Ozone initiated reactions and human comfort in indoor environments

Tamas, Gyöngyi

Publication date: 2006

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Ozone Initiated Reactions and Human Comfort in Indoor Environments

Ph.D. Thesis
Gyöngyi Tamás

Supervisors:
Prof. P. Ole Fanger
Prof. Charles J. Weschler
Ass. Prof. Jørn Toftum

International Centre for Indoor Environment and Energy
Department of Mechanical Engineering
Technical University of Denmark

December 2005
# Table of Contents

TABLE OF CONTENTS ........................................................................................................... I

PREFACE ............................................................................................................................... III

SHORT SUMMARY ............................................................................................................... V

RESUMÉ ................................................................................................................................. IX

LIST OF PAPERS .................................................................................................................. XIII

THESIS SUMMARY ............................................................................................................. 1

INTRODUCTION .................................................................................................................... 1

FORMATION AND OCCURRENCE OF OZONE ................................................................... 1

INDOOR OZONE AND RELATED CHEMISTRY ................................................................. 3

THE EFFECT OF OZONE AND RELATED CHEMISTRY ON HEALTH AND COMFORT ............... 6

*The direct effect of ozone on humans* .............................................................................. 7

*Reported effects resulting from exposures to the products of ozone-initiated chemistry* ........ 8

AIM AND OBJECTIVES ......................................................................................................... 13

EXPERIMENTAL OVERVIEW ............................................................................................. 14

CONCLUSIONS .................................................................................................................... 25
**Table of Contents**

FUTURE WORK .......................................................................................................................... 29

REFERENCES ............................................................................................................................ 31

PUBLICATIONS .......................................................................................................................... 39

ARTICLES IN PEER-REVIEWED JOURNALS ................................................................. 41

  PAPER 1: INFLUENCE OF OZONE-LIMONENE REACTIONS ON PERCEIVED AIR QUALITY .......... 43
  PAPER 2: THE INFLUENCE OF OZONE/CARPET CHEMISTRY ON PERCEIVED AIR QUALITY ........... 75
  PAPER 3: FACTORS AFFECTING OZONE REMOVAL RATES IN A SIMULATED AIRCRAFT
  ENVIRONMENT ....................................................................................................................... 95
  PAPER 4: PRODUCTS OF OZONE INITIATED CHEMISTRY IN A SIMULATED AIRCRAFT ENVIRONMENT ................................................................................................................................. 131

ORIGINAL ARTICLES IN CONFERENCE PROCEEDINGS .............................................. 143

  PAPER 5: INFLUENCE OF OZONE-LIMONENE REACTIONS ON PERCEIVED AIR QUALITY .......... 145
  PAPER 6: ULTRA-FINE PARTICLES AS INDICATORS OF THE GENERATION OF OXIDIZED PRODUCTS ON
  THE SURFACE OF USED AIR FILTERS .................................................................................. 153
Preface

The present Ph.D. thesis summarizes the author’s research work carried out at the International Centre for Indoor Environment and Energy at the Department of Mechanical Engineering, Technical University of Denmark from January 2002 to December 2005. Supervisors during the Ph.D. study were Professor P. Ole Fanger¹, Professor Charles J. Weschler² and Associate Professor Jørn Toftum¹.

I would like to express my sincere gratitude to my supervisors for their valuable advice and suggestions that helped me to carry out the research work and interpretation of the experimental results. 

I would also like to thank Professor David Wyon for his valuable advice in writing scientific papers and his unlimited good ideas in carrying out my practical investigations.

I want to thank Armin Wisthaler for performing the chemical measurements in most of these studies.

Furthermore, I should acknowledge the research staff, technical-administrative staff, present and former colleagues, and the students at the International Centre for Indoor Environment and Energy who contributed to the accomplishment of the experiments.

I warmly thank my colleagues for their companionship throughout the years of my study.

I also thank the subjects who patiently participated in the subjective evaluations of these experiments.

This work has been supported by the Danish Technical Research Council (STVF) as part of the research program of the International Centre for Indoor Environment and Energy at the Technical University of Denmark and, partly through a sub-contract for the Airliner Cabin Environmental Research (ACER) Center of Excellence set up and funded by the U.S. Federal Aviation Administration.

Last but not least I want to thank Zsolt Bakó-Biró for being my closest not official tutor, for the endless discussions and for carrying out practical work involved in this research. Here I want to thank to my dear father, and all my friends for their support and concern in all these years.

Lyngby, 15 December 2005

Gyöngyi Tamás

¹ International Centre for Indoor Environment and Energy, Technical University of Denmark

² Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers University)
Chemical reactions between ozone and pollutants commonly found indoors have been suggested to cause adverse health and comfort effects among building occupants. Of special interest are reactions with terpenes and other pollutants containing unsaturated carbon-carbon bonds that are fast enough to occur under normal conditions in various indoor settings. These reactions are known to occur both in the gas phase (homogeneous reactions) and on the surfaces of building materials (heterogeneous reactions), producing a number of compounds that can be orders of magnitude more odorous and irritating than their precursors.

The present thesis investigates the effects of ozone-initiated reactions with limonene and with various interior surfaces, including those associated with people, on short-term sensory responses. The evaluations were conducted using a perceived air quality (PAQ) method introduced by Fanger (1988). The experiments, involving hundreds of human subjects and subsequent physical and chemical measurements, were conducted under realistic indoor conditions in unfurnished office-like environments, in stainless-steel chambers and inside a full-scale model of a section of an airplane cabin.

These experiments have shown that the common occurrence of ozone and limonene at typical concentrations and ventilation rates encountered indoors can significantly reduce the perceived air quality even under conditions when these pollutants cannot be sensed if present.
by themselves. Many of the reaction products that are typical for ozone-limonene chemistry have been concomitantly identified with real time measurement using proton-transfer-reaction mass spectrometry (PTR-MS), at concentrations high enough to be responsible for the sensory effects reported. The stabilized reaction products of ozone-limonene chemistry including aldehydes, ketones and carboxylic acids are known to partition between the gas phase and condensed phase according to the vapour pressure specific to each compound. The concentrations of condensed phase products, which can be easily detected by ordinary particle counters, were shown to be proportional to the magnitude of the sensory responses. However, the particles themselves did not appear to be the primary causative agent, but instead are co-varying surrogates for sensory offending gas-phase species.

The experiments involving heterogeneous reactions of ozone with various indoor materials also showed that these reactions can significantly alter the nature of emitted pollutants from indoor surfaces. One set of experiments with various carpet samples showed that although ozone initiated reactions reduced to some extent the initial strong odor of a new carpet, ozone exposure of old carpets significantly enhanced the emissions of odor offending compounds that can persist for hours and days after ozone exposure has ended.

The PTR-MS measurements conducted in the simulated aircraft cabin demonstrated that the presence of ozone had significantly increased the concentrations of numerous oxidized compounds in the air of the cabin environment. The most abundant oxidation products were saturated and unsaturated aldehydes and tentatively identified low-molecular-weight carboxylic acids. Some of these compounds were detected at concentrations high enough to trigger the human olfactory sense. When the cabin contained soiled T-shirts, as well as ozone,
the concentration of products derived from oxidized skin oil was significantly higher than when the cabin contained ozone alone.

Detailed measurements of ozone removal in the aircraft cabin, under systematically varied conditions have shown how different surfaces, including seats, recirculation filters and people themselves contribute to overall ozone removal. People are the largest ozone sink, removing almost 60% of ozone in the cabin and its recirculation system. The aircraft seats, that are contaminated with human bioeffluents and represent a large surface area in the cabin, were the second largest ozone sink, removing about 25% of the ozone. To a smaller extent ventilation filters (~7%) and other surfaces (~10%) also contributed to the removal of ozone.
Resumé

Reaktioner mellem ozon og typiske forureninger i indeluften er en potentielt årsag til negative effekter på menneskers komfort og sundhed. Særligt betydningsfulde er de hurtigt forløbende reaktioner med terpener og andre forureningskomponenter, der indeholder umættede kulstof-kulstof dobbeltbindinger. Disse reaktioner kan forløbe i både gasfase (homogene reaktioner) og på overfladen af materialer i bygninger (heterogene reaktioner), og produkterne omfatter forskellige komponenter, der kan være flere størrelsesordener mere lugtintensive og irriterende end de oprindelige udgangsstoffer.

Denne afhandling omhandler de umiddelbare sensoriske effekter på mennesker, der forårsages af produkter skabt af reaktioner mellem ozon og limonen samt mellem ozon og forskellige overflader i bygninger, inklusive menneskers overflader. Forsøgene har involveret flere hundrede forsøgspersoner samt målinger af fysiske og kemiske parametre under realistiske forhold i simulerede, umøblerede kontorer, i rustfrie stålkamre og i en fuldskala model af en sektion af en flykabine.

Forsøgene viste, at den samtidige tilstedeværelse af ozon og limonen i typiske koncentrationer og med typiske ventilationsrater kan forværre den opleved luftkvalitet sammenlignet med situationer, hvor henholdsvis ozon eller limonen optræder alene. Mange af de produkter, der er typiske for reaktioner mellem ozon og limonen er blevet identificeret via real-tids målinger.
Resumé

med proton-transfer-reaction mass spectrometry (PTR-MS) og produkternes høje koncentration var årsag til de observerede sensoriske effekter. De stabile reaktionsprodukter omfattede bl.a. aldehyder, ketoner og carboxyl syrer, som fordelte sig i gasfase og i flydende fase (partikler) i forhold til partialtrykket for den enkelte komponent. Koncentrationen af komponenter i flydende fase, som blev målt med en partikeltæller, var endvidere proportional med det sensoriske respons. Partikelkoncentrationen var i sig selv ikke den vigtigste faktor for det sensoriske respons, men anvendtes til at kvantificere koncentrationen af gas-fase produkter, der resulterede i oplevelsen af dårlig luftkvalitet.

Forsøgene der omhandlede heterogene reaktioner mellem ozon og forskellige byggematerialer viste, at reaktionerne kan ændre karakteren af forurenende stoffer, der emitteres fra byggematerialer. En forsøgsrække med forskellige gulvtæpper viste, at selvom ozon i nogen grad kan forbedre den ubehagelige lugt fra et nyt tæppe kan emissionen af forurenende komponenter fra gamle gulvtæpper blive forøget, en effekt der kan have betydning i selv timer og dage efter at ozonekspansionen er ophørt.

PTR-MS målingerne der blev gennemført i den simulerede flykabine viste, at ozon forøgede koncentrationen af adskillige oxiderede komponenter i luften i flykabinen. De hyppigst forekommende oxidationsprodukter var møttede og umøttede aldehyder, og de foreløbige analyser peger endvidere på carboxyl syrer med lav molekylmasse. Koncentrationen af nogle af disse komponenter var højere end menneskers lugttaerskel. Med brugte T-shirts i kabinen og samtidig dosering af ozon var koncentrationen af reaktionsprodukter fra oxidert hudfedt endvidere højere end med kun ozon i kabinen.
Detaljerede målinger af ozonnedbrydning i flykabinen under systematisk varierede forhold viste, hvordan forskellige overflader som sæder, recirkulationsfiltre og menneskers overflade reagerer med ozon. Mennesker fjernede den største andel af ozonen i luften i kabinen og dens ventilationssystem, næsten 60%. Flykabinens sæder, der var forurenset med bioefluenter og som repræsenterede et stort overfladeareal, fjernede næsten 25% af ozonen.

Ventilationsfiltrene fjernede ca. 7% og de øvrige overflader ca. 10%.
List of papers

The present thesis is based on published or submitted papers to peer-reviewed journals and to international conferences as listed below:

**Articles in peer-reviewed journals**

**Paper 1** / First author

*Influence of Ozone-Limonene Reactions on Perceived Air Quality*
Tamás, Gy., Weschler, C.J., Toftum, J., Fanger, P.O.

*In press, Indoor Air, 2005.*

**Paper 2** / First author

*The Influence of Ozone/Carpet Chemistry on Perceived Air Quality*
Tamás, Gy., Weschler, C.J., Toftum, J.

*Submitted to Indoor Air, in 2005.*

**Paper 3** / First author

*Factors Affecting Ozone Removal Rates in a Simulated Aircraft Environment*
Tamás, Gy., Weschler, C.J., Bakó-Birá, Zs., Wyon, D.P., Strøm-Tejsen, P.

*Submitted to Atmospheric Environment, in 2005.*

**Paper 4** / Joint first author

*Products of Ozone Initiated Chemistry in a Simulated Aircraft Environment*

**Original articles in conference proceedings**

**Paper 5** / First author

*Influence of Ozone-Limonene Reactions on Perceived Air Quality*

Tamás, Gy., Weschler, C.J., Toftum, J., Fanger, P.O.


**Paper 6** / Joint first author

*Ultra-fine Particles as Indicators of the Generation of Oxidized Products on the Surface of Used Air Filters*

Bekő, G., Tamás, Gy., Halás, O., Clausen, G., Weschler, C.J.,

INTRODUCTION

FORMATION AND OCCURRENCE OF OZONE

The word ozone comes from the Greek word “οζειν” meaning “to smell”, which reflects ozone’s sharp, irritating odour. Christian Friedrich Schönbein, professor at the University of Basel, Switzerland, discovered it in 1839 but J. L. Soret gave the chemical formulation a few years later in 1865 (Rubin, 2001). Ozone has a pungent odour and is often detected after a thunderstorm or when close to a poorly filtered photocopier.

In the stratosphere ozone is produced when ordinary oxygen molecules are split by ultraviolet radiation (\(\lambda<242\text{nm}\)) and the excited atoms then recombine with other oxygen molecules to make a molecule with three oxygen atoms. In turn, ozone absorbs certain kinds of ultraviolet light (200<\(\lambda<310\text{nm}\)) that are potentially harmful to living creatures. The highest concentration of ozone, about 10 ppm (parts per million) is reached between 15 and 30 km in the stratosphere. The average thickness of the ozone layer is about 50 km, but if compressed to sea-level pressures, it would be only a few millimeters thick (Finlayson-Pitts and Pitts, 1999).
At ground level most of the ozone results from photochemical reactions between substances of anthropogenic or natural origin. These reactions involve Volatile Organic Compounds (VOCs), and oxides of nitrogen (NOx) in the presence of sunlight (Logan, 1985). Contributions to ground level ozone concentrations may also include downward mixing of ozone from the stratosphere and to some extent lightning and ozone transport from other locations (Weschler, 2000). Hence, outdoor ozone levels tend to be highest in densely populated areas with abundant sunshine and also in areas that experience frequent meteorological inversions. Typical outdoor concentrations of ozone are between 10 and 100 parts per billion (ppb) at various locations. The concentrations are lower in winter time (<40 ppb) and higher in the summer, as the solar flux also varies with season. However, it is not unusual to have concentrations above 100 ppb in highly polluted cities, e.g. Mexico City, where ozone levels above 400 ppb have been measured (DEFRA, 1994; Finlayson-Pitts and Pitts, 1999; Weschler, 2000).

Ozone is commonly found in various indoor settings as a result of outdoor-to-indoor transport or direct emission from indoor sources. In some countries ozone generators are sold as “air purifiers”. Electrical devices may all act as source of ozone if corona discharge occurs during operation or malfunction. Concentrations of 20-40 ppb ozone are commonly reported indoors, but in extreme cases when outdoor concentration is high levels can exceed 100 ppb (Sabersky et al., 1973; Weschler et al., 1989; Weschler, 2000).

The chemical bond between the di-oxygen atoms can be artificially broken up by several methods including electric discharge, ultraviolet irradiation or chemical reaction. For the production of ozone the first two methods are commonly used in various applications. In the ozone production process both atmospheric and pure oxygen (e.g., from a compressed gas cylinder) can be used. When pure oxygen is used, a higher concentration of ozone is
produced. The preferred ozone generation method in the present experiments was irradiation with UV light, since this minimizes the production of nitrogen oxide by-products.

**INDOOR OZONE AND RELATED CHEMISTRY**

In the absence of indoor sources, indoor ozone concentrations are lower than concurrent outdoor concentrations due to removal by indoor surfaces, i.e. heterogeneous reactions and deposition (Cano-Ruiz et al., 1993), and, to a lesser extent, gas-phase reactions with ozone-reactive volatile organic compounds (VOCs) (Weschler, 2000). For a given indoor environment, at a constant air exchange rate and absent varying indoor sources, the indoor ozone concentration divided by the outdoor ozone concentration (I/O ozone) remains relatively constant in the range of 0.2 to 0.7 (Weschler, 2000 and references therein). According to Weschler (2000) the I/O ratio can be approximated by the ratio of the air exchange rate to the sum of the air exchange rate and the surface removal rate, \( \nu_d(A/V) \).

\[
\frac{I}{O} = \frac{ACH}{\nu_d\left(\frac{A}{V}\right) + ACH}
\]

where

ACH is the rate at which the indoor air is replaced with outdoor air (air exchange rate), [h\(^{-1}\)];

\( \nu_d \) is the ozone deposition velocity, [m/h];

A is the total surface area within the room, [m\(^2\)];

V is the volume of the room, [m\(^3\)].
Weschler also gives an equation for indoor ozone levels that accounts for airborne chemical reactions that remove ozone from the indoor air beside various sinks, and also for possible indoor sources in a space that would be ventilated without filtration.

\[
\frac{dO_3^{\text{indoors}}}{dt} = ACH \cdot O_3^{\text{outdoors}} + s(t) - O_3^{\text{indoors}} \left[ v_d \left( \frac{A}{V} \right) + ACH + \sum k_i(\text{chem}_i) \right]
\]

where

- \(O_3^{\text{indoors}}\) is the indoor ozone concentration, [ppb];
- \(O_3^{\text{outdoors}}\) is the outdoor ozone concentration, [ppb];
- \(s(t)\) is the time-varying rate at which ozone is being generated within the room, [ppb/h];
- \(\text{chem}_i\) is the concentration of the \(i^{th}\) (1st, 2nd, 3rd, etc.) chemical in the room air that reacts with ozone, [ppb];
- \(k_i\) is the second order rate constant for the reaction between ozone and the \(i^{th}\) chemical in the room air, [ppb/h].

