

Ozone consumption and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing fabrics

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Abstract

We measured ozone consumption and byproduct formation on materials commonly found in aircraft cabins at flight-relevant conditions. Two series of small-chamber experiments were conducted, with most runs at low relative humidity (10%) and high air-exchange rate ($\sim 20 \text{ h}^{-1}$). New and used cabin materials (seat fabric, carpet, and plastics) and laundered and worn clothing fabrics (cotton, polyester, and wool) were studied. We first measured ozone deposition to many material samples, and then we measured ozone uptake and primary and secondary emissions of volatile organic compounds (VOCs) from a subset of samples. Deposition velocities ranged from 0.06 to 0.54 cm s^{-1} . Emissions of VOCs were higher with ozone than without ozone in every case. The most commonly emitted compounds were C_1 through C_{10} saturated aldehydes and the squalene oxidation product 6-methyl-5-hepten-2-one. For the compounds measured, summed VOC emission rates in the presence of 55-128 ppb (residual level) ozone ranged from 1.0 to 8.5 $\mu\text{mol h}^{-1} \text{ m}^{-2}$. Total byproduct yield ranged from 0.07 to 0.24 moles of product volatilized per mole of ozone consumed. Results were used to estimate the relative contribution of different

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materials to ozone deposition and byproduct emissions in a typical aircraft cabin. The dominant contributor to both was clothing fabrics, followed by seat fabric. Results indicate that ozone reactions with surfaces substantially reduce the ozone concentration in the cabin but also generate volatile byproducts.

Keywords

cabin air quality, indoor chemistry, ozone deposition, surfaces, byproducts

1. Introduction

Passenger flights typically cruise at an altitude of 9 to 12 km, which is in the upper troposphere or the lower stratosphere. At this height, the air is virtually free of most pollutants; however, the natural level of ozone may be elevated, ranging up to hundreds of ppb (Newchurch et al., 2003). When the ozone level is high outside the plane, the ozone level may also be elevated in the cabin since airplanes are continuously ventilated at high air-exchange rates using ambient air.

As summarized in a National Research Council report (NRC, 2002), several investigations were published in the 1960s and 1970s, documenting that ozone levels posing health concerns occurred in aircraft cabins on some flights, especially those flying at high altitudes, high latitudes, and during the late winter and spring months. The Federal Aviation Administration adopted cabin ozone concentration limits in 1980. The regulations state that ozone can be controlled by means of route planning or through the use of ozone converters. Currently, not all planes have ozone converters and, even when present, there is no consistent protocol in place to ensure their effective performance. There have been very few studies on ozone in the cabin environment since the early 1980s. One recently published study measured in-flight cabin ozone concentrations using passive samplers and reported an average level of 80

ppb, suggesting elevated ozone is still an issue of potential concern in aircraft cabins (Spengler et al., 2004).

The cabin environment is characterized by low relative humidity (~ 10-20%), high air-exchange rate (~ 10-20 h⁻¹) and reduced cabin air pressure (~ 0.8 atm) (NRC, 2002). Relative to most occupied microenvironments, the occupant density and surface-to-volume ratio in the cabin are high; on a full flight there may be only 1-2 m³ per occupant, including shared spaces.

As with other indoor spaces, the ozone level inside the plane is lower than the level in outside air because ozone is consumed by reactions, principally occurring on surfaces (Weschler, 2000). While reactions with surfaces reduce the level of ozone in cabin air, the byproducts of those reactions may be more irritating or toxic than ozone itself (Weschler, 2004). Studies conducted in a simulated cabin have confirmed that surfaces, including those associated with passengers, are the dominant contributors to ozone consumption and byproduct formation in airplane cabins (Wisthaler et al., 2005; Tamás et al., 2006).

Ozone deposition has been characterized in indoor spaces such as homes and offices (as summarized by Weschler, 2000), and ozone deposition to common residential and commercial indoor materials have been studied in chamber experiments and modeled (e.g., Grøntoft and Raychaudhuri, 2004; Morrison and Nazaroff, 2002). Byproducts of ozone reactions with surfaces have been measured for some typical home furnishings (Weschler et al., 1992; Morrison and Nazaroff, 2002; Wang and Morrison, 2006). Byproducts measured included toxic air contaminants, such as formaldehyde and acetaldehyde, and compounds with low odor thresholds, such as hexanal, heptanal, nonanal, and various nonenal isomers.

Our objective was to measure ozone-surface reactions for individual materials common to the cabin environment at flight-relevant conditions. We carried out experiments in a small

chamber where cabin materials (seat fabric, carpet, and plastics) and clothing fabrics (polyester, wool, and cotton) were individually exposed to ozone at low relative humidity and high air exchange rate. The experimental data were interpreted to quantify ozone uptake rate, to characterize formation of volatile organic byproducts of ozone-initiated chemistry, and to quantify byproduct emission rates and yields.

2. Methods

2.1. Evaluating ozone deposition and byproduct emissions

A parameter indicating the degree of ozone loss in the cabin is the retention ratio, R , which is defined as the mole fraction of ozone in the cabin air normalized by the mole fraction of ozone in the ambient air in the absence of deliberate control devices (NRC, 2002). If ozone deposition to surfaces dominates consumption, a steady-state mass balance applied to the aircraft interior results in the following equation for R .

$$R = \frac{1}{1 + \frac{N}{VQ} \sum v_d S} \quad (1)$$

Here, S is the nominal surface area of a given material, v_d is the deposition velocity of ozone to that material, the summation is carried out over all ozone-reactive materials, N is the number of moles of cabin air, Q is the molar ventilation rate, and V is the cabin volume. Values for N , V , and Q can be calculated from aircraft specifications and basic flight attributes (i.e., ventilation rate and pressure). To obtain values for the remaining two parameters, the amount and reactivity of each surface type must be evaluated. The only known measurements of retention ratio, 0.465 and 0.825, are from a study conducted by Nastrom et al. (1980). Occupancy was not reported in that study and it is not clear how well the conditions studied then reflect today's aircraft cabin.

