear that significant particle generations were observed despite the ozone concentration being only 22 ppb.

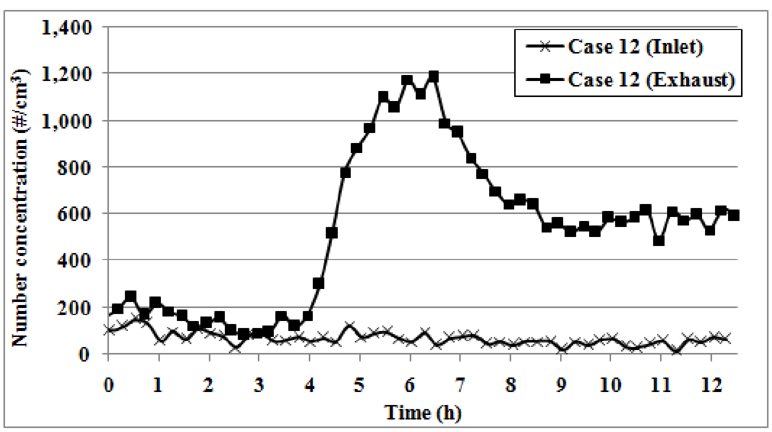

Fig. S5. Ozone-initiated particle number generation under a typical building condition on a poor air quality day

Exposure to ozone-initiated ultrafine particles in building conditions

We analyzed the contributions of ozone-initiated particle generation in realistic indoor conditions. It was assumed that the particle number concentration reaches steady state (as seen in Figure S5), the chamber air was well mixed, and deposition was negligible, then:

$$S \times A = Q \times (N_{exhaust} - N_{inlet}) \quad \text{(S1)}$$

where S is the particle number generation per unit time per unit area of the human surface; A the area of the T-shirt; Q the outdoor airflow rate to the chamber; and N_{inlet} and $N_{exhaust}$ the particle number concentrations at inlet and exhaust, respectively.

For Case 12 that corresponded to a typical building condition on a poor air quality day (22 ppb ozone and 0.5 ACH outdoor air change rate):

$A = 0.9\ m^2$, $Q = 2.55\ m^3/h$, $N_{inlet} \approx 0$, and $N_{exhaust} \approx 600\ \#/cm^3$

$\Rightarrow S = 472222\ \#/m^2\text{-s}$ (from Eq. S(1))

Next, we estimated the particle generation from the ozone reaction with human surfaces for a full-scale building environment by assuming that conditions for Case 12 were applicable. It was further assumed that the building is occupied by M occupants and each occupant contributes an area of 1.7 m^2 (total area = 1.7×M m^2) for the ozone reactions. From Eq. (S1):

$$S \times A = Q \times (N_{exhaust} - N_{inlet})$$
$$\Rightarrow S \times 1.7 \times M = M \times R_p \times (N_{exhaust} - N_{inlet})$$
$$\Rightarrow (N_{exhaust} - N_{inlet}) = \Delta N = (S \times 1.7)/R_p \quad \text{(S2)}$$

where ΔN is the increase in particle number concentrations due to the ozone reactions and R_p is the outdoor airflow rate per person. We used Eq. (S2) to calculate $\Delta N = 80 - 160\ \#/cm^3$ for R_p between 5 - 10 L/s.