The rate at which different surfaces remove ozone is highly dependent on the nature of the indoor surfaces as well as by the surface to volume ratio for a given material. The potential of various materials to remove/react with ozone has been reported in a number of studies. The ozone uptake of various sinks has been studied both in real environments (see Weschler, 2000 and references therein; Grøntoft and Raychaudhuri, 2004) and under special laboratory conditions (Klenø et al., 2001). These values are often reported to be between 1 h\(^{-1}\) and 8 h\(^{-1}\) depending on whether the surfaces are smooth (glass, steel) or fleecy (carpets, weave) and also whether chemical reaction can occur on them.
To indicate the net effect of a surface on the ozone removal in a space it is more useful to work with ozone deposition velocities that are dependent mainly on the nature of the indoor materials. For a reactive gas such as ozone, the deposition velocity depends on the mass transfer coefficient, defined as the ratio between the mass flux of ozone to a surface (µg/m²·h) and its concentration (µg/m³) in the boundary layer of the surface, and by the rate of ozone reaction with the surface (Cano-Ruiz, et al., 1993; Morrison et al., 2000 and references therein). Apart from the nature of the surfaces, the deposition velocity is influenced by several climatic factors, such as indoor temperature (slight effect), relative humidity and indoor air flow conditions (Nazaroff et al., 1993; Grøntoft and Raychaudhuri, 2004). Typical values of deposition velocities to different indoor surfaces range between 0.01 and 0.08 cm s⁻¹ (Nazaroff et al., 1993). For specific materials, measured ozone deposition velocities cover an even wider range -- from 0.0007 (lacquered ash) to 1.5 (office paper) cm s⁻¹ (Klenø et al., 2001).

Finally indoor ozone levels are also influenced by chemical reactions occurring in the gas phase. These are limited by the value of the second order rate constant between ozone and a chemical in room air. For a homogeneous chemical reaction to influence an indoor setting, it must occur at a rate that is comparable to, or faster, than the air exchange rate (Weschler and Shields, 2000). Only a subset of organic compounds in indoor air reacts fast enough with ozone to compete with typical air exchange rates. Air exchange rate also influences the concentration of reactants and hence the reaction rate. It should be noted that increasing the indoor ventilation rate has a beneficial effect since this reduces the concentration of indoor pollutants and the time available for gas-phase reactions, although increased ventilation means more ozone is transported indoors. The chemicals that do react with ozone at a sufficiently fast rate for the reaction to be completed within the chemicals’ residence time
contain one or more unsaturated (double) carbon-carbon bonds (e.g., terpenes). The reaction with ozone leads to the breaking of the double bond and the reaction proceeds with the formation of an unstable ozonide called a molozonide. These ozonides quickly decompose, forming Criegee biradicals and primary products containing a carbonyl group. The energy rich Criegee intermediates then rearrange or may be involved in multiple reaction steps to give further products. The stable oxidation products include a number of aldehydes (saturated and unsaturated) and organic acids with low odour thresholds (Criegee, 1975; Geletneky and Berger, 1998). The intermediate reactions have been demonstrated also to produce highly reactive species such as hydroxyl radicals (OH) and hydrogen peroxide (H$_2$O$_2$), which in turn can further react with compounds that originally would not be oxidized by ozone itself (Weschler and Shields, 1997a, 1997b; Fick et al., 2002; Sarwar et al., 2002; Fan et al., 2003). Both primary and secondary products can exist in the gas phase and in the condensed phase; the distribution between these phases depends on the vapor pressure of the compound and the surface area of existing airborne particles. Low vapor pressure products condense and absorb on pre-existing particles and smaller particles, to a lesser extent, coagulate to form larger particles. This mechanism contributes to the size and mass growth of particles (Weschler and Shields, 1999 and 2003; Wainman et al., 2000; Long et al., 2000; Rohr et al., 2003; Sarwar et al., 2003). These particles are often referred to as Secondary Organic Aerosols (SOA).

**THE EFFECT OF OZONE AND RELATED CHEMISTRY ON HEALTH AND COMFORT**

Ozone may affect the health of building occupants through different pathways. Due to its molecular structure ozone is a strong oxidant and is, by itself, a potential hazard to all living creatures, including humans. Ozone can also react with other substances commonly found
indoors, as described above, to produce compounds that are more odourous and irritating than their precursors.

The direct effect of ozone on humans

The severity of adverse effects caused by ozone depends on both concentration and the duration of exposure. Since people spend most of their time in buildings, their indoor ozone exposure (concentration x time) is often larger than their outdoor exposure, even though ozone concentrations are usually lower indoors than outdoors (Weschler et al., 1989; Zhang and Lioy, 1994). Traditionally, the decrement in lung function was the most-studied parameter of ozone effects (WHO, 1995). Exposure to low concentrations of ozone initially increases the reactivity of the airways to other inhaled substances (bronchial hyper-responsiveness) and causes an inflammatory response in the respiratory tracts. Furthermore, ozone aggravates chronic diseases such as emphysema, bronchitis and asthma and makes it more difficult for the lungs to fight off infections (US EPA, 1996). The negative effects of ozone become more pronounced during exercise or at elevated work levels. Ambient ozone levels were also shown to cause increased daily mortality and hospitalisation due to respiratory dysfunctions. Bell et al. (2004) estimated a 0.52% increase in daily mortality and a 0.64% increase in daily mortality in cardiovascular and respiratory mortality in 95 large US communities during a 14 year period for a 10 ppb increase in the previous week’s local ambient ozone level. To prevent the risks associated with ozone exposure indoors, occupational limits have been derived in different parts of the world (Table 1).
Table 1. Ozone occupational exposure limits

<table>
<thead>
<tr>
<th>Country</th>
<th>TWA ppb (mg/m³)</th>
<th>STEL ppb (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denmark (IPCS)¹</td>
<td>100 (0.2)</td>
<td></td>
</tr>
<tr>
<td>Sweden (IPCS)</td>
<td>100 (0.2)</td>
<td>300 (0.6)</td>
</tr>
<tr>
<td>USA (ACGIH²)</td>
<td>80 (0.16)</td>
<td></td>
</tr>
<tr>
<td>USA (NIOSH³/OSHA⁴)</td>
<td>100 (0.2)</td>
<td>300 (0.6)</td>
</tr>
<tr>
<td>USA (EPA⁵)</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>WHO⁶</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td></td>
<td>60</td>
</tr>
</tbody>
</table>

¹ International Programme on Chemical Safety (IPCS)
² American Conference of Governmental Industrial Hygienists (ACGIH), 2000
³ National Institute for Occupational Safety and Health, 2005
⁴ Occupational Safety & Health Administration, 1989
⁵ Environmental Protection Agency, 1996
⁶ World Health Organisation, 1997

TWA = Time Weighted Average for 8 work hours
STEL = Short Term Exposure Limit

Reported effects resulting from exposures to the products of ozone-initiated chemistry

Several studies conducted over the past few years indicate that the chemical emission of compounds from various indoor materials can be substantially altered at ozone levels typically occurring indoors. Weschler et al., (1992) showed that the concentrations of compounds (including styrene, 4-vinylcyclohexene, and 4-phenylcyclohexene) originating from various carpet samples were considerably reduced inside a 20 m³ chamber when ozone was present at concentrations between 30 and 50 ppb. However, this decrease was accompanied by an increase in the concentration of a series of aldehydes, such as formaldehyde, acetaldehyde, benzaldehyde and C5- to C10-aldehydes. These findings were later confirmed by Morrison and Nazaroff (2002) who indicated that the reaction products also included carboxylic acids and mostly originated from surface chemistry and to a lesser extent from gas phase reactions. The authors also underlined that 2-nonenal, a highly
odourous compound resulting from ozone-carpet chemistry, may negatively affect perceived air quality over years after a new carpet is installed in buildings.

Many studies and reviews of the literature (Mendell, 1993; Wargocki et al., 1999; Peijersen et al., 2001; Mathisen et al., 2002; Mendell and Heath, 2005), acknowledged the negative impact of carpets on perceived air quality and health symptoms of building occupants. However, in most of these studies ozone levels were not measured or reported and therefore little is known to what extent the complaints are due to chemical compounds originating from indoor ozone chemistry. Knudsen et al. (2003) studied the interaction of ozone with unused carpets and other building materials and also the effects of the reaction products on the air quality assessed by human subjects in 50 L test chambers. They found that their carpet sample showed significantly higher odour intensity when exposed to ozone; the ozone-exposed sample had a clear negative sensory evaluation. They also showed that the ozone removal was caused primarily by interactions with the carpet’s surfaces and only to a minor extent by gas-phase reactions. In another investigation Knudsen et al. (2002) showed that a previous 50 ppb ozone exposure in an office ventilated with $0.3h^{-1}$ outdoor air negatively affected perceived air quality 16 hours after the ozone exposure ceased. Moreover, when samples of rug and papers were introduced into a low polluting office environment the perceived air quality (PAQ) was deteriorated to a larger extent after ozone exposure (at about 50 ppb) compared to a condition when ozone was absent. At higher air change rates ($1.0$ and $3.0 h^{-1}$) the PAQ was unaffected by ozone and the ozone-limonene combination.

Several other studies have shown that ozone initiated chemistry causes significant changes in emissions from materials containing linseed oil or other natural oil based products containing chemicals with unsaturated carbon bonds and may also induce negative sensory responses
(Jensen et al., 1996; Morrison and Nazaroff, 2002, Knudsen et al., 2003). Apart from building materials ozone initiated chemistry can also occur on the surface of used ventilation filters (Hyttinen, 2003; Bekö et al., 2005). Based on their studies, Bekö et al. have hypothesized that ozone chemistry is one of the causal factors of the reduced PAQ downstream of ventilation filters that has been commonly reported (Clausen 2004, and references therein). A negative interaction between ozone and house dust particles has recently been reported (Mølhave et al., 2005). The authors found that simultaneous exposure to ozone and dust in the air causes a larger increase in discomfort measures and a larger subsequent decrease in peak expiratory flow than either ozone or dust exposures separately.

As mentioned in the previous sections, the stable products originating from gas-phase reactions of ozone with various indoor pollutants partition between the gas phase and the condensed phase. Since these two phases continue to co-exist in the environment after the reactions occur, it is difficult to differentiate their individual contributions to the health and comfort effects attributed to such chemistry. In addition to that most of the reaction products are sensory offending and potential irritants, the exposure to elevated ultra fine particle concentration could represent an additional health hazard (see later in this section on the effects of particles).

The simultaneous occurrence of ozone and terpenes such as d-limonene and α-pinene and thus the likelihood of their airborne reaction in an indoor environment is relatively common. Scented products such as air fresheners, cosmetics and household cleaners can represent significant sources of terpenes indoors. These products are widely used in homes and non-industrial work places to impart pleasant odours and to counteract malodours originating from a variety of indoor sources, including human activities. In addition to their intended benefits,
these products emit significant quantities of chemicals that may cause adverse health effects or may react to yield harmful secondary products (Nazaroff and Weschler, 2004). Research to investigate related health and comfort effects has mainly focused on the reaction products resulting from ozone-limonene and ozone - α-pinene because of the fast reaction kinetics and substantial contribution to the formation of ultra fine particles indoors (Fan et al., 2003). Limonene oxidation products have been shown to cause eye irritation and increased blinking frequency of male subjects exposed for 20 minutes (Klenø and Wolkoff, 2004; Klenø-Nøjgaard et al., 2005). Knudsen et al. (2002) also found that decreasing the air change rate from 1.0 to 0.3 h⁻¹ in an office-like environment deteriorated the PAQ, and the effect was most pronounced in the presence of ozone and limonene compared to the conditions where ozone and limonene were individually introduced. The health effects of ozone gas phase reaction products were also investigated in another extensive experiment (Fiedler et al., 2005; Laumbach et al., 2005 and Fan et al., 2003 and 2005). Although this study confirmed the formation of respirable particles as a result of reaction between ozone and a VOC mixture that contained d-limonene and α-pinene, no significant increase in the studied symptoms and clinical measures of 130 healthy women was observed as a result of exposure to the reaction products relative to a condition when only VOCs were present.

At present, the health effects of particles originating from the gas-phase reaction with indoor pollutants are little known. Historically there is great interest in airborne particles due to the health disasters resulting from ambient air pollution involving particles in the middle of the last century (Brimblecombe, 1977; Firket, 1936; Mills, 1950, Ministry of Health, 1954). More recently a number of epidemiological studies have shown a correlation between increased levels of airborne particles and increased morbidity and mortality. Such correlations have been observed even at particle concentrations below current US and European standards.
Thesis Summary

(Dockery et. al. 1993, Schwartz et al. 1996). In spite of the correlations reported in the epidemiological literature, there is no clear information about the effects of indoor particles on human health (Schneider, 2003). A major review of the literature (Wallace, 1996) on particle concentrations and sources showed that indoor particle levels may be even higher than outdoors due to a number of important sources such as smoking, cooking and in some case kerosene heaters that sometimes are present in US homes. Higher indoor levels of PM compared to outdoor levels at different sites were also indicated by the measurements conducted in the Harvard 6 City Study (Dockery et. al. 1993). A possible explanation to the observed discrepancies between the indoor and outdoor PM level, even if there are no apparent indoor sources present, may be given by the ozone-initiated chemistry that results in significant SOA production indoors.
AIM AND OBJECTIVES

In spite of the ongoing research investigating many aspects of ozone-initiated chemistry, there is only limited knowledge available on the occurrence of such chemistry in real indoor environments that evaluate the subsequent subjective effects on humans. Data are even scarcer regarding the effects of ozone chemistry in special environments with high ozone levels, such as in aircraft cabins. Ozone deposition on various surfaces has been measured and adequate models have been developed and reported in the literature. However little is known about how occupants contribute to ozone depletion through their surfaces and inhalation.

The main objective of this Ph.D.-study was to investigate the associations between exposure to products of ozone initiated chemistry and human sensory evaluations of air quality, with subsequent measurements to characterize the physical and chemical processes occurring in realistic indoor environments.

The specific objectives were:

- To examine the sensory effects of ozone-limonene chemistry at various concentrations of the reactants in a realistic environment. (Papers 1 and 5)
- To evaluate the sensory effect of ozone exposure on the emissions from new and old carpet samples in 30 m$^3$ chamber environments. (Paper 2)
- To study ozone dynamics in an aircraft environment. (Paper 3)
- To evaluate in real time the chemical products originating from surface and gas-phase chemistry. (Paper 4)
- To examine effects of ozone initiated chemistry on ventilation filters. (Paper 6)
EXPERIMENTAL OVERVIEW

The experiments described in the present PhD research were carried out in the facilities of the International Centre for Indoor Environment and Energy (ICIEE) at DTU in three main locations: four low polluting adjacent test offices, two stainless steel twin chambers and a simulated aircraft cabin. Overviews of the experiments, their locations, objectives and main conclusions are summarized in Table 2. This table also contains the identities of the publications where the results from the experiments are presented. The experiments investigated two broad areas of ozone-initiated chemistry: the first set of experiments was designed to evaluate the sensory effects of reaction products originating from ozone-limonene chemistry; the second set of experiments was designed to investigate interactions of ozone with various surfaces, including humans and their bioeffluents, and the subsequent effects on perceived air quality.