Deposition velocity parameterizes uptake of pollutants on surfaces and is formally defined as the flux to a surface divided by the free stream concentration. It is possible to obtain the deposition velocity for a specific material by exposing it to ozone in a chamber void of other reactive material. At steady state, the deposition velocity is given by equation 2 (Morrison and Nazaroff, 2000).

$$v_d = \frac{Q_{chamber}}{[O_3]_{chamber} A} ([O_3]_{supply} - [O_3]_{chamber}) \quad (2)$$

where $[O_3]_{chamber}$ is the ozone level inside the chamber, $[O_3]_{supply}$ is the ozone level in the supply, $Q_{chamber}$ is the flow rate through the chamber (units of volume per time), and A is the nominal surface area of the sample. Deposition velocity is a situation-specific parameter in that it may depend on the flow conditions under which the measurements were made. Efforts to unravel this dependence have yielded a simplified two-resistor model of ozone uptake (Cano-Ruiz et al., 1993). The core of an interior space is considered to be well mixed and separated from each ozone-reactive surface by a thin concentration boundary layer. The analogy of two resistors in series describes the rates of two key processes controlling surface uptake: transport to the surface and surface reaction kinetics. The transport resistance, r_t , is the inverse of the mass-transport limited velocity, v_t , and the uptake resistance, r_s , can be expressed as $4/(\gamma \langle v \rangle)$ so that the deposition velocity is given by equation 3.

$$\frac{1}{v_d} = r_t + r_s = \left(\frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle} \right) \quad (3)$$

Here, $\langle v \rangle$ is the Boltzmann velocity, which has a value of $3.6 \times 10^4 \text{ cm s}^{-1}$ for ozone at 293 K.

The reaction probability, γ , is defined as the fraction of collisions of ozone molecules at the surface that result in irreversible uptake. By measuring the deposition velocity, v_d , and the transport-limited deposition velocity, v_t , to a surface, one can extract the flow-independent

parameter, γ . The uptake coefficient can be combined with information about the flow conditions in the environment of interest, in this case the cabin environment, to translate the deposition velocity measured in the laboratory to the expected value in the real environment. Equation 4, based on equation 3, shows how the reaction probability is calculated given the deposition and mass-transport-limited deposition velocity measured in a chamber.

$$\gamma = \left(\frac{\langle v \rangle}{4} \left(\frac{1}{v_d} - \frac{1}{v_t} \right) \right)^{-1} \quad (4)$$

The mass transport-limited deposition velocity is obtained experimentally by eliminating uptake resistance at the surface. In practice this is achieved by coating the material with potassium iodide, a substance that is considered to be a perfect sink for ozone (Parmar and Grosjean, 1990). In the research reported here, experiments identical to ones conducted to measure v_d were also conducted with the material coated in potassium iodide to measure v_t .

In addition to determining how much ozone was consumed in reactions with surfaces, the types and amounts of gas-phase byproducts formed from ozone-initiated reactions were measured. One parameter used to characterize product formation is the molar yield, Y_i , which is defined as moles of product of a species i formed per mole of ozone consumed. Molar yields of volatile byproducts were calculated using equation 5.

$$Y_i = \frac{[\text{prod}]_i}{([\text{O}_3]_{\text{supply}} - [\text{O}_3]_{\text{chamber}})} \quad (5)$$

where $[\text{prod}]_i$ is the gas-phase concentrations of species i . Another byproduct formation parameter is emissions flux, which was calculated using equation 6.

$$E_i = \frac{[\text{prod}]_i Q_{\text{chamber}}}{A} \quad (6)$$

2.2. *Materials*

An inventory of the typical types and amounts of surface materials was determined for a few representative aircraft cabins by personal correspondence with Boeing employees. New and used samples of the most prevalent surfaces (carpet, plastics, and seat fabric) were obtained from the manufacturers via Boeing. Many types of plastic are used, but in this study four new manufacturers' samples were investigated: two samples of plastic-coated wall covering and two types of plastic used in passenger service units (overhead panel housing passenger lights and gaspers). One used plastic sample, a folding tray table that had been in service for an unknown period of time, was also tested. Eight samples of new carpet and two used carpets were studied. One of the used carpets was a runner that had been in service for approximately 18 months since cleaning (total duration in service was unknown). The other used carpet, visibly worn and dirty, had an unknown service life and was stored approximately two years. A swatch of new seat fabric and a used seat covering that had been in service for 18 months since its last cleaning were tested.

Common clothing fabrics (cotton, wool, and polyester) were also included because, under high occupancy, the amount of surface area associated with passenger clothing is significant relative to the amount of surface area associated with "fixed" cabin surfaces. Also, clothing may contain skin oils, which are reactive with ozone (Fruekilde et al., 1998). Both laundered and soiled samples were investigated to evaluate the influence of skin oil on ozone consumption and byproduct formation. Laundered cloth samples were washed in a fragrance and dye free detergent and then stored, and were handled only with gloved hands. Soiled cloth samples were laundered materials that were worn next to the skin by a male, age 25, while sleeping for ~ 8 h

just prior to testing. Ozone reactions with human skin and aircraft ventilation ductwork were not investigated.

2.3. *Experimental apparatus*

Experiments were conducted in a 10.5 L electropolished stainless steel chamber housed in an incubating enclosure, as described in Morrison et al. (1998). The chamber temperature was maintained at 23 ± 1 °C. “Zero” grade air was humidified by means of running a portion of the air stream through a sparger. Relative humidity (RH) was set to $10 \pm 1\%$. Temperature and RH were measured every minute inside the chamber with a probe (Model HMD30YB; Vaisala). Experiments were performed at standard pressure. Ozone was generated by means of UV irradiation of a 0.3 L min^{-1} air stream, which made up part of a total flow of $3\text{-}4 \text{ L min}^{-1}$, depending on the experiment. Ozone in chamber air was continuously monitored with a photometric ozone analyzer (Model 400E; Advanced Pollution Instrumentation, Inc.). All material samples placed in the chamber were encased in or laid on a foil backing to isolate exposure to one primary surface. Gas samples were collected at the chamber exhaust.

2.4. *Chemical sampling and analysis*

Volatile organic compound (VOC) samples were collected on TenaxTA-filled tubes (P/N CP-16251; Varian, Inc.) and analyzed by thermal desorption-gas chromatography-mass spectrometry (TD/GC/MS) using a thermal desorber and cryogenic trap (Model CP-4020 TCT; Varian, Inc.) and an HP6890 GC interfaced to a HP5973 mass selection detector. Carbonyl samples were collected on dinitro-phenyl-hydrazine (DNPH) coated silica cartridges (P/N WAT037500; Waters Corp.), extracted with acetonitrile, and analyzed for formaldehyde, acetaldehyde, and acetone by high-pressure liquid chromatography (Model 1200; Agilent). Details of the analytical methods are given elsewhere (Destailats et al., 2006a). All gas samples

were collected and analyzed in duplicate, and background samples were run periodically. Two “background” experiments were conducted, one with the chamber empty and one where the chamber contained only the backing. Background levels of the sum of all compounds except acetone were less than the equivalent of $0.25 \mu\text{mol h}^{-1} \text{m}^{-2}$ without ozone and $0.5 \mu\text{mol h}^{-1} \text{m}^{-2}$ with ozone, and acetone emissions were less than $0.5 \mu\text{mol h}^{-1} \text{m}^{-2}$ with or without ozone.

Inline ozone scrubbers were used for VOC collection to avoid ozone-sampling artifacts (Fick et al., 2001; Calogirou et al., 1996). Some of the first experiments in this series were conducted with a commercial, potassium iodide-filled scrubber (P/N WAT054420; Waters Corp.) attached upstream of the Tenax and DNPH samplers. The commercial scrubber introduced many unwanted compounds onto the Tenax. Although scrubber artifacts appeared not to interfere with analysis of with target analytes, an in-house scrubber was developed for use with the Tenax samplers. The scrubbers comprised glass tubes with potassium iodide (KI) held in place with glass wool plugs. The in-house scrubber was tested in a side-by-side comparison with the commercial scrubber using various representative compounds. The in-house scrubber was highly effective at scrubbing ozone and did not result in significant positive or negative artifacts of the target compounds (with or without ozone) or the appearance of many unwanted compounds in the chromatograms.

2.5. Experimental protocol

First, all of the materials obtained from the aircraft manufacturers and the clothing fabrics were screened for ozone reactivity. Samples of each material were exposed to ozone in the chamber for a period of 3 h or more to gauge the magnitude of ozone reactivity and determine variation within groups of samples.

In screening experiments, the chamber was quenched by introducing a high ozone concentration in the supply air (~ 350 ppb) until the concentration at the exhaust equaled the concentration in the supply. Then the chamber was ventilated with clean air for 15 minutes, after which the material specimen was introduced and exposed to 80 ± 3 ppb (supply level) for a period of 3 h or more. The specimen was left in the chamber until the ozone level was steady (changing less than 2 ppb per 10 minutes). Flow rate and sample size were adjusted according to the flow-to-surface ratio of the material in a typical aircraft. For materials other than carpet, specimens were approximately 250 cm^2 and were exposed at a chamber airflow rate of $4.0 \pm 0.1 \text{ L min}^{-1}$. Owing to limited materials, carpet specimens were 70 cm^2 and were exposed with $3.0 \pm 1 \text{ L min}^{-1}$.

The 3-h average deposition velocity was calculated with equation 2 where $C_{chamber}$ was the average ozone level collected 15 minutes to 195 minutes after sample introduction. The first 15 minutes of data were discarded to allow for re-equilibration after opening the chamber. The uncertainty associated with deposition velocities was determined from error propagation analysis to be <5-10%. Variation between specimens was expected to be the larger source of error and was determined to be <15% from duplicate and triplicate experiments of a subset of materials.

A second series of experiments was conducted to characterize primary emissions and ozone-reaction byproducts from cabin materials and clothing. One new and one used specimen of each material (seat fabric, carpet, and plastics) and one laundered and one soiled specimen of each type of the clothing fabric (cotton, polyester, and wool) were tested. Each experiment was run at the same conditions: $10 \pm 1\%$ RH, $23 \pm 1^\circ\text{C}$, $4.0 \pm 0.1 \text{ L min}^{-1}$, 160 ± 4 ppb ozone in the supply air. The chamber was first quenched and aired as in the screening experiments. The material was then placed in the chamber and conditioned for 3 h with clean air, after which the

ozone was turned on for 1.5 h or more. During conditioning, duplicate 3-h, 100 mL min⁻¹ samples were collected on Tenax-filled glass samplers and 3-h samples were collected on DNPH, one at 0.4 L min⁻¹ and the other at 1.0 L min⁻¹. Another set of samples was collected during the 1.5 h period of ozone exposure. Average emission rates were calculated using equation 6 where [prod]_{*i*} is equal to the concentration of a species *i* measured during a sampling period minus a background concentration from blank experiments. Across all experiments, the average relative standard deviations (RSD) for formaldehyde, acetaldehyde, acetone, and 6-MHO were 40%, 50%, 55%, and 30%. For all other compounds the average RSD was less than 15%.

3. Results and Discussion

3.1 Ozone deposition

The initial, final, and 3-h average deposition velocities ($v_{d, 15 \text{ min}}$, $v_{d, 195 \text{ min}}$, and $v_{d, av}$, respectively) for the 22 materials in the screening experiments are shown in Table 1. The 3-h average deposition velocities for all materials range from 0.06 to 0.54 cm s⁻¹. The 3-h average reaction probability, γ_{av} , values were calculated for each material according to equation 4 using the mass-transfer-limited deposition velocity indicated in Table 1. A limited number of KI-coated materials was tested because mass-transfer-limited deposition velocities were found to be relatively uniform within a category. A limitation of the KI-coating method should be noted: KI tends to recrystallize when dried on a smooth surface causing uneven coverage and creating a new surface microstructure that could conceivably affect mass transport.

Table 1 illustrates several points. First, all of the materials exhibited similar ozone reactivity in that all deposition velocities were within an order of magnitude. Second, the carpet samples (all different carpets) exhibited similar deposition rates except for New Carpet 5, which

had an unusually high deposition velocity. From BET analysis, this carpet did not possess a significantly higher area than the other carpet samples so the increased reactivity is likely due to a difference in surface treatment or backing (Morrison and Nazaroff, 2002). Third, used samples were slightly more reactive than new ones in the case of carpet and seat fabric. It is possible that accretion of an organic film caused the increase in reactivity (Liu et al., 2003). Fourth, soiled clothing samples were more reactive than freshly laundered samples. Figure 1 shows the deposition velocities for the laundered, soiled, and KI-coated clothing fabrics. Wearing the fabric increased its reactivity to near the maximum (KI-coated) level. Squalene, a major component of skin oil and a triterpene (Yeo and Shibamoto, 1992), is likely responsible for the increase owing to its six unsaturated carbon bonds (Fruekilde et al., 1998).

The deposition velocities measured in this study are higher than values reported in other studies of similar materials (Cano-Ruiz et al., 1993; Morrison and Nazaroff, 2000). Likely, these higher values are a result of the much higher air-exchange used rate to simulate the cabin environment. Figure 2 compares the data to a model of deposition velocity as a function of reaction probability and friction velocity (Cano-Ruiz et al., 1993; Morrison and Nazaroff, 2002). The model is described by equation (7):

$$v_d = \frac{\gamma \langle v \rangle u^*}{\Gamma \gamma \langle v \rangle + 4u^*} \quad (7)$$

where u^* is the friction velocity and Γ is a parameter equal to 13.3 for the conditions in this chamber (Morrison and Nazaroff, 2002). A least-squares fit of the model to the data indicates a friction velocity of 7 cm s^{-1} in the chamber. Lai and Nazaroff (2000) suggested that $0.3\text{--}3 \text{ cm s}^{-1}$ might span the range expected for indoor environments, but their analysis did not take into account the complex topographies of real indoor surfaces and may be biased low, especially for conditions in an aircraft cabin.