In these investigations short-term sensory responses were used to evaluate the effects of ozone-initiated reactions on people. The evaluations in most of the experiments included assessment of perceived air quality (PAQ), odour intensity, air freshness and dryness on adequate subjective scales commonly used (Fanger, 1988, Clausen, 2000). In each experiment a panel of 20-30 staff members and students from the ICIEE were included in the sensory evaluations. The various aspects of the air quality were assessed individually by each subject shortly after they walked into the test environment and spent no more than 1-2 minutes to complete the questionnaires.
<table>
<thead>
<tr>
<th>No</th>
<th>Experiment</th>
<th>Date</th>
<th>Environment</th>
<th>Aim</th>
<th>Findings</th>
<th>Publication*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ozone-limonene sensory evaluation</td>
<td>2003 Spring</td>
<td>4 low polluting, unfurnished test rooms</td>
<td>Direct sensory comparison of ozone /limonene reaction products with precursors using different ozone and limonene concentrations</td>
<td>The PAQ was poorer when ozone and limonene were present together compared to when only ozone or only limonene was present</td>
<td>Paper 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Paper 5</td>
</tr>
<tr>
<td>2</td>
<td>Limonene odour recognition</td>
<td>2003 Summer</td>
<td>3 low polluting, unfurnished test rooms</td>
<td>Direct sensory comparison of three limonene concentrations</td>
<td>The odour of limonene was recognized by more than 50% of the sensory panel at 85 ppb, a level that is lower than the detection limits in some of the older literature</td>
<td>Paper 1</td>
</tr>
<tr>
<td>3</td>
<td>Ozone-limonene sensory evaluation with filtration</td>
<td>2003 Summer</td>
<td>2 low polluting, unfurnished test rooms</td>
<td>Direct sensory and objective comparisons of unfiltered / filtered reaction air</td>
<td>The filtration of ozone-limonene products removed a fraction of the condensed-phase species as well as a fraction of the gas phase pollutants; this improved the perceived air quality</td>
<td>Paper 1</td>
</tr>
<tr>
<td>4</td>
<td>Ozone-limonene sensory evaluation with different ozone generation methods</td>
<td>2005 Summer</td>
<td>2 stainless-steel chambers</td>
<td>Direct sensory and objective comparisons of two ozone generation methods (with room air vs. tank oxygen)</td>
<td>Ozone generation using room air resulted in a higher particle yields and better perceived air quality compared to the method using pure oxygen</td>
<td>Paper 1</td>
</tr>
</tbody>
</table>
### Table 2 (Continued)

<table>
<thead>
<tr>
<th>No</th>
<th>Experiment</th>
<th>Date</th>
<th>Environment</th>
<th>Aim</th>
<th>Findings</th>
<th>Publication*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Ozone carpet sensory evaluation</td>
<td>2005 Spring</td>
<td>2 stainless-steel chambers</td>
<td>Direct sensory comparisons of emissions from carpet in the presence and absence of ozone; objective measurement of ozone removal rates &amp; deposition velocities</td>
<td>Ozone exposure diminishes new carpet’s odour, however, it significantly increases the emission of sensory offending secondary pollutants during most of a carpet’s service life</td>
<td>Paper 2</td>
</tr>
<tr>
<td>6</td>
<td>SOA measurements downstream of an ozone exposed loaded filter</td>
<td>2004 Autumn</td>
<td>low polluting, unfurnished test room and test-rig</td>
<td>Objective comparison of particle counts downstream of a loaded filter in the presence and absence of ozone</td>
<td>The downstream / upstream ratio of ultra fine particles was higher when ozone was present – evidence of chemistry occurring on filter</td>
<td>Paper 6</td>
</tr>
<tr>
<td>7</td>
<td>Ozone exposure of soiled T-shirt with human bioeffluents</td>
<td>2003 Autumn</td>
<td>simulated aircraft cabin</td>
<td>Objective comparisons of products originating from ozone / surface chemistry in the presence and absence of soiled T-shirts</td>
<td>The addition of ozone to the environment increased the concentration of numerous pollutants. This was more pronounced in the presence of soiled T-shirts</td>
<td>Paper 3, Paper 4</td>
</tr>
<tr>
<td>8</td>
<td>Ozone dynamics</td>
<td>2004-2005</td>
<td>simulated aircraft cabin</td>
<td>Evaluation of ozone removal rates under different conditions related to filtration and to the presence of people</td>
<td>Ozone removal in simulated aircraft: people (59%), seats (26%), loaded HEPA filter (7%), other surfaces (10%)</td>
<td>Paper 3</td>
</tr>
</tbody>
</table>

* See the section entitled: “List of papers” (Page xiii-xiv) for the title of the papers
In Experiment 1 (Table 2) short-term assessment of perceived air quality was carried out for six different realistic concentrations of ozone and limonene, separately or together, in room air. The evaluations were made in four identical 40 m$^3$ unfurnished low-polluting test offices ventilated with outdoor air at 1.4 h$^{-1}$. One office where neither ozone nor limonene was introduced was always used as a reference exposure. A second office contained different levels of ozone. In a third office different levels of limonene were maintained (using a pump, a bubbler and a flow meter to achieve a controlled flow of limonene-saturated air from the bubbler). In the fourth office ozone and limonene were generated at the same rates as ozone in the second and limonene in the third room.

The results showed a clear negative effect on the perceived air quality when ozone and limonene co-existed in the room air. The negative effects were attributed to the reaction products originating from the ozone limonene homogeneous chemistry, which are consistent with the findings of earlier research studies (Knudsen et al., 2002; Klenø and Wolkoff, 2004; Klenø-Nøjgaard et al., 2005). Besides the above results, a correlation was observed between the number of secondary organic aerosols produced by a given ozone/limonene condition in the test offices and the sensory pollution load for that condition. However, the results of Experiment 1 raised several issues that initiated further investigations:

- Based on the assessments of air quality in the test rooms containing only limonene was observed that limonene’s odour alone altered to some extent PAQ in the test rooms even at concentrations below some reported odour threshold limits (Devos et al., 1990). However, this effect was much lower in magnitude than those attributed to the reaction products resulting from the related ozone-limonene chemistry.
• Questions were also raised whether simple filtration of air containing ozone-limonene reaction products would have beneficial effects on the pollutant levels and sensory evaluations.

• In Experiment 1 ozone was photochemically generated using a UV lamp contained in a small glass box placed in, and drawing its air from, the test room. Hence, in the test rooms in which ozone was generated using room air a small fraction of air (1/30th of the outdoor airflow rate) was photolized in the generator that may have affected the ozone-limonene chemistry and possibly the resulting sensory effects as well.

Subsequent investigations (Experiment 2, 3; Table 2) addressing the first two questions were conducted in the same test facilities. To determine the range of odour recognition for limonene, the same concentrations were reproduced as in the initial experiments in the absence of ozone. The sensory panel voted at this time for the character of the odour, such as no odour, metal, wood, fruit, car exhaust and “other” odours. A subject marking “fruit” was considered to have recognized the odour of limonene. The results revealed that the odour of limonene was recognized by more than 50% of the sensory panel at 85 ppb, a level that is lower than some detection limits reported in the literature (e.g., 438 ppb; Devos et al., 1990) and are more consistent with the odour threshold of 40 ppb reported in Nagata et al. (2003).

The effect of filtration was studied in two adjacent offices (Experiment 3, Table 2). In one of the offices ozone and limonene were generated at rates that would result in concentrations of 45 ppb and 115 ppb, respectively, if only ozone or only limonene had been present in the office. The air from this room (containing the reaction products of ozone-limonene) was transported through a standard EU-7 bag filter to the adjacent office by means of a simple duct system and fan. This investigation showed that the filter removed a fraction of the condensed-phase species as well as a fraction of the gas phase pollutants; this improved the
perceived air quality. The concentration of secondary organic aerosols was less in the room containing filtered air not only because some aerosol was removed by filtration, but also due to less ongoing generation of SOA given the lower concentration of ozone.

The third question regarding the effects of ozone generation method was studied in a follow-up experiment at a later time (Experiment 4) and it was not possible to use the same test facilities as those in the initial experiments. This experiment was carried out in two adjacent stainless-steel chambers designed for air quality studies. The chambers were served by to independent ventilation systems that allowed direct comparison of various conditions set in the chambers. In these chambers two different methods of ozone generation were compared: the method used in the initial experiments and a method in which ultra-pure oxygen from a compressed gas cylinder flowed directly into the ozone-generator. The first method is similar to situations in which ozone is generated in a room using an ozone-generator, an air-ionizer or a photocopier. The second method is a reasonable model for ozone entering a room as a consequence of outdoor-to-indoor transport. The level of ozone generated in both chambers by these methods was identical, but varied with the experimental conditions. The generation of limonene was done as mentioned in the initial experiments.

The results of this experiment showed that the ozone generation method with room air produced more SOA, creating a mixture with less sensory offending pollutants compared to mixtures in the room where the ozone was generated with pure oxygen. This suggests that photochemistry promotes additional secondary oxidation (by OH radicals) leading to more high molecular weight products with low vapour pressures – hence, more SOA is produced, resulting in a nonlinear increase in SOA yields (Odum et al., 1996). Furthermore, the sensory results obtained in the chamber experiments, in the view of the earlier findings, indicated that
the odour of limonene (at high concentrations) and the various gas phase oxidation products both contribute to the sensory effects of ozone limonene reactions, while condensed phase products do not appear to directly contribute to sensory effects, but rather indicate the presence of odourous gas phase reaction products.

Although the health consequences of long-term exposures to the products of ozone-limonene initiated indoor chemistry remain to be determined, we judge that the sensory offending nature of selected products provides an additional reason to limit indoor ozone levels. Devices that emit ozone at significant rates should not be used indoors. Ozone-filtration of make-up air should also be beneficial in mechanically ventilated buildings located in regions that repeatedly violate outdoor ozone standards. Additionally, the use of limonene containing products should be curtailed during periods when indoor ozone levels are elevated.

A set of other experiments were designed in the current PhD research to study ozone interactions with various surfaces (Experiments 5-6, Table 2) and within special environments (Experiments 7-8), and to evaluate the subsequent sensory effects that result mainly from heterogeneous reactions on the surfaces and to a lesser extent from homogeneous chemistry in the air.

The primary objective of Experiment 5 was to evaluate changes in emissions of sensory offending pollutants resulting from exposure of carpet samples to moderate ozone levels. Full-scale air quality assessments were carried out in the absence and presence of ozone for three carpet samples that were different in age, constituent materials and origin. The results showed that ozone exposure reduced the sensory pollution load of the new carpet presumably as a consequence of the oxidation of odourous primary emissions to less odourous products.
However ozone exposure of the old, soiled carpets significantly increased the sensory pollution load and this affected perceived air quality in a negative way.

Based on the results of the present study it was concluded that early in a carpet’s service life, ozone exposure may diminish a new carpet’s odour. However, during most of a carpet’s service life, after the more volatile primary emissions have decayed, even moderate ozone exposure will significantly increase the emission of sensory offending secondary pollutants and these negatively affect the perceived air quality of carpeted environments.

Oxidation reactions occurring on filter surfaces are assumed to be similar to ozone-initiated indoor chemistry and may lead to the growth of ultrafine airborne particles downstream of used ventilation filters. The objective of the Experiment 6 (Table 2) was to see if it was possible to detect an increase in the concentration of ultrafine particles downstream of a used ventilation filter when ozone was present in the airstream compared to when it was not. Such an increase would be further evidence that ozone reacts with organic compounds on the surface of the filter to generate oxidation products that subsequently are desorbed and recondensed on particles immediately downstream of the filter. The experiment was done using small-scale test equipment in a low-polluting office with a very low background ozone level. Ultrafine particle concentrations were measured upstream and downstream of filter samples when the air passing through the filters either did or did not contain ozone.

The results of the experiment provided evidence for the formation of oxidation products as the loaded ventilation filters scavenge ozone. The increase of secondary organic aerosols observed downstream of the filter when ozone is present in the air stream is not, in itself, of
great concern. The actual increase in particle mass concentration as a consequence of this chemistry is quite small.

The significance of the observation is that it supports the hypothesis that ozone can initiate oxidation processes on the surface of loaded filters. We suspect that these oxidation processes can change the mix of chemicals in the air downstream of a loaded filter and may result in ventilation air that is less acceptable, in terms of sensory perceptions, than the air would have been if such oxidative chemical transformations had not occurred.

The last two experiments of the current PhD research was conducted inside a purpose-built section of an aircraft cabin at full scale. At typical cruising altitudes the concentration of ozone in the cabin of a commercial aircraft can be significantly higher than that for normal indoor built environments. Hence, ozone-initiated reactions can be of great importance to identify the causing factors of human complaints that are often reported during transcontinental flights.

In Experiment 7 proton-transfer-reaction mass spectrometry (PTR-MS) was used to examine the products formed when ozone reacted with the materials in a simulated aircraft cabin, including a loaded high-efficiency particulate air (HEPA) filter in the return air system. Four conditions were examined: cabin (baseline), cabin plus ozone, cabin plus soiled T-shirts (surrogates for human occupants), and cabin plus soiled T-shirts plus ozone. The addition of ozone to the cabin without T-shirts, at concentrations typically encountered during commercial air travel, increased the concentration of detected pollutants (from 35 ppb to 80 ppb). Most of this increase was due to the production of saturated and unsaturated aldehydes and tentatively identified low-molecular-weight carboxylic acids. A slight increment in the
concentration of detected compounds was also shown with the addition of soiled T-shirts, with no ozone present. However, the combination of soiled T-shirts and ozone caused the greatest increase in the mixing ratio of detected pollutants to 110 ppb, with more than 20 ppb originating from squalene (a common constituent of human skin oil) oxidation products (acetone, 4-oxopentanal, and 6-methyl-5-hepten-2-one). The odour thresholds of certain products were exceeded. The results also showed that the introduction of soiled T-shirt with human bioeffluents in the cabin environment doubled the ozone surface removal rate constant. This does not appear to be caused by simple deposition on the increased surface area due to the presence of T-shirts in the cabin; ozone has been also removed by chemical processes as indicated by the PTR-MS evaluation.

Experiment 8 was designed entirely to investigate ozone removal rates in the simulated aircraft environment. By systematically varying the presence or absence of people, soiled T-shirts, aircraft seats and a soiled HEPA filter enabled to isolate the contribution of these and other factors to the removal of ozone from the cabin air. This experiment consisted of 24 different measurements carried out at different stages during two years. The results showed that in the case of this simulated aircraft, people were responsible for almost 60% of the ozone removal occurring within the cabin and recirculation system; the aircraft seats about 25%; the loaded HEPA filter 7%; and the other surfaces 10%. The removal of ozone by people was equivalent to a Clean Air Delivery Rate, with respect to ozone, of 12 to 14 m$^3$ h$^{-1}$ per person or a deposition velocity of 0.20 to 0.22 cm s$^{-1}$. Respiration can only have been responsible for about 4% of this removal. A T-shirt that had been slept in overnight removed roughly 70% as much ozone as a person, indicating the importance of skin oils in ozone removal. The presence of the used HEPA filter in the recirculated air stream reduced the perceived air quality. When the cabin surfaces were exposed to elevated ozone levels for an
extended period of time (~ 5 h), the overall ozone surface removal rate decreased at ~ 3% per hour. With people present, the measured ozone retention ratios (0.15 to 0.21) were smaller than levels reported in the literature.

Taken together, these measurements provide a more complete picture of the parameters that remove ozone as it is transported from outside the aircraft to the breathing zone of passengers and crew. Ozone removal is desirable in terms of reducing the exposure of passengers and crew to ozone, but ozone removal by surfaces is not without consequences. To a large extent, this removal of ozone is due to reactions with organic compounds on the surfaces. The more volatile oxidation products can subsequently desorb from the surfaces and become part of the mix of chemicals within the cabin to which passengers and crew are exposed. Retention ratios measured in this study are lower than the default value used by the FAA in deciding whether or not ozone-removing devices should be used on aircraft. However, this should not be construed as an extra “margin of protection”. For the reasons outlined above, a low retention ratio indicates significant surface chemistry and, potentially, significant exposures to the consequent oxidation products that desorb from surfaces. The ozone removal associated with people produces products to which other passengers are exposed. From the T-shirt experiments we know that these products include the squalene oxidation products acetone, 6-methyl-5-heptene-2-one and 4-oxopentanal. We do not know the nature of the major products generated from clothing. Regardless, since the chemistry involves the passengers and crew themselves, the only way to minimize people’s exposure to both ozone and the products of ozone-initiated chemistry is to minimize the concentration of ozone in the cabin. This fact underscores the need for efficient filtration of ambient ozone from the air supply system of an aircraft.
CONCLUSIONS

The results of the experiments included in the present PhD research work highlighted the importance of ozone-initiated chemistry in indoor environment and the subsequent negative effects on human perception given by short-term subjective evaluations. Both homogeneous and heterogeneous reactions of ozone with pollutants commonly found indoors have lead to deterioration of air quality. Although the main focus was given to subjective evaluations the negative effects were also shown by objective chemical measurements. These interactions involve not only the building materials but the building occupants as well. The importance of human factor in such chemistry has been clearly indicated; people were shown to represent one of the largest ozone sinks in indoor environments and the reactions of ozone with human bioeffluents were shown to produce a number of chemical compounds that are more odourous than their precursors. There are certain scenarios when ozone exposure lowers the intensity of unpleasant odours due to decomposition of sensory offending primary emissions of materials (e.g. in case of a new carpet). However, this effect still does not result with good air quality and only occurs at the beginning of the product’s life cycle.

Several methods can be implemented in the future ventilation strategies of buildings and other environments to prevent people’s exposure to ozone and the related chemistry. Increasing the outdoor ventilation rates can be efficient to limit gas-phase reactions by reducing both the concentration of pollutants and the time available for such chemistry. However this strategy would be less efficient to avoid reactions occurring on the surfaces of materials and clothing containing pollutants that can readily react with ozone. Ozone filtration of ventilation air or the use of air cleaning devices with activated carbon filter may present more efficient way to limit the negative effects of ozone-initiated chemistry on people. In addition, ozone-resistant
coating applied on the surface of materials would lower the occurrence of such reactions in indoor environments.