3.2 Byproduct emissions

VOC emissions from the materials were measured in the presence and absence of ozone. The techniques used to collect emissions were capable of detecting a wide range of VOCs. Saturated aldehydes (C_1 through C_{10}), acetone, and 6-MHO were the compounds most commonly detected. Based on previous studies, unsaturated aldehydes such as 2-nonenal were also likely emitted but at levels too low to be detected in the current experiments (Morrison and Nazaroff, 2002; Wisthaler et al., 2005). Emissions were generally higher in the presence of ozone. Presented in Figure 3 are emission rates from cabin materials and clothing fabrics with and without ozone. Although all experiments, unless otherwise indicated, were conducted with the same level of ozone in the supply air, the ozone level that a specimen was effectively exposed to varied with the reactivity of the specimen. Average chamber ozone levels are presented in emissions figures.

New and used plastic emitted acetone at rate of $\sim 0.5 \mu\text{mol h}^{-1} \text{m}^{-2}$ with and without ozone, but emissions of aldehydes were higher in the presence of ozone. Emissions from new plastics were low overall. The secondary emissions profiles of used plastic and used seat fabric were similar, perhaps owing to an accretion of an ozone-reactive organic film during service (Liu et al., 2003). New and used seat fabric had similar primary emissions consisting mainly of formaldehyde and acetone. New seat fabric was the highest emitting cabin material, with total secondary emissions comparable to soiled clothing fabrics; ozone reaction byproducts were dominated by acetone and nonanal.

The dominant species found in secondary emissions from used carpet were acetaldehyde and nonanal. High emissions of acetaldehyde were unique to this material, but uncertainty associated with the acetaldehyde measurement in this experimental run was high, $\sim 100\%$ RSD.

The secondary emissions profile of new carpet was similar to that of laundered clothing fabrics. The unsaturated fatty acids believed to be the precursors of these compounds are naturally present in cotton (Pollock, 1948) and may also be present in carpet owing to the use of plant-derived soaps and oils in carpet fabrication and processing (Morrison and Nazaroff, 2002). The emissions profiles from the carpet samples are comparable to measurements made in similar studies, but are near the lower end of reported values (Morrison and Nazaroff, 2002; Wang and Morrison, 2006).

Emissions profiles for the laundered fabrics were similar to one another although emissions from wool were about half those from cotton or polyester. Emissions profiles were also similar amongst soiled clothing samples, with expected byproducts of ozone reactions with squalene dominating secondary emissions. The lower molecular weight oxidation products of squalene are acetone, 6-methyl-5-hepten-2-one (6-MHO), and 4-oxopentanal (4-OPA) (Fruekilde et al., 1998). As shown in Figure 3, acetone dominates secondary emissions from soiled clothing. Average emissions rates of 6-MHO from soiled cotton, polyester, and wool during the first 1.5 h of ozone exposure (with comparable residual ozone levels) were 2.1, 1.0, and 0.5 $\mu\text{mol h}^{-1} \text{m}^{-2}$, respectively. The emission rates of 6-MHO from cabin surfaces (seat fabric, plastic, and carpet) were low in comparison to the soiled fabrics, ranging from below the detection limit to 0.2 $\mu\text{mol h}^{-1} \text{m}^{-2}$. The GC/MS was not calibrated for 4-OPA analysis at the time of these experiments.

All of the byproducts shown in Figure 3 were included in the total yield calculation. Total molar yield for all of the materials was in the range of 0.07 to 0.23 (Figure 4). The total aldehyde yield for used carpet (0.08) was similar to the yield (0.07) reported for a 10-y old carpet in another study (Wang and Morrison, 2006).

3.3 Effect of environmental factors

To explore the effects of various environmental factors on ozone consumption and byproduct formation, supplementary experiments were conducted where one experimental factor at a time was changed relative to base case conditions. Figure 5 shows emissions from laundered cotton for different ozone supply and RH levels.

Emission rates of ozone reaction byproducts from cotton, except for formaldehyde, were relatively constant across the range of ozone levels tested (90 ppb, 160 ppb, and 320 ppb). This may indicate that surface species are the limiting reagents, i.e. ozone is in excess even at the lowest concentration. That formaldehyde emissions increased with increasing ozone concentration while the other species remain constant may suggest that formaldehyde formation, at least in part, results from ozone reactions with cellulose, which is not a limiting reagent, while other byproducts are formed from ozone reactions with oils or other trace compounds present in the fabric. Formaldehyde formation from cellulose oxidation by ozone has not been measured but is consistent with a proposed reaction mechanism (Lemeune et al., 2004).

Exposing cotton to ozone at 50% rather than 10% RH resulted in an increase in the yield of all byproducts. Emissions of most species increased in proportion to their emissions in the 10% RH case, approximately doubling for the 50% RH case. Exceptions are nonanal and decanal, which increased by five times in the 50% RH case. Increased ozone reactions at the surface of cotton at higher RH have been reported (Destailats et al., 2006b). This result is relevant for the cabin environment because clothing fabric is likely to experience a RH condition higher than the bulk cabin air because of close proximity to human skin.

3.4 Aging and regeneration

Decreasing reactivity of a material with increasing cumulative ozone exposure is termed “aging” (Mueller et al., 1973; Sabersky et al., 1973; Morrison and Nazaroff, 2000). Figure 6 shows ozone concentration measured at the chamber exhaust for four materials during the screening experiments. Since the ozone level in the supply air (80 ppb) and all other experimental conditions were the same, the residual ozone level in the chamber is an indicator of the reactivity of the material. A high residual ozone concentration indicates low ozone reactivity and vice versa. Some materials appear to have persistent reactivity with ozone on this time scale (i.e. used seat fabric), whereas others quickly become quenched (i.e. new plastic-coated wall covering). Most materials exhibited time-varying reactivity profiles between these extremes (as illustrated for wool in Figure 6).

Some emissions experiments were extended to collect an additional integrated samples during ozone exposure (duplicate samples were collected for 3 h while conditioning the material and then during the first 1.5 h and following 2-3 h of ozone exposure). Extended experiments were performed for used carpet, new seat fabric, used seat fabric, soiled cotton and laundered cotton (4 conditions). Average emissions for all materials except used seat fabric were less in the later sampling period, ranging from 20 to 70% of emissions in the earlier period. The used seat fabric emissions were ~20% higher.

Exposed materials can exhibit regeneration, a rebound in reactivity after a period of exposure to ozone-free air (Mueller et al., 1973; Sabersky et al., 1973; Morrison and Nazaroff, 2000). To evaluate regeneration, used seat fabric was exposed to conditions intended to simulate routine plane operations. Following an extended emissions experiment (3 h with clean air, then ozone for 3.5 h), the used seat fabric specimen was then stored in airtight packaging overnight.

The next day the specimen was treated as follows: 3-h conditioning, 1.5-h ozone exposure, 1.5-h conditioning, and 3-h ozone exposure. The ozone concentration in the supply air was 155-160 ppb. This exposure scheme simulates the environment in a plane that has a 7-h flight segment, is grounded overnight, and then flies an 8-h segment in which ozone is encountered intermittently. The initial (15 minutes after ozone was turned on) and 90-minute deposition velocities for the three periods were, in sequential order, 0.389 and 0.354 cm s^{-1} , 0.371 and 0.326 cm s^{-1} , and 0.315 and 0.295 cm s^{-1} . Thus, the material exhibited both aging and regeneration: the 90-minute deposition velocities were lower than initial deposition velocities and the initial deposition velocity in the second exposure period was greater than the 90-min deposition velocity in the first period. Although the average reactivity of the material decreased with each exposure to ozone, the total emissions of C₁ through C₁₀ aldehydes increased slightly in sequential ozone exposures with 1.5-h average emissions of 2.4, 2.7, and 3.1 $\mu\text{mol m}^{-2} \text{h}^{-1}$, respectively, for the three periods.

3.5 Contributions of surface reactivity to cabin air quality

The relative abundance of each material in a cabin environment was estimated based on the interior dimensions of a Boeing 737. To estimate the contribution of passengers to surface area, the plane was assumed to be fully loaded and half of the seat fabric was assumed to be covered. Each passenger was assumed to contribute 1 m^2 of exposed clothing fabric. As shown in Figure 7a, plastic and clothing are the dominant contributors to cabin surface area for these conditions.

Although the deposition velocities in the cabin may differ from those measured in chamber experiments, experimental values reported here can be used to indicate relative reactivity. The product of the material-averaged deposition velocity and the area of that material

in the plane ($v_d \times S$) provides an estimate of the contribution of each surface type to ozone consumption in the cabin. As shown in Figure 7b, clothing and seat fabric are the dominant ozone-consuming surfaces.

Since molar yield expresses the amount of product formed per amount of ozone consumed, multiplying yield by ozone deposition velocity provides a parameter that is proportional to byproduct emission rate. Therefore, an estimate of each material's contribution to byproduct emissions into the cabin can be obtained as the product of three terms: average molar yield for a surface, the average deposition velocity to that surface, and the amount of that surface in the cabin ($Y \times v_d \times S$). The total yield of C₁ through C₁₀ saturated aldehydes, acetone, and 6-MHO, averaged for each material type, was used to produce Figure 7c. This analysis suggests that clothing fabric dominates ozone-initiated byproduct emissions, followed by seat fabric, although all material types make significant contributions. These results are substantiated by relatively good agreement with results from a simulated cabin study (Tamás et al., 2006).

The molar yield can also be used to estimate the concentration of byproducts in the cabin, based on the level of ozone outside the plane, according to equation 8 (NRC, 2002).

$$[\text{prod}]_i = [\text{O}_3]_{\text{ambient}} (1 - R) Y_i \quad (8)$$

where $[\text{prod}]_i$ is the cabin level of species i attributable to byproduct formation (ppb) and $[\text{O}_3]_{\text{ambient}}$ is the ozone level (ppb) outside the plane. For example, using 0.1 for total molar yield of aldehydes, an ambient ozone level of 150 ppb, and a retention ratio of 0.4, the total level of C₁ through C₁₀ aldehydes in the cabin attributable to ozone-initiated chemistry would be $(150 \text{ ppb})(0.6)(0.1) = 9 \text{ ppb}$. Equation 8 applies to a plane without an ozone-converter on the supply air. With a converter present, the right hand side of the equation should be multiplied by $(1 - \eta)$, where η is the fractional removal efficiency of ozone by the control device.

Translating deposition velocities, emission rates, and yields from chamber experiments to the cabin requires information about flow conditions in that environment. Cabin airspeeds are comparable to those in buildings, and surface topographies are probably more complex, suggesting somewhat higher friction velocities (Matthews et al., 1989; Zhang and Chen, 2006).

Although the experiments were conducted at a pressure of 1 atm, rather than at the reduced pressure of the cabin environment, we expect ozone deposition velocities and byproduct yields to be relatively independent of cabin pressure. Byproduct emission fluxes from cabin materials likely scale with the ozone partial pressure, so that the results reported in this paper would be scaled down by the ratio of the cabin air pressure to sea-level air pressure in translating to the cabin environment.

4. Conclusions

The aircraft cabin is different from other indoor environments because of the low relative humidity, high air-exchange rate, high occupant density, high surface-to-volume ratio, underpressurization, and the potential to experience high ozone levels. As in other indoor environments, ozone reactions with surfaces lower the ozone levels but produce secondary volatile products. In this study, ozone uptake and byproduct formation of individual materials were characterized through chamber experiments conducted at flight-relevant conditions. Consistently, VOC levels were higher with ozone than without; measured byproducts included formaldehyde, acetaldehyde, C₃ through C₁₀ saturated aldehydes, and the squalene oxidation products, acetone and 6-MHO. Due to limitations of available methods, only products that are chemically stable can be captured and analyzed using analytical methods employed here. Other, so-called “stealth” products are known to be formed from ozone-initiated chemistry, including radicals and labile organics (Weschler, 2006).

Deposition velocities and molar yields measured from the experiments were combined with the typical proportions of surfaces in the cabin to estimate the relative contributions of surfaces to ozone consumption and emissions. The majority of both could be attributed to seat fabric and clothing, particularly soiled clothing. An important implication of these results is that ozone reactions are occurring on or very near the crew and passengers, which may be significant for exposure. Another important implication is that occupant density in the cabin would likely influence the levels of both ozone and its reaction byproducts in cabin air.

Emissions profiles measured in the chamber experiments were consistent with those measured in a simulated cabin environment (Wisthaler et al., 2005). Certain aspects of surface-ozone chemistry can be explored in chamber experiments with the advantage that materials can be isolated and efficiently tested under many well-controlled conditions. The present results advance our understanding of the role of ozone-initiated chemistry in influencing cabin air quality.

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Figure Captions

Fig. 1. Ozone deposition velocity (3-h average) to three common fabrics: cotton, wool, and polyester. The “laundered” sample was washed a few days prior to being exposed to ozone, the “soiled” sample was worn near the skin for 8 h prior to exposing it to ozone, and the “KI-coated” sample represents the maximum reactivity of a material for the given experimental conditions.