The conclusions of the present work are detailed as follows:

- The products of ozone-initiated reactions with limonene negatively affected short-term evaluations of perceived air quality. This is consistent with results from other studies (Knudsen et al., 2002; Klenø and Wolkoff, 2004; Klenø-Nøjgaard et al., 2005).
- The filtration of ozone-limonene products removed a fraction of the condensed-phase species as well as a fraction of the gas phase pollutants; this improved the perceived air quality.
- The odour of limonene was recognized by more than 50% of the sensory panel at 85 ppb, a level that is lower than the detection limit reported in some of the older literature.
- The odour of limonene (at high concentrations) and the various gas phase oxidation products both contribute to the sensory effects of ozone-limonene reactions.
- In ozone-limonene reactions the condensed phase products do not appear to directly contribute to sensory effects, but rather indicate the presence of odourous gas phase reaction products.
- In ozone-limonene reactions a correlation was found between particle concentrations and sensory pollution loads; this reflects the co-generation of condensed phase products and sensory offending gas phase products.
- The perceived air quality significantly improved after ozone exposure of a new carpet; this can be attributed to ozone-initiated reactions that altered the primary emission of sensory offending compounds.
• In case of used carpets with low primary emissions, ozone exposure significantly increased the release of sensory offending secondary pollutants.

• Ozone retention ratios measured in a simulated aircraft environment in the presence of humans were lower (0.15 – 0.21) than the default value used by the U.S. Federal Aviation Administration (FAA) in deciding whether or not ozone-removing devices should be used on aircraft.

• In a simulated aircraft environment, people were responsible for almost 60% of the ozone removal occurring within the cabin and recirculation system. The aircraft seats contributed about 25%; the loaded HEPA filter, 7%; and the other surfaces, 10% to the total ozone removal. The effects of used and new HEPA filters on the overall ozone removal rate were found to be similar in magnitude.

• In a simulated aircraft environment the perceived air quality was significantly poorer with the used HEPA filter in the system compared to no HEPA filter in the system. This is consistent with results from numerous other studies indicating that a loaded ventilation filter adversely impacts the quality of the air that passes through it.

• The deposition velocity associated with people in the simulated cabin was between 0.20 and 0.22 cm s\(^{-1}\); for the T-shirts and aircraft seats the deposition velocities were between 0.19 - 0.27 cm s\(^{-1}\) and between 0.10 - 0.11 cm s\(^{-1}\), respectively. The deposition velocity for the T-shirts and people is at, or slightly beyond, the upper limit of such values, given mass transport constraints.

• A T-shirt that had been slept in overnight removed roughly 70% as much ozone in the simulated aircraft as a person, indicating the importance of skin oils in ozone removal.

• The addition of ozone to a simulated aircraft environment at concentrations typically encountered during commercial air travel increased the concentration of detected pollutants from 35 ppb to 80 ppb. Most of this increase was due to the production of
saturated and unsaturated aldehydes and tentatively identified low-molecular-weight carboxylic acids.

- The addition of ozone to a simulated aircraft environment containing soiled T-shirts increased the concentration of detected pollutants from 45 ppb to 110 ppb, with more than 20 ppb originating from squalene oxidation products (acetone, 4-oxopentanal, and 6-methyl-5-hepten-2-one); the addition of soiled T-shirts alone, with no ozone present only slightly contributed to the concentration of pollutants in the cabin air.

- In a simulated ozone exposed aircraft environment, both in the presence and absence of soiled T-shirts, the more-abundant oxidation products included acetone/propanal (8-20 ppb), formaldehyde (8-10 ppb), nonanal (~6 ppb), 4-oxopentanal (3-7 ppb), acetic acid (~7 ppb), formic acid (~3 ppb), and 6-methyl-5-hepten-2-one (0.5-2.5 ppb), as well as compounds tentatively identified as acrolein (0.6-1 ppb) and crotonaldehyde (0.6-0.8 ppb).

- The downstream/upstream ultra fine particle concentration ratio of a loaded filter was found to be higher when the air stream contained ozone than when it didn’t. These findings confirm an earlier hypothesis regarding the generation of oxidized products on the surface of used air filters.
FUTURE WORK

The findings from this thesis show that ozone-initiated reactions, occurring both on surfaces and in the gas phase, have a clear negative effect on short-term evaluations of perceived air quality. It is anticipated that this negative effect would persist during longer exposures and would contribute to an increase in symptom intensity of those who were exposed. Further analyses of our latest data and possibly further investigations are needed to confirm the hypothesis in the previous sentence.

In the present experiments limonene was generated using bubblers containing the pure compound. Commercial products, such as air fresheners and surface cleaners contain a number of other terpenoids that could also react with ozone to produce odour offending compounds. Further experiments are essential to evaluate the sensory effects expected from ozone reactions with terpenoid containing products commonly used in various indoor environments.

Clothing may substantially affect ozone removal rates associated with people. Similarly, ozone removal may also be affected by various cosmetics, perfumes, and lotions applied on the skin. Future experiments should also evaluate these factors since people are present in most indoor environments.

Ozone deposition velocities calculated for T-shirts and people in these experiments were at the upper limit anticipated from mass transport considerations. This suggests that ozone, in addition to being removed by surface processes, was also removed by gas phase chemistry related to the presence of people. Further studies are warranted to examine this issue.
References


(http://www.defra.gov.uk/environment/airquality/aqs/ozone/index.htm)


References


Publications
Articles in peer-reviewed journals
PAPER 1: INFLUENCE OF OZONE-LIMONENE REACTIONS ON
PERCEIVED AIR QUALITY
INFLUENCE OF OZONE-LIMONENE REACTIONS ON PERCEIVED
AIR QUALITY

Gyöngyi Tamás¹, Charles J. Weschler¹,², Jørn Toftum¹ and P Ole Fanger¹

¹International Centre for Indoor Environment and Energy (ICIEE), Technical University of
Denmark, 2800-Kgs. Lyngby, Denmark
²Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical
School & Rutgers Univ.), Piscataway, NJ 08854 USA

Correspondence to:
Charles J. Weschler
Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical
School & Rutgers Univ.), 170 Frelinghuysen Rd., Piscataway, NJ 08854, USA
Phone: 732 235-4114    Fax: 732 235-4569
e-mail: weschlch@umdnj.edu
ABSTRACT

This study conducted short-term assessments of perceived air quality for six different realistic concentrations of ozone and limonene, separately or together, in room air. The impact of filtration and the influence of the ozone generation method were also examined. The evaluations were made in four identical 40 m$^3$ low-polluting test offices ventilated at 1.4 h$^{-1}$ or in two identical 30 m$^3$ stainless-steel chambers ventilated at 1.9 h$^{-1}$. Concentrations of ozone, total volatile organic compounds and size-fractionated particles were continuously monitored in each experiment. The results indicate that, for each of the six conditions, the perceived air quality was poorer when ozone and limonene were present together compared to when only ozone or only limonene was present. In the test offices a correlation was observed between the number of secondary organic aerosols produced by a given ozone/limonene condition and the sensory pollution load for that condition. The particles themselves do not appear to be the primary causative agents, but instead are co-varying surrogates for sensory offending gas-phase species.

KEY WORDS

Indoor air chemistry, Ozone, Limonene, Secondary organic aerosols, Perceived air quality, Odor recognition

PRACTICAL IMPLICATIONS

Although the health consequences of long-term exposures to the products of ozone-initiated indoor chemistry remain to be determined, we judge that the sensory offending nature of selected products provides an additional reason to limit indoor ozone levels. Devices that emit
ozone at significant rates should not be used indoors. Ozone-filtration of make-up air should also be beneficial in mechanically ventilated buildings located in regions that repeatedly violate outdoor ozone standards. Additionally, the use of limonene containing products should be curtailed during periods when indoor ozone levels are elevated.

**INTRODUCTION**

Scented products such as air fresheners, cosmetics and household cleaners are widely used in homes and non-industrial work places to impart pleasant odors and to counteract malodors originating from a variety of indoor sources, including human activities. In addition to their intended benefits, these products emit significant quantities of chemicals that may cause adverse health effects or may react to yield harmful secondary products (Nazaroff and Weschler, 2004). Of special note are terpenes such as d-limonene and a-pinene, whose reactions with ozone are fast enough to compete with normal air change rates (Weschler, 2000). Average indoor levels of 5-15 ppb limonene have been reported in a number of studies (Seifert et al., 1989; Fellin and Otson, 1994), but levels may reach several hundreds of ppb during and immediately after product use (Wainman et al., 2000; Singer et al., 2005). Similarly ozone is commonly found in various indoor settings as a result of outdoor-to-indoor transport or direct emission from indoor sources. Concentrations of 20-40 ppb ozone are commonly reported indoors, but in extreme cases levels can exceed 100 ppb (Sabersky et al., 1973; Weschler et al., 1989; Weschler, 2000). Ozone/d-limonene reactions produce both stable species and reactive free radicals. The free radicals, in turn, react to generate additional species. The oxidation products include a number of aldehydes (saturated and unsaturated) and organic acids with low odor thresholds. Some of these products are anticipated to be more irritating than their precursors. Both primary and secondary products can exist in the gas phase and in the condensed phase; the distribution between these phases depends on the vapor
pressure of the compound and the surface area of existing airborne particles. Low vapor pressure products contribute to the growth of secondary organic aerosols indoors (Weschler and Shields, 1999; Wainman et al., 2000; Long et al., 2000; Rohr et al., 2003; Sarwar et al., 2003). Although indoor ozone/terpene reactions have been investigated in a number of studies, only a few have evaluated the human sensory effects of ozone/terpene initiated reaction products (Fiedler et al., 2002; Knudsen et al., 2002; Kleno and Wolkoff, 2004; Kleno-Nojgaard et al., 2005).

Fiedler et al. (2002) tested the effects of ozone-VOC reaction products on symptoms, neurobehavioral performance, nasal inflammation and lung function. The VOC mixture consisted of 23 compounds including d-limonene. The secondary products of the reaction confirmed the formation of respirable particles in the case where ozone and VOCs were present together. However, there was no increase in the studied symptoms during exposure of 75 healthy women relative to the “VOCs only” condition. Symptoms may have been less distinguishable against the strong background odor from the VOC mixture itself.

Terpene-ozone reaction products, at realistic indoor concentrations, cause an increase in blink frequency (Kleno and Wolkoff, 2004; Kleno-Nojgaard et al., 2005). In one set of experiments Kleno and Wolkoff exposed the left eye of 8 male subjects for 20 minutes to limonene oxidation products, residual reactants and pure air. The subjects reported eye irritation and increased blinking activities when they were exposed to the oxidation products. The blinking frequency was unaffected by exposure to ozone and slightly reduced in the case of limonene. The exposure to pure limonene and to the oxidation products resulted in weak subjective eye irritation, but the perceptions differed.
Knudsen et al. (2002) investigated the effects of ozone, limonene and ozone-limonene reaction products on perceived air quality (PAQ) in three typical low polluting offices at realistic air change rates (ACH). They found that decreasing the air change rate from 1.0 to 0.3 h\(^{-1}\) deteriorated the PAQ, and the effect was most pronounced in the presence of ozone. At higher air change rates (1.0 and 3.0 h\(^{-1}\)) the PAQ was unaffected by ozone and the ozone-limonene combination.

The present experiments, summarized in Table 1, were designed to evaluate the impact of ozone-limonene reaction products on perceived air quality under realistic indoor conditions using different relative concentrations of ozone and limonene. Two different ozone generation methods were compared with respect to sensory effects and secondary aerosol formation. As part of these experiments, the odor recognition of limonene was evaluated at different concentrations.

**METHODS**

**Initial Experiments**

The measurements were carried out in four identical and adjacent non-furnished low polluting offices (Figure 1) ventilated at 1.4 h\(^{-1}\) (± 0.1 h\(^{-1}\)). In each room the outdoor air was supplied by an axial fan mounted in the window, connected to a damper followed by an activated charcoal filter to remove ambient ozone. The temperature and humidity were maintained at 22.3°C (± 0.4°C) and 51 % (± 6%) RH, respectively. Several small fans were used to achieve good mixing inside each room. The polluted air was extracted by another axial fan mounted in each window. The corridor was well ventilated and used as the space where subjects refreshed their olfactory sense between assessments of the air in the rooms.
One office where neither ozone nor limonene was introduced was always used as a reference exposure. A second office contained different levels of ozone. In a third office different levels of limonene were maintained using a pump, a bubbler and a flow meter to achieve a controlled flow of limonene-saturated air from the bubbler. In the fourth office ozone and limonene were generated at the same rates as ozone in the second and limonene in the third room (Figure 1). In these initial experiments ozone was photochemically generated using a UV lamp contained in a small glass box placed in, and drawing its air from, the test room. Hence, in the test rooms in which ozone was generated using room air a small fraction of air (1/30th of the outdoor airflow rate) was photolized in the generator. As subsequent experiments revealed (see below) this influenced the chemistry.

Figure 1. Schematic of the experimental arrangement
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Condition</th>
<th>Ozone&lt;sup&gt;a&lt;/sup&gt; [ppb]</th>
<th>Lim&lt;sup&gt;a&lt;/sup&gt; [ppb]</th>
<th>Location</th>
<th>V [m&lt;sup&gt;3&lt;/sup&gt;]</th>
<th>ACH [h&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Aim</th>
<th>Subjects</th>
<th>Measured parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1</td>
<td>10</td>
<td>115</td>
<td>4 low polluting, unfurnished</td>
<td>40</td>
<td>1.4</td>
<td>Direct sensory comparison of ozone /limonene reaction products with precursors using different ozone and limonene concentrations</td>
<td>20 untrained staff members and students</td>
<td>Air acceptability, Ozone, TVOC, Particles&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Odor character</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>30</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Limonene&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>45</td>
<td>40</td>
<td>test rooms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>30</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>45</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odor recognition</td>
<td>I</td>
<td>--</td>
<td>115</td>
<td>3 low polluting, unfurnished</td>
<td>40</td>
<td>1.4</td>
<td>Direct sensory comparison of three limonene concentrations</td>
<td>39 untrained staff members and students</td>
<td>Odor character</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>--</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>--</td>
<td>50</td>
<td>unfurnished test rooms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtration</td>
<td>7</td>
<td>45</td>
<td>115</td>
<td>2 low polluting, unfurnished test rooms</td>
<td>40</td>
<td>1.4</td>
<td>Direct sensory and objective comparisons of unfiltered / filtered reaction air</td>
<td>16 untrained staff members</td>
<td>Air acceptability, Ozone, TVOC, Particles</td>
</tr>
<tr>
<td>Follow-up</td>
<td>1</td>
<td>10</td>
<td>115</td>
<td>2 stainless-steel chambers</td>
<td>30</td>
<td>1.9</td>
<td>Direct sensory and objective comparisons of two ozone generation methods (with room air vs. tank oxygen)</td>
<td>24 untrained staff members and students</td>
<td>Air acceptability, Ozone, TVOC, Particles</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>45</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Concentration in the test room or chamber if there were no reaction between ozone and limonene.

<sup>b</sup> See text for details.
Table 1 (Initial experiments) shows the intended steady-state ozone and limonene concentrations in the offices containing only ozone or only limonene. Conditions 5 and 6 were designed to initially yield three times as much product as Conditions 1 and 2, respectively.

**Subjects and procedure:** During the experiments a panel of untrained subjects consisting of approximately twenty staff members and students (age 22-60 years) from the ICIEE assessed the air quality shortly after entering each of the test rooms; this was done using a pseudo-continuous acceptability scale (Clausen, 2000). The evaluation order of the rooms was randomized and there was a two-minute break between each assessment. The experiments were carried out during two weeks in June 2003. On each experimental day a different condition (Table 1, Initial experiments) was evaluated. The order in which the conditions were established in the rooms was also randomized. Assessments were conducted after steady-state conditions had been achieved.

**Data analysis:** The mean acceptability ratings were transformed to Percent Dissatisfied (PD) according to Gunnarsen and Fanger (1992) and subsequently into decipol units (Fanger, 1988). Using the comfort model given by Fanger (1988), coupled with the measured ventilation rates and assuming that perfect mixing had been achieved, the total sensory pollution loads in the test offices were calculated in units of “olf’s” (Clausen, 2000). The sensory pollution load can be viewed as a measure of the emission rate (i.e., mass per unit time) of sensory pollutants. All data obtained from questionnaires were tested for normality using the Shapiro-Wilks’ W test with the rejection region of $p<0.01$. For normally distributed data, one-way analysis of variance (ANOVA) supplemented with Duncan’s post-hoc comparison or paired t-test was applied to evaluate differences between the conditions. All reported p-values are 1-tailed.
**Physical measurements:** Temperature and RH values were monitored continuously during the experiment. The outdoor air supply rate was measured in each office before each experiment started using the tracer decay method. The ozone concentration in the two offices where ozone was generated was continuously measured with ozone meters (Dasibi 1003-AH and 1003-RS). Limonene concentrations, in test rooms containing only limonene, were determined after steady-state conditions had been achieved. Samples of room air were pumped through sorbent tubes for two hours at an average rate of 146 ml/min. The tubes were subsequently thermally desorbed and analyzed using a gas chromatograph equipped with a mass spectrometer (GC/MS) operated in full scan mode. In each of the sampled rooms, a duplicate sample was collected after a 1.5 hour break. The number concentrations of particles [part/cm\(^3\)] were measured with a P-Trak condensation nuclei counter (0.02-1 µm diameter size range) and a Lasair optical particle counter (0.1-0.2; 0.2-0.3; 0.3-0.4; 0.4-0.5; 0.5-0.7; 0.7-1; 1-2; and > 2 µm diameter size ranges). Based on the number concentration, and assuming that the particle mass is distributed according to a lognormal distribution, the mass concentrations [µg/m\(^3\)] were calculated using the geometric mean diameter of the particle size range and 1.2 g/cm\(^3\) density (Turpin and Lim, 2001). Real-time TVOC levels were estimated with a B&K 1302 Multigas monitor (a photoacoustic spectrometer) using the UA987 filter.