Fig. 2. Screening experiment data mapped onto deposition velocity model (Cano-Ruiz et al., 1993).

Fig. 3. Emission rates of selected volatile organic compounds from (a) new and used common cabin materials and (b) laundered and soiled clothing fabrics. For each material presented, the left bar represents the average emissions without ozone during a 180-minute conditioning period (no ozone), and the right bar represents the average emissions during the initial 90-minute ozone exposure period. The number above the right bar is the 90-minute average residual ozone concentration in ppb. Error bar indicates plus one standard deviation from analysis of replicate integrated samples.

Fig. 4. Molar yields of the sum of C₁ through C₁₀ saturated aldehydes, acetone, and 6-MHO from new and used cabin materials and laundered and soiled clothing fabrics during first 90 minutes of exposure to 160 ppb ozone (supply level) at 10% RH.

Fig. 5. Emission rates from cotton exposed to varying levels of ozone under different relative humidity conditions. For each material, the left bar represents the average emission rates without ozone during a 180-minute conditioning period (no ozone), and the right bar represents the average emissions during the initial 90-minute ozone exposure period. The number above the right bar is the 90-minute average residual ozone concentration in ppb. Error bar indicates plus one standard deviation from analysis of replicate integrated samples.

Fig. 6. Ozone reactivity profile of four materials exposed to a consistent set of conditions. Residual ozone level is the ozone level measured at the exhaust of the chamber; the supply level was 80 ppb.

Fig. 7. Contribution of major cabin surfaces to (a) total cabin surface area, (b) ozone consumption, and (c) byproduct emissions. Surface areas are estimated for a fully occupied Boeing 737 plane.

Figure 1

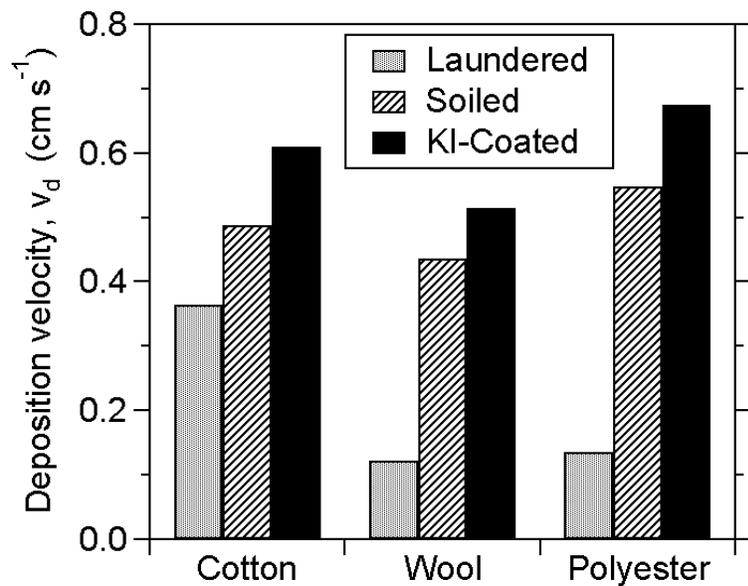


Figure 2

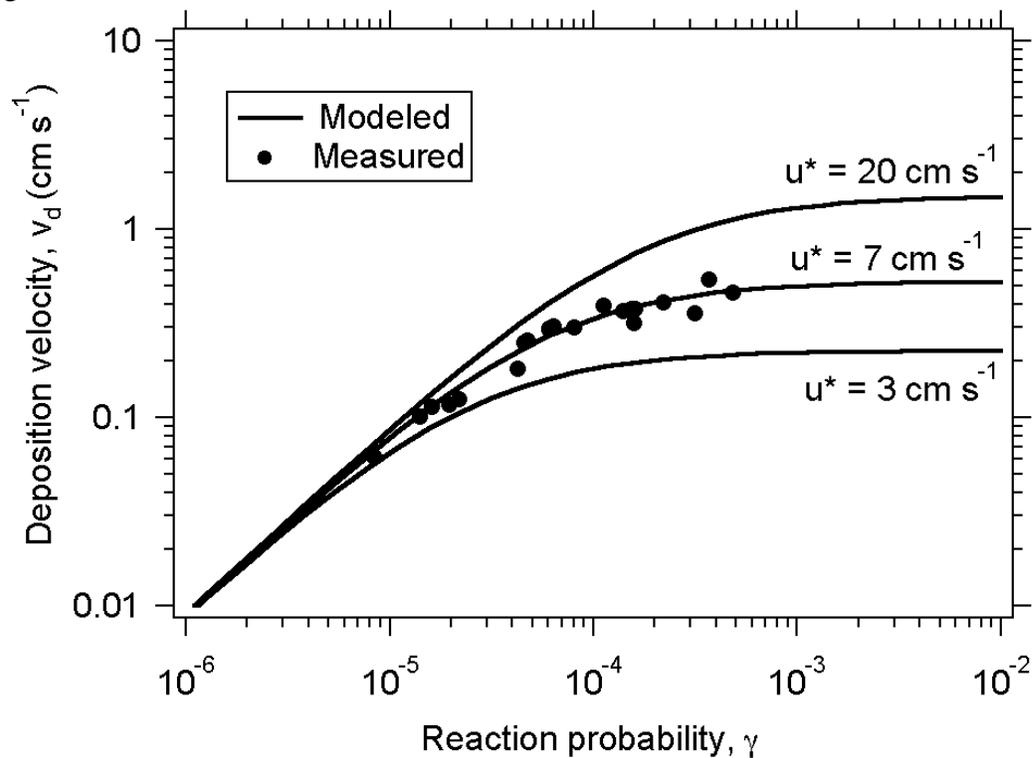


Figure 3

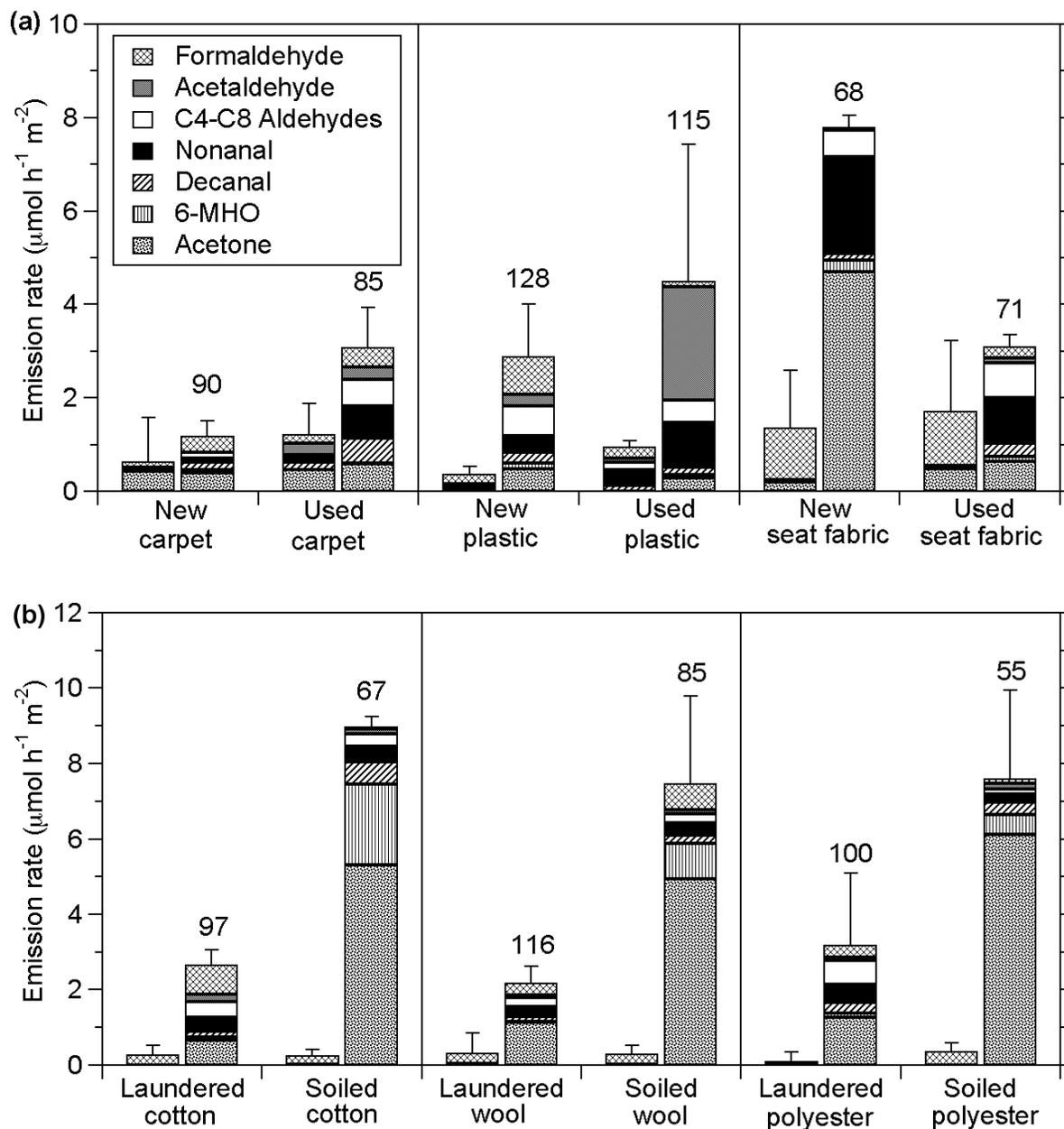


Figure 4

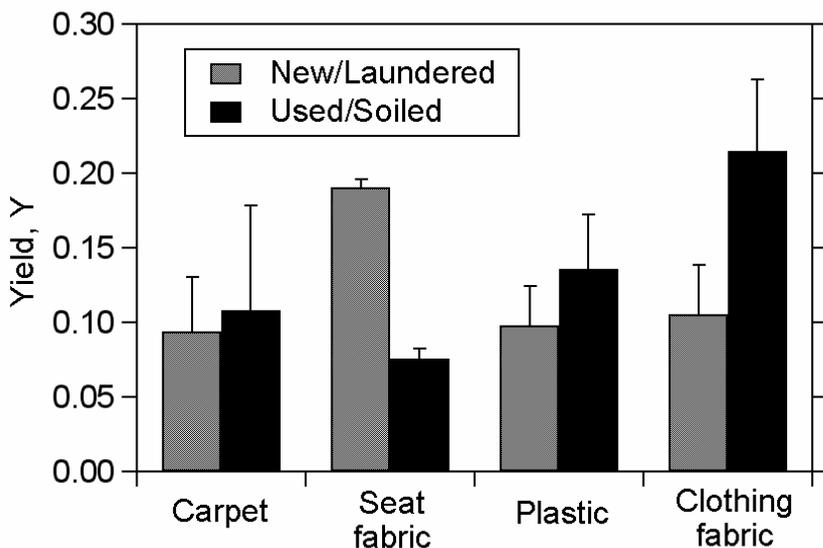


Figure 5

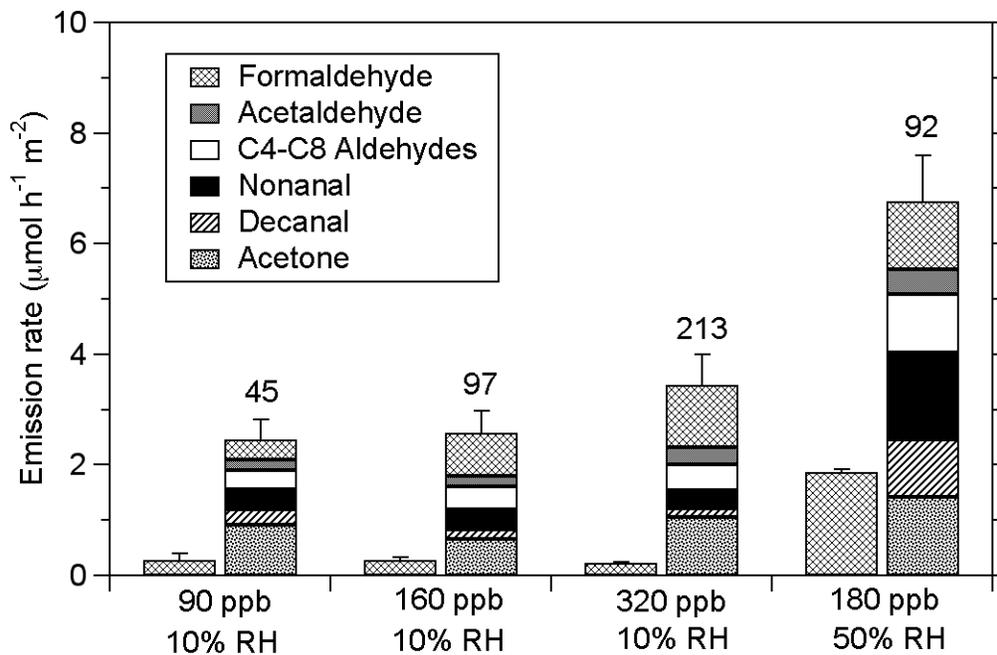


Figure 6

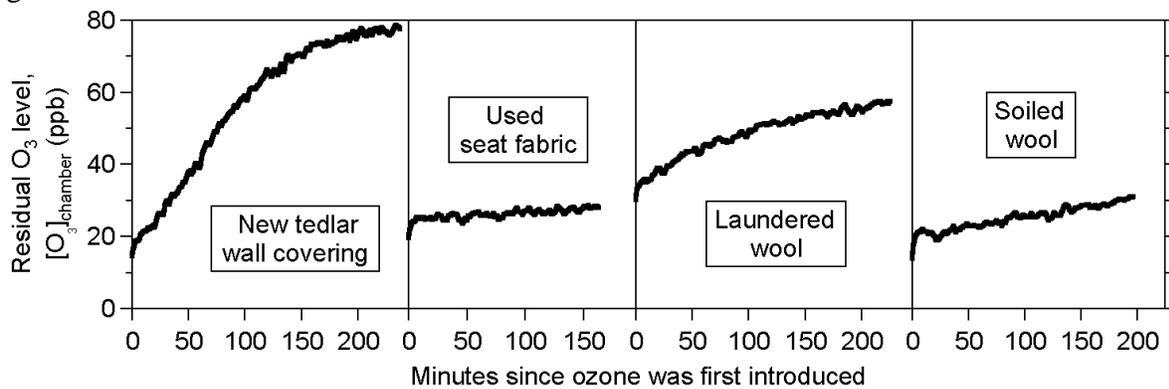
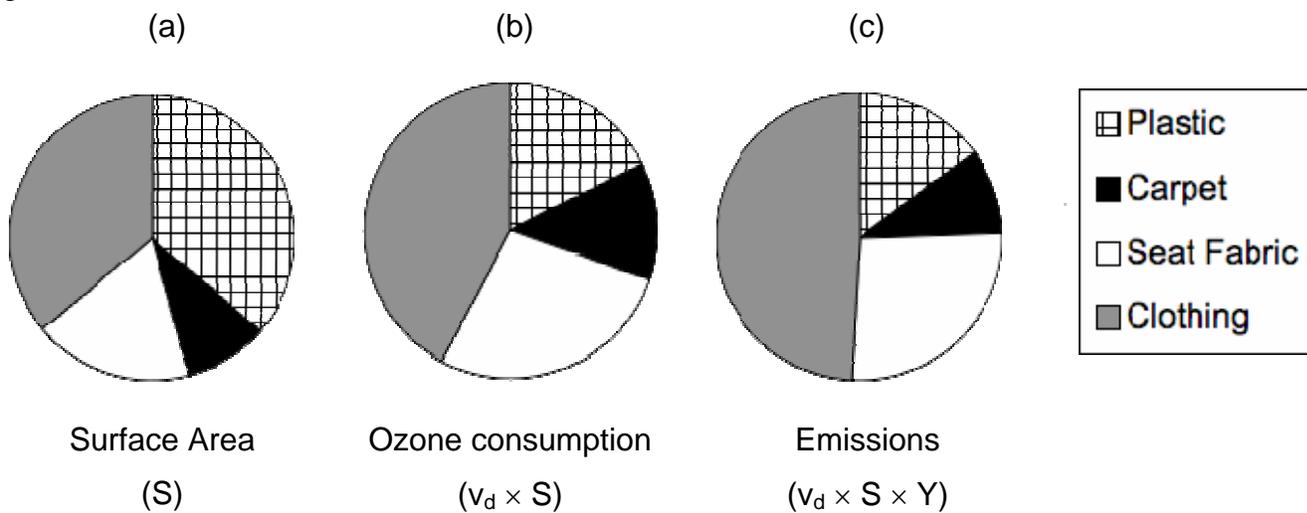


Figure 7



Tables

Table 1: Initial, final and 3-h average ozone deposition velocities ($v_{d,15\text{ min}}$, $v_{d,195\text{ min}}$, and $v_{d,av}$, respectively) and 3-h average reaction probability (γ_{av}) for 22 cabin materials. The reaction probability was calculated using equation 4 where the 3-h average deposition velocity was used for v_d .

Material Category	Material Description	$v_{d,15\text{ min}}$ (cm s^{-1})	$v_{d,195\text{ min}}$ (cm s^{-1})	$v_{d,av}$ (cm s^{-1})	γ_{av}^*
Carpet	New Carpet 1	0.61	0.17	0.30	6.3×10^{-5}
	New Carpet 2	0.68	0.30	0.39	1.1×10^{-4}
	New Carpet 3	0.87	0.11	0.30	6.4×10^{-5}
	New Carpet 4	0.49	0.21	0.26	4.7×10^{-5}
	New Carpet 5	0.95	0.38	0.54	3.7×10^{-4}
	New Carpet 6	0.68	0.14	0.30	6.1×10^{-5}
	New Carpet 7	0.38	0.22	0.25	4.6×10^{-5}