**Odor recognition:** In a separate set of experiments, limonene concentrations of 115, 85 and 50 ppb were established in three of the test rooms. The same temperature, relative humidity and air change rate were maintained as in the previous experiments. Ozone was again filtered from the incoming air. A panel of 39 untrained subjects consisting of staff members and students between the ages of 19 and 69 assessed the quality of the air in the offices and voted for the character of the odor: no odor, metal, wood, fruit, car exhaust and “other”. A subject marking “fruit” was considered to have recognized the odor of limonene. The same panel
again accessed the air quality and odor character of the rooms one day after the limonene generation had been terminated.

**Sensory evaluation of filtered reaction air:** In a subsequent experiment using two of the above-described offices configured at the same temperature, relative humidity and air change rate, the effect of filtration on pollutant levels and sensory evaluations was investigated. In one of the offices ozone and limonene were generated at rates that would result in concentrations of 45 ppb and 115 ppb, respectively, if only ozone or only limonene had been present in the office. The air from this room was transported through a standard EU-7 bag filter (equivalent to an ASHRAE 85 dust spot filter with 42% efficiency for 0.1 µm particles and 95% efficiency for 1.8 µm particles; Hanley et al., 1994) to the adjacent office by means of a simple duct system and fan. The air change rate in the two offices was identical. The ozone, TVOC and particle levels were continuously monitored in both offices using the instrumentation described above. In this experiment, the sensory panel used for air quality assessments consisted of staff members.

**Follow-up Experiments**

As noted in the “Initial Experiments” sub-section, a small fraction of air (1/30th of the outdoor airflow) passed through the ozone-generator and, hence, was photolyzed with light from the mercury vapor lamp. We were concerned that this might have an impact on the production of gas and condensed phase oxidation products, as well as the sensory evaluation of the room air. To investigate this issue, we conducted a series of follow-up experiments in which two different methods of ozone generation were compared: the method used in the original experiments and a method in which ultra-pure oxygen from a compressed gas cylinder flowed directly into the ozone-generator. By the time the follow-up experiments
were conducted, the test rooms were no longer available. Consequently, these follow-up experiments were conducted in a pair of adjacent stainless-steel chambers, designed specifically for indoor air quality studies (Albrechtsen, 1988). Each chamber has a volume of 30 m$^3$ (including re-circulation ducts), is served by a completely separate HVAC system, and was operated at 22 ± 0.1°C and 33.6 ± 7.2 RH. The air in the chambers is distributed through a perforated floor, extracted at the ceiling and re-circulated at a high rate to obtain good mixing of the pollutants emitted in the chamber. The total rate (recirculated and outdoor air) at which air in the chambers was exchanged was 50 h$^{-1}$, while the rate at which the chamber air was exchanged with outdoor air was 1.87 ± 0.26 h$^{-1}$ for both chambers.

Ozone and limonene were generated at the same rate in both chambers to obtain two distinct experimental conditions corresponding to Conditions 1 and 4 (Table 1, Initial experiments). In the two chambers the two separate ozone generation methods were employed as described above. When ozone was generated using room air, the fraction of air photolyzed in the generator compared to the outdoor air flow was 1/31, roughly the same as in the initial experiments. The flow of limonene-saturated air from the bubbler was adjusted to obtain an estimated concentration in the chamber corresponding to 40 or 115 ppb assuming that the surface removal is similar to that of the previously described test offices at similar air change rates. The evaluation of the two conditions was made on two separate days with a one-day break in between. On the morning of each experimental day, first the ozone concentration was adjusted to the desired level and then limonene generation began. The subjective evaluations were made after steady-state conditions had been established in both chambers. Twenty-four subjects participated in the evaluation of air acceptability; votes were also registered for the empty chambers prior to the establishment of the experimental conditions. The instrumentation used for the physical measurements was the same as previously described.
RESULTS

Initial Experiments

Physical measurements: Figure 2a shows the evolving nature of the particle concentrations for the different size ranges in the room where ozone and limonene were generated together under Conditions 1; Figure 2b shows analogous data for Condition 4. The results are typical of those observed under the other conditions listed in Table 1. For each condition the largest particle number concentrations were observed in the 0.02-0.2 µm size range.

In the offices where either ozone or limonene were present separately or nothing was generated, the background level of particles was low, typically less than 1000 part/cm³, although on a few occasions the level was 10 times higher. Compared to these levels, the particle concentration in the ozone-limonene office increased one to two orders of magnitude, depending on the ozone and limonene concentrations (Table 2). Background TVOC levels, as measured by the multigas monitor, were similar in each office (between 3.5 and 5 mg/m³), and did not change when only ozone was added to a test room. On the other hand, for Conditions 1, 2, 5 and 6, TVOC concentrations detectably increased when limonene was added to the rooms. After initiating the addition of limonene, the concentration of ozone in the ozone/limonene offices decreased by 17-45%, depending on the condition.

Table 2 contains a summary of the ozone, TVOC and total particle concentrations (0.02-1 µm) measured during the sensory assessments in the offices where ozone and limonene were simultaneously present.
Figure 2. Particle concentrations prior to and during the sensory assessments in the ozone-limonene room

a.) Condition 1 (Ozone 10 ppb, Limonene 115 ppb);
b.) Condition 4 (Ozone 45 ppb, Limonene 40 ppb)
Table 2. Ozone, TVOC, and total particle concentrations (mean ± SD) measured during the
assessment period in the ozone-limonene rooms

<table>
<thead>
<tr>
<th>O$_3$/Lim$^a$ (ppb)</th>
<th>Residual O$_3$$^b$ (ppb)</th>
<th>TVOC (mg/m$^3$)</th>
<th>Particles (part/cm$^3$)</th>
<th>Particles (µg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test Rooms, initial experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/115</td>
<td>4.1 ± 0.3</td>
<td>7.7 ± 0.3</td>
<td>107000 ± 7300</td>
<td>15.5 ± 0.9</td>
</tr>
<tr>
<td>15/85</td>
<td>7.8 ± 0.5</td>
<td>5.7 ± 0.1</td>
<td>31000 ± 1200</td>
<td>11.1 ± 1.9</td>
</tr>
<tr>
<td>30/50</td>
<td>21.0 ± 0.6</td>
<td>5.4 ± 0.2</td>
<td>15000 ± 700</td>
<td>14.2 ± 0.9</td>
</tr>
<tr>
<td>A 45/40</td>
<td>31.6 ± 1.4</td>
<td>5.9 ± 0.1</td>
<td>50000 ± 4400</td>
<td>11.3 ± 1.0</td>
</tr>
<tr>
<td>30/115</td>
<td>15.2 ± 0.8</td>
<td>7.0 ± 0.3</td>
<td>96000 ± 5000</td>
<td>21.9 ± 1.0</td>
</tr>
<tr>
<td>45/85</td>
<td>4.1 ± 0.3</td>
<td>5.5 ± 0.3</td>
<td>138000 ± 7300</td>
<td>21.2 ± 1.4</td>
</tr>
<tr>
<td>Test Rooms, filtration experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45/115</td>
<td>27.2 ± 0.8</td>
<td>6.0 ± 0.2</td>
<td>122000 ± 1500</td>
<td>18.3 ± 0.5</td>
</tr>
<tr>
<td>filtered</td>
<td>3.0 ± 0.3</td>
<td>5.1 ± 0.2</td>
<td>2200 ± 40</td>
<td>2.2 ± 0.4</td>
</tr>
<tr>
<td>Steel Chambers, follow-up experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 45$^c$/40</td>
<td>25.4 ± 2.6</td>
<td>5.5 ± 0.3</td>
<td>670 ± 200</td>
<td>--</td>
</tr>
<tr>
<td>C 45/40</td>
<td>32.6 ± 4.1</td>
<td>5.2 ± 0.2</td>
<td>1220 ± 540</td>
<td>--</td>
</tr>
<tr>
<td>10$^f$/115</td>
<td>3.2 ± 0.7</td>
<td>7.5 ± 0.4</td>
<td>1090 ± 520</td>
<td>--</td>
</tr>
<tr>
<td>10/115</td>
<td>3.6 ± 0.7</td>
<td>7.3 ± 0.2</td>
<td>22800 ± 4200</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$“O$_3$/Lim” are the concentrations of ozone and limonene that would be in the test room or chamber if there was no reaction between ozone and limonene.

$^b$“Residual O$_3$” is the concentration of ozone that was measured in the test office or in the chamber during steady-state conditions when both ozone and limonene were present.

$^c$Ozone generated using 99.9999% O$_2$ from a compressed gas cylinder; no photochemistry within chamber.
Table 3. Air acceptability and Percent Dissatisfied as assessed for each experimental condition in the test-rooms and stainless-steel chambers. Air acceptability based on a linear scale: 1 = clearly acceptable, 0 = just acceptable / not acceptable, -1 = clearly not acceptable.

<table>
<thead>
<tr>
<th>O₃/Lim¹ (ppb)</th>
<th>No generation</th>
<th>Ozone</th>
<th>Limonene</th>
<th>Ozone + Limonene</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/115</td>
<td>0.24 ± 0.21</td>
<td>0.21 ± 0.19</td>
<td>0.04 ± 0.18</td>
<td>-0.23 ± 0.20</td>
</tr>
<tr>
<td>15/85</td>
<td>0.29 ± 0.19</td>
<td>0.19 ± 0.14</td>
<td>0.11 ± 0.18</td>
<td>-0.20 ± 0.23</td>
</tr>
<tr>
<td>30/50</td>
<td>0.55 ± 0.12</td>
<td>0.17 ± 0.24</td>
<td>0.13 ± 0.12</td>
<td>-0.07 ± 0.24</td>
</tr>
<tr>
<td>A 45/40</td>
<td>0.44 ± 0.18</td>
<td>0.26 ± 0.25</td>
<td>0.48 ± 0.22</td>
<td>-0.06 ± 0.23</td>
</tr>
<tr>
<td>30/115</td>
<td>0.23 ± 0.16</td>
<td>0.44 ± 0.15</td>
<td>0.04 ± 0.15</td>
<td>-0.32 ± 0.21</td>
</tr>
<tr>
<td>45/85</td>
<td>0.50 ± 0.09</td>
<td>0.16 ± 0.13</td>
<td>0.11 ± 0.15</td>
<td>-0.32 ± 0.19</td>
</tr>
</tbody>
</table>

Test Rooms, filtration experiments

<table>
<thead>
<tr>
<th>O₃/Lim¹ (ppb)</th>
<th>No generation</th>
<th>Ozone</th>
<th>Limonene</th>
<th>Ozone + Limonene</th>
</tr>
</thead>
<tbody>
<tr>
<td>45/115</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>-0.29 ± 0.25</td>
</tr>
<tr>
<td>filtered</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.07 ± 0.25</td>
</tr>
</tbody>
</table>

Stainless-steel Chambers, follow-up experiments

<table>
<thead>
<tr>
<th>O₃/Lim¹ (ppb)</th>
<th>No generation</th>
<th>Ozone</th>
<th>Limonene</th>
<th>Ozone + Limonene</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 45⁵/40</td>
<td>0.32 ± 0.17</td>
<td>--</td>
<td>--</td>
<td>-0.12 ± 0.26</td>
</tr>
<tr>
<td>C 45/40</td>
<td>0.29 ± 0.19</td>
<td>--</td>
<td>--</td>
<td>0.34 ± 0.19</td>
</tr>
<tr>
<td>10⁵/115</td>
<td>0.32 ± 0.17</td>
<td>--</td>
<td>--</td>
<td>-0.26 ± 0.23</td>
</tr>
<tr>
<td>10/115</td>
<td>0.29 ± 0.19</td>
<td>--</td>
<td>--</td>
<td>-0.30 ± 0.19</td>
</tr>
</tbody>
</table>

¹ “O₃/Lim” are the concentrations of ozone and limonene that would be in the test room or chamber if there was no reaction between ozone and limonene.

² Sensory pollution load, calculated in units of “olf” from Percent Dissatisfied; see text.

³ Ozone generated using 99.9999% O₂ from a compressed gas cylinder; no photochemistry within chamber.
Subjective measurements: Table 3 presents sensory assessment results for each experimental condition in the test rooms and the steel chambers. Based on the air acceptability results, the percent dissatisfied with the perceived air quality in the office where nothing was generated (Office 4 in Fig. 1) averaged 10%. Compared to this level, the quality of the air in the office where only ozone was generated (Office 3 in Fig. 1) was slightly less acceptable, but the difference was only significant ($p < 0.035$) when the ozone concentration reached 30 or 45 ppb. The presence of limonene (Office 2 in Fig. 1) also negatively affected the air acceptability compared to the office where nothing was generated; the acceptability decreased significantly ($p < 0.05$) at limonene concentrations of 50, 83 and 115 ppb. In the office where ozone and limonene were present together (Office 1 in Fig. 1) the air acceptability sharply decreased ($p < 0.001$) compared to the office where nothing was generated, resulting in more than 50% dissatisfied with the perceived air quality under all six experimental conditions.

Figure 3. For each of the six initial conditions shown in Table 1, the sensory pollution load (olf) measured in rooms with only ozone, only limonene or ozone & limonene together. The values have been corrected for the loads measured in the respective empty offices.
Figure 3 shows the sensory pollution load above background, in units of “olf”, in each office under each of the six initial conditions. The sensory pollution load was modestly affected by the presence of ozone alone and affected to a greater extent by the presence of limonene, varying in magnitude with the limonene concentration. When ozone and limonene were present together the sensory pollution load was always much higher than that for ozone alone (p < 0.025) or limonene alone (p < 0.05). The sensory pollution load for ozone and limonene together was highest in Conditions 5 and 6 (29 and 30 olfs, respectively).

**Correlation between objective and subjective measurements**: The sensory pollution loads obtained in the test room with the different combinations of ozone and limonene concentrations correlated reasonably well with the particle levels measured in the size ranges of 0.02-0.1 µm (p < 0.01, $R^2=0.77$) and 0.1-0.2 µm (p < 0.005, $R^2=0.81$) (Figure 4). This correlation may reflect a direct effect of particles on sensory perception, or the particles may simply be a surrogate for offending gas phase products. The latter appears to be the case (see Discussion Section).

**Figure 4.** Correlation between the sensory pollution load and the particle number concentrations in (a) the 0.02-0.1 um and (b) the 0.1-0.2 um size ranges
**Odor recognition:** Figure 5 shows that more than 50% of the sensory panel recognized a fruit odor when the limonene concentration exceeded 85 ppb, while only 16% recognized a fruit odor at 40 ppb. About 24 hours after the limonene generation ceased, 9% of the sensory panel still recognized the odor in the office that had had the highest concentration of limonene, while in the office that had had the lowest concentration no subjects identified a fruit-like odor. The results indicate that the odor of limonene can be detected at lower levels than indicated in certain older literature (e.g., 438 ppb; Devos et al., 1990) and are more consistent with the odor threshold of 40 ppb reported in Nagata et al. (2003).

![Odor recognition chart](image)

*Figure 5. Percentage of people (out of 37 total subjects) who recognized a fruity odor for different limonene concentrations in the test rooms*

**Sensory evaluation of filtered air:** As noted in the Experimental Section, the effect of filtration on pollutant levels and sensory evaluations was investigated in a separate experiment. The results of the objective and subjective measurements from this experiment are summarized in the middle portion of Tables 2 and 3. In the office that received air from the ozone plus limonene polluted office through an EU-7 bag filter, not only the particle levels but also the TVOC and ozone concentrations were lower than in the ozone/limonene

---

**Paper 1**

P - 63
polluted office. In the subjective measurements, the percentage of dissatisfied was half (p<0.01) that in the ozone/limonene office.

**Follow-up Experiments**

Results from the follow-up experiments in the stainless-steel chambers (during the assessment period) are summarized in the bottom portions of Tables 2 and 3. Prior to the assessments in the empty chambers, as well as during periods when only ozone was generated, the level of particles was low (typically less than 500 part/cm$^3$). During the ozone/limonene generation period, a large increase in the particle concentration (up to 35000 part/cm$^3$) occurred only under the high limonene condition when the ozone was generated using chamber air. The background TVOC levels were similar in both chambers (between 4 and 5 mg/m$^3$), and increased slightly during the period when only ozone was added to a chamber. An increase in TVOC level due to the introduction of limonene was detectable only at “115 ppb” and resulted in close to 7 mg/m$^3$ TVOC in both chambers before the assessment period started. For Condition 1 (10 ppb of ozone initially in the chambers), when limonene was added to the chamber in which the ozone was generated using oxygen, the concentration of ozone decreased by 76%, while it only decreased by 67% when limonene was added to the chamber in which the ozone was generated using chamber air. The same trend was observed for Condition 4 (45 ppb of ozone initially in the chambers), with ozone decreasing by 32% in the chamber in which it was generated using oxygen, compared to 21% in the chamber in which it was generated using room air.