	New Carpet 8	0.60	0.18	0.30	6.0×10^{-5}
	Used Carpet 1	0.73	0.18	0.32	1.6×10^{-4}
	Used Carpet 2	1.08	0.18	0.36	3.1×10^{-4}
Clothing Fabric	Laundered Cotton	0.40	0.22	0.30	8.0×10^{-5}
	Soiled Cotton	0.73	0.31	0.41	2.2×10^{-4}
	Laundered Wool	0.22	0.06	0.10	1.4×10^{-5}
	Soiled Wool	0.52	0.28	0.37	1.4×10^{-4}
	Laundered Polyester	0.37	0.05	0.11	1.6×10^{-5}
	Soiled Polyester	0.55	0.37	0.46	4.8×10^{-4}
Seat fabric	New Seat Fabric	0.37	0.33	0.38	1.5×10^{-4}
	Used Seat Fabric	0.36	0.36	0.38	1.6×10^{-4}
Plastic	New Tedlar Wall Covering 1	0.77	0.02	0.13	2.2×10^{-5}
	New Tedlar Wall Covering 2	0.46	0.02	0.12	2.0×10^{-5}
	New Plastic 1	0.89	0.02	0.18	4.2×10^{-5}
	New Plastic 2	0.72	0.01	0.06	8.4×10^{-6}

* Mass transport limited deposition velocity used to calculate reaction probability for each material type: new carpet, $v_t = 0.65 \text{ cm s}^{-1}$; used carpet, $v_t = 0.32 \text{ cm s}^{-1}$; cotton, $v_t = 0.52 \text{ cm s}^{-1}$; wool, $v_t = 0.46 \text{ cm s}^{-1}$; polyester, $v_t = 0.57 \text{ cm s}^{-1}$; seat fabric, $v_t = 0.52 \text{ cm s}^{-1}$; plastic, $v_t = 0.34 \text{ cm s}^{-1}$