The subjective votes (Table 3) indicated that the background air quality in the chambers was similar, with no more than 16% dissatisfied (equivalent to 1.2 olf). In the condition with 40 ppb ozone / 45 ppb limonene the perceived air quality was significantly lower (p < 0.0001)
when the ozone was generated with oxygen (equivalent to 16 olf above background level) compared with the method in which ozone was generated using room-air (only slightly above the background level, < 1 olf). In the condition with 10 ppb ozone / 115 ppb limonene, the quality of the air was assessed to be equally poor in both chambers (on average 24 olf above background level), with more than 70% dissatisfied; this was significantly worse than for either of the other chamber conditions (no p larger than 0.03).

DISCUSSION

Sensory evaluations in the test rooms

As reported in the Results Section, the simultaneous presence of ozone and limonene negatively affected the perceived air quality. The most striking condition (40 ppb limonene / 45 ppb ozone) was that in which the limonene concentration in the absence of ozone did not affect the perceived air quality, but the combination of limonene and ozone (32 ppb residual ozone) caused more than 50% to be dissatisfied with the air quality. This suggests that chemical reactions resulting from ozone-terpene chemistry may substantially deteriorate perceived air quality. Knudsen et al. (2002) applying a delayed exposure process (subjects assessed the air quality a couple of hours after ozone had been introduced into a limonene cleaned room) also observed degradation of perceived air quality while exposing people to ozone limonene reaction products, but only at a relatively low air change rate (0.3 h⁻¹).

Particle concentrations were considerably higher at low ozone and high limonene concentrations than under the reverse conditions. This partially reflects secondary oxidation by hydroxyl radicals that also contribute to the formation of particles (Fan et al., 2003). In these experiments, when a small fraction of the room air passed over a UV lamp, elevated
concentrations of sub-micron particles were observed even when the ozone and limonene concentrations were at relatively low levels.

**Sensory evaluation of filtered air**

The filtration of air containing the products of ozone-limonene reactions was effective in reducing the concentration of secondary organic aerosols (SOA). The concentration of the gaseous pollutants in the filtered office also decreased, as indicated by the ozone and TVOC measurements. The concentration of secondary organic aerosols is less in the room containing filtered air not only because some aerosol was removed by the filter, but also due to less ongoing generation of SOA given the lower concentration of ozone. The perceived air quality in the filtered office improved as shown by the subjective results. The decrease in the residual ozone concentration does not appear to be a major contributor to this improvement. The residual ozone concentration in the unfiltered office (27 ppb) was lower than levels that produced no significant sensory effects in the Initial experiments (see Ozone column in Table 3). Instead, the improvement of perceived air quality in the filtered office compared to the unfiltered office appears to be due to the lower concentration of reaction products. However, these measurements do not resolve the question of whether gas phase or condensed phase reaction products contributed more to the sensory effects (see below for additional discussion of this issue). Real time chemical analysis of the air in both the filtered and un-filtered offices would aid in evaluating the effects of such filtration on the gas-phase and condensed phase products.

**Sensory evaluations in the stainless steel chambers**

In the stainless-steel chamber experiments two methods of ozone generation were compared, reproducing Condition 1 or 4 of the Initial Experiments (see Table 1). In the first method
ozone was produced within the chamber using a UV-generator drawing air from its surroundings; in the second method ozone was produced in a sealed UV-generator drawing high purity oxygen from a cylinder, with the resulting ozone subsequently mixed with the chamber air (see Methods Section). The first method is similar to situations in which ozone is generated in a room using an ozone-generator, an air-ionizer or a photocopier. The second method is a reasonable model for ozone entering a room as a consequence of outdoor-to-indoor transport.

When ozone was generated in the steel chambers using room air, the residual ozone and TVOC concentrations were similar to what had earlier been measured in the test rooms using the same ozone generation method. This indicates that the reaction proceeded to approximately the same steady-state in both cases. However, the resulting particle concentrations in the steel chambers differed from those in the test rooms. One of the factors influencing the concentration of particles is the surface removal rate, which is affected by the nature of the surfaces and the airflow. Although the stainless steel surface is expected to interact with the air pollutants to a smaller degree than other common material surfaces, the surface removal rate of particles in the steel-chambers was higher than in the test-rooms due to the larger surface area in the recirculation ducts, the high speed recirculation fan operating at an elevated temperature, and the more turbulent flow conditions created by the recirculation system.

The lower particle concentrations for the two conditions when ozone was generated using oxygen compared to the method using room air, indicates that smaller concentrations of low-vapor pressure products were created. This suggests that photochemistry promotes additional secondary oxidation (by OH radicals) leading to more high molecular weight products with
low vapor pressures – hence, more SOA is produced, resulting in a nonlinear increase in SOA yields (Odum et al., 1996).

Further comparing the two methods of ozone generation, photochemistry may also partially explain the difference in the amount of ozone consumed after limonene was introduced into the chambers (see Results Section). When ozone was generated by the method that used chamber air, a fraction of the limonene or unsaturated reaction products that passed in front of the UV lamp may have been photolyzed, reducing the total concentration of species available to react with ozone. Hence, less ozone would be consumed than in the method where ozone had been generated using oxygen. A related difference was also observed during the human subject assessment period when the TVOC concentration increased due to subject emissions in the chamber. The TVOC concentration in the chamber where ozone was generated using oxygen conspicuously overtook the TVOC concentration in the other chamber where ozone was generated using room air. That is, a fraction of the human bioeffluents appears to have been photochemically decomposed in the one case but not in the other.

In the 45 ppb ozone/40 ppb limonene experiments in the stainless-steel chambers (“B” and “C” in Table 3), when almost exclusively gas phase products were present (particle concentrations < 1500 part/cm$^3$), the sensory results indicated that the perceived air quality was significantly worse in the case of ozone generation with oxygen (16 olf) than with room air (< 1 olf). This indicates that gas phase species contribute to the sensory effects caused by the reaction products and, also, tentatively supports the above speculation that some gas phase sensory pollutants were consumed by photochemistry when passing near the UV lamp. Assuming that there was equilibrium between gas phase and condensed phase products, some
gas phase products also would be purged by particle removal, with consequent improvement in the acceptability of the air.

The combination of gas phase products and a low particle concentration produced a pollution load (16 olf) in the chamber environment (“B” in Tables 2 and 3) that was twice the pollution load (8 olf) caused by the combination of gas phase products and a high particle concentration in the office environment (“A” in Tables 2 and 3). This further suggests that gas phase products, and not particles, are primarily responsible for the degradation of air quality when this reaction occurs indoors.

In the office environment during the condition with 45 ppb ozone/40 ppb limonene (“A” in Tables 2 and 3), the degradation of the air quality relative to the background (8 olf) was larger than that (< 1 olf) for the same ozone-limonene condition in the stainless-steel chamber (“C” in Tables 2 and 3). The particle and TVOC concentrations measured during experiment C indicate that the recirculation loop in the stainless steel chamber scavenged both particles (50000 part/cm$^3$ in the test room vs. 1220 part/cm$^3$ in the stainless-steel chamber) and gas-phase species (5.9 in the test room vs. 5.2 mg/m$^3$ in the stainless-steel chamber). Since the comparisons presented in the preceding paragraphs indicate that the higher particle concentrations do not make a significant contribution to short-term sensory effects, this indicates that some of the scavenged gas phase species are sensory pollutants.

To sum up the observations derived from the 45 ppb ozone/40 ppb limonene experiments, we can say that the presence of ozone–limonene mixtures in indoor air leads to the degradation of air quality. Furthermore, we speculate that the greater the extent of secondary organic aerosol formation, the less sensory offending the product mixture. The ozone generation method with
room air produced more SOA, creating a mixture with less sensory offending pollutants compared to mixtures in the room where the ozone was generated with pure oxygen. Based on these results we infer that the ozone generation method with oxygen, if used in the test rooms, would have resulted in stronger sensory effects than the room air generation method. The gas phase products are primarily responsible for the degradation of air quality. Since condensed phase products always coexist with gas phase products, increased particle concentrations resulting from indoor ozone reactions indicate less acceptable air quality (see Figure 4); however, low particle concentrations cannot guarantee acceptable air quality.

In the 10 ppb ozone/115 ppb limonene condition the scents of limonene and of the related reaction products were very strong in both steel chambers due to the high limonene concentration, making it difficult to observe sensory differences between the two ozone generation methods.

CONCLUSIONS

Ozone has direct, adverse effects on human health (Bell et al., 2004 and references therein). Ozone also initiates reactions that produce potentially irritating products. The current study, using concentrations of ozone and limonene known to occur in indoor settings, demonstrates that the products of ozone-initiated reactions with limonene negatively affect short-term evaluations of perceived air quality. This corresponds to other studies (Knudsen et al., 2002; Kleno and Wolkoff, 2004; Kleno-Nojgaard et al., 2005) that also report negative effects of exposure to the products of ozone/limonene reactions.

The filtration of ozone-limonene products removed a fraction of the condensed-phase species as well as a fraction of the gas phase pollutants; this improved the perceived air quality.
The odor of limonene was recognized by more than 50% of the sensory panel at 85 ppb, a level that is lower than the current detection limits reported in the literature. The odor of limonene (at high concentrations) and the various gas phase oxidation products both contribute to the sensory effects of ozone limonene reactions, while condensed phase products do not appear to directly contribute to sensory effects, but rather indicate the presence of odorous gas phase reaction products. The correlations shown in Figure 4 between particle concentrations and sensory pollution loads reflects the co-generation of condensed phase products and sensory offending gas phase products.

ACKNOWLEDGEMENTS

The authors thank the subjects for their participation in the experiments. This work has been supported by the Danish Technical Research Council (STVF) as part of the research programme of the International Centre for Indoor Environment and Energy at the Technical University of Denmark.

REFERENCES


PAPER 2: THE INFLUENCE OF OZONE/CARPET CHEMISTRY ON
PERCEIVED AIR QUALITY
THE INFLUENCE OF OZONE/CARPET CHEMISTRY ON
PERCEIVED AIR QUALITY

Gyöngyi Tamás\textsuperscript{1}, Charles J. Weschler\textsuperscript{1,2}, Jørn Toftum\textsuperscript{1}

\textsuperscript{1}International Centre for Indoor Environment and Energy (ICIEE), Technical University of Denmark, 2800-Kgs. Lyngby, Denmark

\textsuperscript{2}Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers Univ.), Piscataway, NJ 08854 USA

Correspondence to:

Charles J. Weschler

Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers Univ.), 170 Frelinghuysen Rd., Piscataway, NJ 08854, USA

Phone: 732 235-4114    Fax: 732 235-4569

e-mail: weschlch@umdnj.edu
ABSTRACT

Full-scale air quality assessments were carried out in the absence and presence of ozone (18 to 28 ppb) for three carpet samples that were different in age, constituent materials and origin. Area-specific emission rates of sensory pollutants and area-specific carpet surface removal rates were calculated. The results show that ozone exposure reduced the sensory pollution load of the new carpet (from 2.6 to 1.6 olf/m$^2$), presumably as a consequence of the oxidation of odorous primary emissions to less odorous products. However, ozone exposure of the old, soiled carpets significantly increased the sensory pollution load -- from about 0.2 to 1 olf/m$^2$ in case of a synthetic carpet and from 0.4 to 2.3 olf/m$^2$ for a carpet made of wool. Ozone deposition velocities were between 0.028 and 0.054 cm/s and increased as the sensory emission from the carpets increased. The present result shows that even moderate ozone levels may significantly alter the perceived air quality of carpeted environments.

KEY WORDS

Ozone, Carpet, Indoor air chemistry, Perceived air quality, Ozone removal rate, Deposition velocity

INTRODUCTION

Ozone is commonly found in various indoor settings as a result of outdoor-to-indoor transport or direct emission from indoor sources. Concentrations of 20-40 ppb ozone are commonly reported indoors, but in extreme cases levels can exceed 100 ppb (Sabersky et al., 1973; Weschler et al., 1989; Weschler, 2000). In the absence of indoor sources, indoor ozone
concentration are lower than concurrent outdoor concentrations due to removal by indoor surfaces, i.e. heterogeneous reactions and deposition (Cano-Ruiz et al., 1993), and, to a lesser extent, gas-phase reactions with ozone-reactive volatile organic compounds (VOCs) (Weschler, 2000). Since people spend most of their time in buildings, their indoor exposure can actually be larger than their outdoor exposure, even though ozone concentrations are usually lower indoors than outdoors (Weschler et al., 1989). The direct effects of ozone on health are well recognized. When inhaled, ozone can damage the lung cells and aggravate chronic diseases such as emphysema, bronchitis and asthma (US EPA, 1996). Bell et al. (2004) estimated a 0.52% increase in daily mortality for a 10 ppb increase in the ambient ozone level. The US EPA health-based standard for ozone is 120 ppb and 80 ppb for 1 h and for 8 h exposures, respectively (US EPA, 1996). An occupational threshold limit of 80 ppb also has been established (ACGIH, 2000).

Floor materials, and in particular carpets, are of special interest in air quality investigations because they are recognized as major VOC sources indoors. Since carpets may have up to 60-70 times larger surface areas than the floor area that they cover (Morrison and Nazaroff, 2000), the potential to significantly impact indoor air quality is especially large. Primary emissions from carpets (i.e. physical release of VOCs from the carpet pile, backing and backing adhesives) contain a number of potentially odorous and/or irritating compounds (e.g., 4-phenylcyclohexene, styrene, and 4-vinylcyclohexene (Hodgson et al., 1992)). However, the VOC emissions from a carpet may be significantly altered in an ozone rich environment, and ozone-initiated chemistry produces a set of other odorous and/or irritating compounds, such as formaldehyde, acetaldehyde and C5-C10 aldehydes, which are released from the carpet surface into the air (Weschler et al., 1992; Morrison and Nazaroff, 2000; 2002a). In real life carpets act as a huge reservoir for other organic substances associated with dust and grim that
accumulate over time, and which may also interact with ozone. The secondary emissions from a used carpet may involve more complex chemistry than in the case of a new product. Carpets are widely used in buildings throughout the world (Potting and Blok, 1995). The negative impacts of carpets on perceived air quality, health symptoms and work performance have been acknowledged in many studies and reviews of the literature (Mendell, 1993; Wargocki et al., 1999; Pejtersen et al., 2001; Mathisen et al., 2002; Mendell and Heath, 2005). The ozone uptake of carpets and the resulting reaction products have been measured both in real environments and under special laboratory conditions (Weschler et al., 1992; Moriske et al., 1998; Jakobi and Fabian, 1997; Klenø et al., 2001; Morrison and Nazaroff, 2002a, 2002b). Knudsen et al. (2003) studied the interaction of ozone with unused carpets and other building materials and also the effects of the reaction products on the air quality assessed by human subjects in 50 L test chambers. They found that their carpet sample showed significantly higher odor intensity when exposed to ozone; the ozone-exposed sample had a clear negative sensory evaluation. They also showed that the ozone removal was caused primarily by interactions with the carpet’s surfaces and only to a minor extent by gas-phase reactions.

The primary objective of this study was to evaluate changes in emissions of sensory offending pollutants resulting from exposure of carpet samples to moderate ozone levels (18-28 ppb in presence of the carpet). An ancillary objective was to measure ozone’s deposition velocity to these samples and compare the results with earlier measurements.

METHODS

Experimental conditions and procedure

Air quality assessments of emissions from carpet samples were conducted to evaluate the effect on perceived air quality of ozone-initiated reactions occurring on the carpet surfaces.
and in the gas phase. The sensory assessments took place in climate chambers both at moderate ozone levels and in an ozone free environment.

**Carpet samples:** Three types of carpet samples (Table 1), one new and two old, were examined. One of the old carpets (Town Hall Carpet) was taken from an office building in Denmark where it had been situated for 20 years (Pejtersen et al., 2001). The other old carpet (Aircraft Carpet) had been in use in a passenger aircraft for the duration of its normal service life. The new carpet (New Carpet) was of a type that is commonly used in office buildings in Denmark, and was purchased one year before the experiments. The new carpet had never been laid down for normal use. The area of the Town Hall Carpet and the New Carpet was 10 m², corresponding to the floor area of the steel-chambers, but only 6.5 m² of the Aircraft Carpet were available.

**Table 1.** Characteristics of carpet samples.

<table>
<thead>
<tr>
<th></th>
<th>Town Hall Carpet</th>
<th>Aircraft Carpet</th>
<th>New Carpet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction</td>
<td>textured loop</td>
<td>textured loop</td>
<td>textured loop</td>
</tr>
<tr>
<td>Fiber</td>
<td>polyamid</td>
<td>wool</td>
<td>polyamid</td>
</tr>
<tr>
<td>Dye method</td>
<td>unknown</td>
<td>unknown</td>
<td>solution</td>
</tr>
<tr>
<td>Fiber treatment</td>
<td>Scotchguard</td>
<td>no treatment</td>
<td>static control</td>
</tr>
<tr>
<td>Backing</td>
<td>rubber</td>
<td>canvas</td>
<td>Graphlex</td>
</tr>
<tr>
<td>Backing fixation</td>
<td>SBR latex adhesive</td>
<td>sewn on a machine</td>
<td>unknown adhesive</td>
</tr>
<tr>
<td>Form</td>
<td>roll</td>
<td>roll</td>
<td>tiles</td>
</tr>
</tbody>
</table>

**Chambers:** The air quality assessments of the three carpet samples were conducted in a pair of adjacent stainless-steel chambers, designed specifically for indoor air quality studies (Albrechtsen, 1988). Each chamber has a volume of 30 m³ (including re-circulation ducts), 10 m² floor area and is served by a completely separate HVAC system. The chambers were
operated at 22 ± 0.1°C and 35.4 ± 5.2 % RH. The air in the chambers was distributed through a perforated floor, extracted at the ceiling and re-circulated at a high rate to obtain good mixing of the pollutants emitted in the chamber. The total rate (recirculated and outdoor air) at which air in the chambers was exchanged was 50 h⁻¹, while the rate at which the chamber air was exchanged with outdoor air was 1.6 h⁻¹ ± 0.1 h⁻¹ for both chambers.

**Ozone:** During the period when the assessments were carried out an activated charcoal filter was installed in the supply air system for each chamber to remove ambient ozone. For conditions with ozone, it was generated using ultra-pure oxygen from a compressed gas cylinder that flowed directly into the ozone-generator (UV lamp in a sealed housing) and then into the chamber.

**Procedure:** The assessments were conducted on three separate days during a week in April 2005 with full-day breaks between each assessment. The full-day breaks were used to ventilate (refresh) the carpet samples. During the “recovery period” they hung on stainless-steel racks for 24 hours in a neighboring chamber. On each of the three assessment days approximately 40 ppb of ozone was generated in one of the steel chambers. In the other chamber no ozone was generated. The selection of the chamber where ozone was generated was randomized. When the ozone concentration reached steady state, the same kind and the same amount of carpet samples were placed into both chambers, behind a partition. The carpet samples were fixed back-to-back to each other to reduce emissions from and reactions with the backing of the carpet. Two hours after the carpets had been placed in the chambers the ozone levels had decreased to between 18 and 28 ppb (Table 2); at this point a panel of untrained subjects consisting of approximately twenty staff members and students (age 22-60 years) from the ICIEE began assessing the air quality. The assessments were made, one by
one, immediately upon entering the chamber. This was done using a pseudo-continuous acceptability scale (Clausen, 2000). After the 45-60 minute assessment period, the ozone generator was shut off, and 1.5 hours later another assessment round took place using the same panel. The air quality in the chambers in the absence of carpets and ozone was also evaluated on a separate day by the same panel.

After the week of sensory measurements the ozone removal rates in the chamber with and without carpet samples were measured. During this part of the study the activated charcoal filter was removed from the air supply system and ozone was transported with the outdoor air into the chambers. The carpet samples that had not been exposed to ozone during the sensory assessments were used. All other parameters were kept unchanged.

**Physical measurements:** Temperature and relative humidity were monitored continuously during the experiments. The outdoor air change rate was measured with the tracer gas decay method each morning prior to the experimental session. The ozone concentrations in the chambers were continuously measured with two UV photometric analyzers operating at 254 nm (Dasibi 1003-AH and Dasibi 1003-RS). These instruments have a range of 0 – 500 ppb, a sensitivity of 1 ppb and a precision of 1 ppb or +/- 1 %, whichever is greater. The sampling points of the ozone instruments were close to the central location of the chambers at a height of 1.5 m.

**DATA ANALYSIS**

Using the comfort model presented by Fanger (1988), coupled with the measured ventilation rates and assuming that good mixing had been achieved, the total sensory pollution loads in
the chambers were calculated in units of “olf”s” (Clausen, 2000). The sensory pollution load can be viewed as a measure of the emission rate (i.e., mass per unit time) of sensory pollutants. All data obtained from questionnaires were tested for normality using the Shapiro-Wilks’ W test with the rejection region of p<0.01. For normally distributed data, one-way analysis of variance (ANOVA), supplemented with Duncan’s post-hoc comparison or paired t-test, was applied to evaluate differences between the conditions. All reported p-values are 1-tailed. Differences were assumed significant at a p level of <0.05.

RESULTS

The results of the sensory evaluations are summarized in Table 2. The air in the chambers when neither carpet nor ozone were present was perceived to be better than that in the presence of any carpet samples, regardless of the ozone condition, and was very similar in the two chambers (+0.29 vs. +0.32).

Statistical analysis of the acceptability results indicates that during the morning sessions, when the same kind of carpets were compared in the presence and absence of ozone, a significant difference was found only for the New Carpet; the air quality in the chamber containing New Carpet and ozone was more acceptable than that in the chamber containing only New Carpet (p<0.042). During the afternoon sessions, 1.5 hours after the ozone generator was shut off, significant differences were found between all three pairs of ozonized/non-ozonized carpet samples (p<0.004 for Town Hall Carpet, p<0.005 for Aircraft Carpet and p<0.014 for New Carpet).
Table 2. Results from sensory evaluations of chamber air. Significant differences are at p<0.05.

<table>
<thead>
<tr>
<th>Carpet size [m²]</th>
<th>ACH [h⁻¹]</th>
<th>Ozone level [ppb]</th>
<th>Ozone</th>
<th>Acceptability (± 95% c.i.)</th>
<th>Area Specific Sensory Pollution Load [olf/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Town Hall Carpet</td>
<td>10</td>
<td>1.64</td>
<td>27.7 ± 2.3</td>
<td>present</td>
<td>0.17 ± 0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>absent</td>
<td>-0.11 ± 0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.13 ± 0.17</td>
</tr>
<tr>
<td>Aircraft Carpet</td>
<td>6.5</td>
<td>1.63</td>
<td>18.0 ± 3.1</td>
<td>present</td>
<td>-0.06 ± 0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>absent</td>
<td>-0.18 ± 0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.13 ± 0.22</td>
</tr>
<tr>
<td>New Carpet</td>
<td>10</td>
<td>1.59</td>
<td>25.3 ± 2.8</td>
<td>present</td>
<td>-0.27 ± 0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>absent</td>
<td>-0.20 ± 0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.40 ± 0.23</td>
</tr>
<tr>
<td>Ch 1 alone</td>
<td>--</td>
<td>1.62</td>
<td>--</td>
<td>absent</td>
<td>0.32 ± 0.17</td>
</tr>
<tr>
<td>Ch 2 alone</td>
<td>--</td>
<td>1.49</td>
<td>--</td>
<td>absent</td>
<td>0.29 ± 0.19</td>
</tr>
</tbody>
</table>

* Average during assessment period.

Table 3. Indoor/Outdoor ozone ratios, removal rates and deposition velocities based on measurements in the steel-chambers. See text for details.

<table>
<thead>
<tr>
<th>Size [m²]</th>
<th>I/O w/o carpet</th>
<th>I/O with carpet</th>
<th>R w/o carpet [h⁻¹]</th>
<th>R with carpet [h⁻¹]</th>
<th>Normalized Rₚ [h⁻¹/m²]</th>
<th>Vₚ [cm s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Town Hall Carpet</td>
<td>10.0</td>
<td>0.52 ± 0.04</td>
<td>0.48 ± 0.03</td>
<td>1.49</td>
<td>1.78</td>
<td>0.029</td>
</tr>
<tr>
<td>Aircraft Carpet</td>
<td>6.5</td>
<td>0.53 ± 0.04</td>
<td>0.46 ± 0.03</td>
<td>1.30</td>
<td>1.69</td>
<td>0.065</td>
</tr>
<tr>
<td>New Carpet</td>
<td>10.0</td>
<td>0.52 ± 0.04</td>
<td>0.44 ± 0.02</td>
<td>1.49</td>
<td>2.04</td>
<td>0.055</td>
</tr>
</tbody>
</table>
In the case of the non-ozonized samples, the acceptability of air was similar in the morning and afternoon assessments, as expected. In the case of the ozonized samples, the assessments in the afternoon, absent ozone, differed from those in the morning. The old carpets were less acceptable in the afternoon compared to the morning evaluations (p<0.003 for Town Hall Carpet and p<0.123 for Aircraft Carpet), while the new carpet was slightly more acceptable. In addition to acceptability results, Table 2 also presents the area-specific sensory pollution loads both for the carpet samples and the empty chambers. Normalizing for surface area, the ozonized Aircraft Carpet is much more polluting than the ozonized Town Hall Carpet. The ozonized Aircraft Carpet is even more polluting than the ozonized New Carpet, although the non-ozonized Aircraft Carpet was much less polluting than the non-ozonized New Carpet.

Table 3 shows indoor/outdoor ozone ratios in the steel chambers when carpet samples are absent and present. In these experiments ozone was not deliberately added to the air, but was simply the ozone present in the outdoor air on the day of the experiment. The area-specific carpet surface removal rates (2nd to last column in Table 3) were calculated from the ozone I/O ratios. These, in turn, were converted to deposition velocities by multiplying by the volume of the stainless-steel chamber (30 m$^3$). The deposition velocities of the Aircraft Carpet and the New Carpet were similar and about twice as high as that of the Town Hall Carpet.

**DISCUSSION**

It is instructive to compare the sensory assessments of the air in the empty chamber with the air when the chamber contained carpet, but no ozone. In the case of the New Carpet, the acceptability decreased from +0.30 to –0.41; in the case of the old Town Hall carpet, it decreased from +0.30 to +0.13; in the case of the old Aircraft Carpet, it decreased from +0.30
to +0.11. Absent ozone, the New Carpet was emitting sensory pollutants at a much larger rate than either of the old carpets (2.6 olf/m² vs. less than 0.4 olf/m²).

The morning sensory assessments that were conducted in the presence of ozone are difficult to evaluate. At concentrations above its odor detection limit (20-50 ppb) ozone may inhibit the sense of smell due to its paralyzing effect on terminal olfactory nerves (Horváth et al., 1985). This phenomenon manifests itself as reduced sensitivity to certain odors in the presence of ozone. Hence, during the morning sessions in the presence of ozone, ozone attenuated the subjects’ evaluations of the primary carpet emissions as well as the secondary emissions resulting from ozone-initiated chemistry. The sensory evaluations of the ozonized carpets conducted in the afternoon, when no ozone was present to alter the sense of smell, are more straightforward to interpret.

From the afternoon assessments, it is apparent that ozone exposure affected the sensory evaluations, and hence the pollution load, of the old and the new carpets in different ways. In the case of the old carpets, the assessments indicate that ozone exposure had produced sensory offending compounds that continued to desorb from the carpet after ozone was no longer present in the chamber air. This is consistent with earlier studies that have reported continued emission of ozone derived oxidation products from carpets for hours, days and weeks after the period of ozone exposure was over. For example, the C6-C10 aldehydes were still detected in chamber air one day after their ozone-induced production had ceased (Weschler et al., 1992). Weschler et al. speculated that these aldehydes had sorbed to the carpet surfaces during the period when their steady-state concentrations were elevated (i.e., when ozone was present). Then, in the absence of ozone, the carpets served as a source of these aldehydes as they desorbed from carpet surfaces. Morrison et al. (2002a) also reported
that ozone induced aldehydes continued to be emitted 24-60 hours after carpet samples were exposed to ozone; this was true for each of the 4 carpets they examined.

In the case of the New Carpet, the afternoon assessments indicate that ozone exposure had decreased the emission of sensory offending compounds. Presumably, the New Carpet contains volatile, sensory offending primary emissions that react with ozone (e.g., 4-PCH and 4-VCH; see Weschler et al., 1992; Morrison and Nazaroff, 2002a). Although it is known that oxidation products result from reactions between primary emission products and ozone, the results indicate that the sensory response was driven by the primary emissions as opposed to the oxidation products. It appears that, during the morning exposures, ozone diffused into the carpet, reacting with reservoirs of volatile unsaturated sensory pollutants, reducing their emission rates. We expect that after one or two days the emission rates returned to a level close to those before the ozone exposure, taking into account the fact that primary emissions decrease as a carpet ages (Hodgson et al., 1992).

From Table 3 it is apparent that, during the morning experiments, the Aircraft Carpet removed more ozone per square meter than either the New Carpet or the Town Hall Carpet. Comparing the two old carpets, in the morning experiments the ozone deposition velocity was larger for the Aircraft Carpet (0.054 vs. 0.024 cm s$^{-1}$) and in the afternoon it emitted more sensory pollutants (2.3 vs. 1.1 olf m$^{2}$).

The ozone deposition velocity measured in the current study for the Town Hall Carpet can be compared with that measured 7 years earlier for this same carpet. In the earlier study, Wargocki et al. (1999) reported outdoor and indoor levels of ozone in an occupied 108 m$^{3}$ office ventilated at 2 h$^{-1}$ in the presence and absence of 36 m$^{2}$ of the Town Hall Carpet. Based
on these conditions, the ozone deposition velocity for the Town Hall Carpet was calculated to be 0.083 cm s\(^{-1}\) in 1998 compared with 0.024 cm s\(^{-1}\) in 2005. Some of the difference reflects differences in humidity levels between the two studies (RH 35\% vs. 50\%). An increase in ozone deposition velocities due to higher humidity levels has been reported in other studies (Nazaroff et al., 1993). Grøntoft et al., 2004 reported an increase in the ozone deposition velocity from 0.069 to 0.081 cm s\(^{-1}\) for a synthetic carpet sample when the relative humidity increased from 30 to 50 \%. However, we expect that much of this difference was caused by the gradual evaporation of sensory offending compounds coupled with the ozone consumption of reactive sensory offending compounds over the intervening 7 years.

**CONCLUSIONS AND PRACTICAL IMPLICATIONS**

Based on the results of the present study we can conclude that early in a carpet’s service life, ozone exposure may diminish a new carpet’s odor. However, during most of a carpet’s service life, after the more volatile primary emissions have decayed, ozone exposure will significantly increase the emission of sensory offending secondary pollutants. For example, in a typical carpeted office with 10 m\(^2\)/person occupancy, the total pollution load from a recently ozone-exposed carpet may contribute 10-20 times more to the pollution load than a standard person.

**ACKNOWLEDGEMENTS**

The authors thank the subjects for participating in these experiments and Pawel Wargocki for helpful discussions.
This work has been supported by the Danish Technical Research Council (STVF) as part of the research program of the International Centre for Indoor Environment and Energy at the Technical University of Denmark.

REFERENCES

ACGIH (American Conference of Governmental Industrial Hygienists), (2000) “TLV’s and BEI’s, 2000. Threshold Limit for Chemical Substances and Physical Agents and Biological Exposure Indices”. Cincinnati, OH, American Conference of Governmental Industrial Hygienists.


PAPER 3: FACTORS AFFECTING OZONE REMOVAL RATES IN A SIMULATED AIRCRAFT ENVIRONMENT
FACTORS AFFECTING OZONE REMOVAL RATES IN A SIMULATED AIRCRAFT ENVIRONMENT

Gyöngyi Tamás¹, Charles J. Weschler¹,², Zsolt Bakó-Biró¹, David P. Wyon¹ and Peter Strøm-Tejsen¹

¹International Centre for Indoor Environment and Energy (ICIEE), Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
²Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers Univ.), Piscataway, NJ 08854 USA

Correspondence to:
Charles J. Weschler
Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers Univ.), 170 Frelinghuysen Rd., Piscataway, NJ 08854, USA
Phone: 732 235-4114  Fax: 732 235-4569
e-mail: weschlch@umdnj.edu
ABSTRACT

Ozone concentrations were measured concurrently inside a simulated aircraft cabin and in the airstream providing ventilation air to the cabin. Ozone decay rates were also measured after cessation of ozone injection into the supply airstream. By systematically varying the presence or absence of people, soiled T-shirts, aircraft seats and a soiled HEPA filter, we have been able in the course of 24 experiments to isolate the contribution of these and other factors to the removal of ozone from the cabin air. In the case of this simulated aircraft, people were responsible for almost 60% of the ozone removal occurring within the cabin and recirculation system; the aircraft seats, about 25%; the loaded HEPA filter, 7%; and the other surfaces, 10%. The removal of ozone by people was equivalent to a Clean Air Delivery Rate, with respect to ozone, of 12 to 14 m$^3$ h$^{-1}$ per person or a deposition velocity of 0.20 to 0.22 cm/s. Respiration can only have been responsible for about 4% of this removal. A T-shirt that had been slept in overnight removed roughly 70% as much ozone as a person, indicating the importance of skin oils in ozone removal. The presence of the used HEPA filter in the recirculated airstream reduced the perceived air quality. When the cabin surfaces were exposed to elevated ozone levels for an extended period of time (~5 h), the overall ozone surface removal rate decreased at ~3% per hour. With people present, the measured ozone retention ratios (0.15 to 0.21) were smaller than levels reported in the literature. These results, coupled with our previous study of the products resulting from ozone-initiated chemistry in this same simulated aircraft, indicate that the optimal way to reduce people’s exposure to both ozone and the products of ozone-initiated chemistry is to efficiently remove ozone from the air supply system of an aircraft.
KEY WORDS

Ozone, Aircraft air quality, Indoor air chemistry, Heterogeneous chemistry, Ozone removal rates, Human bioeffluents

INTRODUCTION

The presence of ozone in the indoor environment has received increased attention over the last decade due to the recognition of its direct effect on human health and its important contribution to indoor chemistry. When inhaled, ozone can damage the lung cells and aggravate chronic diseases such as emphysema, bronchitis and asthma (US EPA, 1996). Based on data from 95 US urban communities during a 14 year period, Bell et al. (2004) estimated a 0.52% increase in daily mortality for a 10 ppb increase in the previous week’s local ambient ozone level. Ozone also initiates reactions that produce known irritants of potential health concern (e.g., Weschler et al., 1992; Morrison and Nazaroff, 2002a; Nazaroff and Weschler, 2004). The negative effects of products originating from some of these reactions have been directly evaluated with human subjects (Klenø-Nøjgaard et al., 2005; Tamás et al., 2005; Laumbach et al., 2005). The US EPA health-based standard for ozone is 120 ppb for 1 h and 80 ppb for 8 h exposures (US EPA, 1996). An occupational threshold limit of 80 ppb has been established (ACGIH, 2000).

At typical cruising altitudes the concentration of ozone in the cabin of a commercial aircraft can be significantly higher than that for normal indoor built environments. This is due to the high concentration (500-800 ppb) of ozone in the outside air at higher altitudes (> 10000 m; SAE International, 2000) that is transported through the aircraft ventilation system to the cockpit and passenger area. A recent study using passive samplers on 106 flight segments reported average concentrations of 80 (± 30) ppb in airplane cabins during winter and early
spring. Twenty percent of the measurements exceeded 100 ppb and eleven percent exceeded 120 ppb (Spengler et al., 2004). Spicer et al. (2004) continuously measured the ozone levels on 4 flights within the continental United States using a real time ozone monitor. On all 4 flights, the authors found that ozone levels increased from takeoff until cruise altitude had been reached. At cruise altitude they measured average levels between 31 and 106 ppb. Both the above studies showed that ozone levels in commercial aircraft can easily approach and exceed the recommended health exposure ceilings.

To reduce the cabin crew and passengers exposure to ozone, catalytic converters are sometimes installed in the air supply system. Absent these converters or when a converter malfunctions, a large amount of ozone may pass into the cabin. The “retention ratio”, defined as the ratio between the ozone concentration in the cabin and in the air outside, is a measure of the fraction of outdoor ozone in the cabin air when no devices are present to deliberately remove it. Average retention ratios of 0.45 and 0.85 have been measured for a Boeing 747-100 and 747SP, respectively (Nastrom et al., 1980). The default retention ratio for demonstrating compliance with the FAA (U.S. Federal Aviation Administration) regulations addressing cabin ozone levels is 0.7 (SAE AIR910 cited in NRC, 2002). Ozone is partly removed when passing through the aircraft air delivery system and air conditioning units, and is further removed by surfaces in the cabin, by the passengers and crew and by surfaces in the recirculation system. The removal is due to simple decomposition and surface reactions (Weschler, 2000; Grøntoft and Raychaudhuri, 2004). Such surface reactions can significantly alter the composition of aircraft cabin air. Wisthaler et al. (2005) examined the products formed when ozone, at concentrations typical of those encountered at cruising altitudes, is present in a simulated commercial aircraft cabin. (The same simulated cabin was used in the present study.) The study was conducted without human occupants. However, T-shirts that
had been worn all night were used as surrogates for some of the less volatile bioeffluents
associated with passengers and crew. Concentrations of monitored organic compounds were
significantly higher when ozone was present, with most of the increase being due to higher
concentrations of aldehydes (saturated and unsaturated) and squalene oxidation products.

The potential of various materials to remove/react with ozone has been reported in a number
of studies. The ozone uptake of various sinks has been studied both in real environments (see
Weschler, 2000; Grøntoft and Raychaudhuri, 2004) and under special laboratory conditions
(Klenø et al., 2001). A few studies have examined the interaction of ozone with ventilation
filters (Bekö et al., 2005a and 2005b; Hyttinen et al., 2003). Relatively sparse data since 1989
exist on ozone removal rates in aircraft cabin environments. The effect of people on ozone
removal has not been systematically investigated, but some data are available from air quality
studies made in indoor environments with and without occupants (Bakó-Biró et al., 2005).

The present study examines the effects of various parameters, (e.g., people and their clothing,
human bioeffluents, surfaces within the cabin, ventilation filters, repeated ozone exposures)
on the ozone removal rate within a simulated aircraft cabin. Ozone removal by such processes
influences the exposure of passengers and crew to both ozone and the products of ozone-
initiated chemistry. Such information can be used to better determine the need and required
efficiency of ozone removal devices in today’s aircraft.
METHODS

Over a two-year period (2004 and 2005) experiments were conducted to study ozone dynamics in a simulated aircraft environment at the Technical University of Denmark. In each of these experiments the simulated aircraft cabin and the integrated ventilation system were exposed to elevated ozone concentrations and possible interactions of ozone with various sinks were evaluated.

**Filters:** A used (i.e. dust-loaded) HEPA filter that had been in a passenger aircraft for 18 months (its maximum recommended service life) was included in the air recirculation system (see Figure 1) in some of the conditions. Two-thirds of its cross-sectional area was blocked off so that the area through which the recirculated air passed was in correct proportion to the length of the cabin section. For comparison, a new HEPA filter was also examined. In some cases, supplementary to the physical measurements of a used HEPA, new HEPA or no HEPA in the system, subjective evaluations of cabin air quality were carried out.

**Bioeffluents:** As a preliminary method to simulate the presence of human bioeffluents in the cabin air, soiled T-shirts were placed over the back of the seats. Later, after obtaining ethics approvals from boards in Denmark and the United States, human subjects were exposed in the cabin environment for several hours.

**Aircraft seats:** Aircraft seats, due to their large surface area, present a significant sink for ozone. To evaluate the magnitude of this effect, measurements were made during a period in which the seats had been taken out of the aircraft cabin.
**Aging effect:** Interior surfaces of the cabin were exposed for approximately 5 hours to elevated O$_3$ concentrations and changes in the ozone removal rate were evaluated.

**Repeated ozone exposure:** During the normal operation of an aircraft, the cabin surfaces may be repeatedly exposed to elevated ozone concentrations, reflecting time in the air and time on the ground. To examine the impact of such cycling, the ozone generators were shut off for different periods of time (30, 60, 90 and 120 minutes) following 60 minute cycles of ozonation.

**Description of simulated aircraft cabin**

The study was conducted within a simulated aircraft cabin containing 21 seats (3 rows of 7). As illustrated in Figure 1, it was installed inside an existing climate chamber that is capable of providing two separately controlled air supply streams. One of these was used to cool the climate chamber, to ensure that the rate of heat loss through the cabin walls was realistic, the other to ventilate the simulated cabin.

![Figure 1. Schematic of the simulated aircraft cabin’s ventilation system.](image)
The total supply airflow, including recirculated air, was always 200 L/s (equivalent to 23 h⁻¹) of which 25-75 L/s (3-8.8 h⁻¹) was outdoor air, depending on the experimental condition. The value for the outdoor airflow rate specified by FAR 25 (Federal Aviation Regulation) is 75 L/s at altitude if this cabin had 16 occupants. The cabin air temperature was controlled by an integrated ventilation system at 23.3 ± 0.3 °C. Relative humidity varied with the experimental conditions and spanned the range from 2-24% (all but three values were below 15%). Experiments were conducted at ground level barometric pressure. The pressure in the simulated cabin was 4 to 8 Pa higher than that in the outer chamber in order to avoid contamination of the cabin air with air that might infiltrate in an uncontrolled manner.

Emissions to the cabin air, other than those described above, occurred from the materials and fittings specified in this paragraph. Used aircraft seats were obtained from a supplier of aftermarket parts. The carpet had been in use in a passenger aircraft for the duration of its normal service life. The total surface area of the carpet was 15.6 m² while that of the aircraft seats was 24.6 m². Six panels from a used aircraft cabin interior, with windows, were used in the walls. For additional details regarding the simulated cabin see Wisthaler et al. (2005).

**Generation of ozone**

All of the outdoor supply air passed first through a 10 m³ pollution chamber (see Figure 1). Pure oxygen (99.999%) from a compressed gas cylinder flowed through six UV ozone generators, providing ozone to this pollution chamber and subsequently to the cabin. Given the high rate of total air supply (200 L/s) relative to the cabin volume, the mixing time is
anticipated to be short (< 5 minutes). The amount of ozone was regulated by turning one or more ozone generators on or off.

**Physical measurements**

Cabin temperature and relative humidity, outdoor air supply rate, total air supply rate and cabin pressure were monitored continuously during the experiment. The ozone concentration in the cabin air and in the pollution chamber was continuously measured with two UV photometric analyzers operating at 254 nm (Dasibi 1003-AH and Dasibi 1003-RS). These instruments have a range of 0 – 500 ppb, a sensitivity of 1 ppb and a precision of 1 ppb or +/- 1 %, whichever is greater. The number concentrations of particles [part/cm$^3$] were measured with two P-Trak condensation nuclei counters (0.02-1 µm diameter size range). The sampling points for the ozone and particle instruments were close to the central location of the cabin at a height of 1.2 m and at the exhaust of the pollution chamber.

**Experimental conditions and procedure**

The experiments are summarized in Table 1.
Table 1. Summary of experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Condition</th>
<th>HEPA</th>
<th>Seats</th>
<th>T-shirts</th>
<th>People</th>
<th>ACH [h⁻¹]</th>
<th>n</th>
<th>Aim</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEPA filter</td>
<td>1</td>
<td>none</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>1</td>
<td>Determine ozone removal rates of used and new HEPA filters at two outdoor air change rates.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>3</td>
<td>Direct measurements of ozone removal efficiencies of used and new HEPA filters at two outdoor air change rates.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>new</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>1</td>
<td>Sensory evaluations of the cabin air with and without a used filter.</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>none</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>6.5</td>
<td>2</td>
<td>Determine ozone removal rates of the aircraft seats at two outdoor air change rates.</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>6.5</td>
<td>1</td>
<td>Examine “surface aging” effect on ozone removal during an extended exposure period.</td>
</tr>
<tr>
<td>HEPA filter</td>
<td>1</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>2</td>
<td>Simulate contribution of human skin oils to ozone removal rates at two outdoor air change rates.</td>
</tr>
<tr>
<td>upstream/downstream</td>
<td>2</td>
<td>new</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>2</td>
<td>Determine ozone removal rates due to people at two outdoor air change rates.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>new</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>HEPA filter sensory</td>
<td>1</td>
<td>none</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Aircraft seats</td>
<td>1</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>used</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>used</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Soiled T-shirts</td>
<td>1</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>3.0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>used</td>
<td>+</td>
<td>17</td>
<td>--</td>
<td>3.0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>none</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>6.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>none</td>
<td>+</td>
<td>17</td>
<td>--</td>
<td>6.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>People</td>
<td>1</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>4.4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>16</td>
<td>4.4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>16</td>
<td>8.8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Aging</td>
<td>1</td>
<td>used</td>
<td>+</td>
<td>--</td>
<td>--</td>
<td>8.8</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
**Effect of HEPA filter on ozone removal.** A total of five experiments, at air exchange rates of either 4.4 or 6.5 h\(^{-1}\), were conducted to evaluate the effect of HEPA filters on ozone removal rates in the cabin. Two of the experiments focused on the influence of a loaded HEPA filter; one experiment used a new HEPA filter; and two experiments were conducted with no HEPA filter installed. The length of the ozonation period ranged from 1 to 2 hours. In four additional experiments, conducted at low and high air change rates with either a used or new HEPA filter in the recirculation system, ozone removal efficiencies were directly determined by measuring ozone concentrations upstream and downstream of the filter.

**The effect of HEPA filter on sensory evaluation of the cabin air.** Sensory evaluation of the cabin air was carried out for two conditions: used HEPA filter or no HEPA filter installed in the recirculation duct of the ventilation system. The outdoor air supply rate to the cabin during the sensory evaluations was 4.4 h\(^{-1}\). To avoid subjects entering the cabin, the air quality assessment took place, after steady-state conditions had been achieved, in an adjacent chamber that was continuously supplied with air (~20 L/s) from the aircraft cabin. The system was exposed to elevated ozone concentrations for at least 2 hours before the sensory assessments began. A panel of untrained subjects consisting of 26 staff members and students (age 22-60 years) from the ICIEE assessed the air quality shortly after entering the chamber on a pseudo-continuous acceptability scale and on an odor intensity scale (Clausen, 2000). The panel was blind to conditions.

**The effect of the aircraft seats.** The contribution of the aircraft seats to ozone removal was evaluated by measuring the ozone removal rates in the presence and absence of seats, keeping all other parameters the same. Such comparisons were made at low and high outdoor air change rates (4.4 and 8.8 h\(^{-1}\)), both times with a used HEPA filter in place.
The effect of soiled T-shirts. The effect of T-shirts on the ozone removal rate was investigated in two separate sets of experiments. The first included two experiments with four-hour continuous ozonation in the presence of a loaded HEPA filter at $3 \text{ h}^{-1}$ outdoor air. In one of the experiments 17 soiled T-shirts were placed over the back of the airplane seats. Male subjects had slept in these T-shirts throughout the previous night. The second set of experiments was made with five repeated exposures in the absence of a HEPA filter, including two experiments at $6.5 \text{ h}^{-1}$ outdoor air. During these two experiments the ozone generators were shut off for different periods of time (30, 60, 90 and 120 minutes) following 60 minutes of ozonation each time. Figure 2 shows the on/off schedule that was used for the ozone generators.

![Figure 2. Ozone generator “on – off” schedule during the repeated ozone exposure experiment](image)

In one of the two intermittent ozonation experiments without a HEPA filter in the system, 17 soiled T-shirts were again placed over the back of the airplane seats. In the other experiment no T-shirts were present in the cabin.
The effect of people. Four experiments were conducted in the presence of a used HEPA filter at air change rates of either 4.4 or 8.8 h\(^{-1}\) while the cabin was empty or while 16 people were present. On each of the four experimental days there were two periods when ozone was generated -- first, for a one-hour period before people entered the cabin; second, after a one-hour break, for a four-hour period in the presence of people.

Aging effect. The effect of surface aging was evaluated in a 5 hour exposure at 8.8 h\(^{-1}\) in the presence of a used HEPA filter, but no people.

Ozone concentrations in the pollution chamber and in the aircraft cabin. The ozone concentrations in the pollution chamber and the cabin environment varied between 96-615 ppb and 41-341 ppb, respectively. The levels were set according to the purpose of each experiment, the outdoor air supply rate and whether the experiment occurred with or without human subjects in the cabin.

DATA ANALYSIS

Ozone removal rate. The ozone removal rate was determined from measurements of ozone’s first-order decay within the cabin when the ozone generator was turned off. This method was augmented with mass-balance calculations (Weschler, 2000) for each pair of cabin/pollution chamber ozone concentrations when steady-state conditions had been achieved (e.g. the aging effect experiment). When comparisons were possible, results obtained by these two different approaches were similar. For most of the data, the first-order decay constants are reported in this paper.
**Sensory assessments.** All data obtained from questionnaires were tested for normality using the Shapiro-Wilks’ W test with the rejection region of $p<0.01$. As all these data were normally distributed, one-way analysis of variance (ANOVA), supplemented with Duncan’s post-hoc comparison, or paired t-tests were used to evaluate differences between the conditions. All reported $p$-values are 1-tailed.

**RESULTS**

Over the relatively small range of relative humidities used in these experiments (from 2-24%), there was no discernable influence of the air humidity on the ozone removal rates.

The background concentration of particles in the cabin remained at very low levels throughout the experiments ($< 2000 \text{ part/cm}^3$) and was little affected by ozone concentrations, the presence of people or other factors, with one exception. That occurred when worn T-shirts were introduced in the cabin environment absent a HEPA filter. This will be further described later in this section.

Based on concurrent ozone levels in the cabin and in the pollution chamber, the ozone retention ratio was calculated. In the presence of a used HEPA filter at a low outdoor air change rate ($4.4 \text{ h}^{-1}$), the retention ratio was 0.15 with people present and 0.33 without people. For similar conditions, but at a high air change rate ($8.8 \text{ h}^{-1}$), the retention ratio was 0.21 with people present and 0.52 without people.
The effect of a used or new HEPA filter

Table 2 summarizes the ozone removal rates in the cabin with and without a HEPA filter installed in the recirculation system. Three different airflow rates were used. The number of independent measurements for a given condition is also shown. When more than one measurement was carried out for the same condition, the ozone removal rate is indicated as the average of the values given by each measurement.

Table 2. Effect of HEPA filter

<table>
<thead>
<tr>
<th>Condition</th>
<th>Airflow [h⁻¹]</th>
<th>Ozone removal rate [h⁻¹]</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total**</td>
<td>Total – Ach.</td>
</tr>
<tr>
<td>No HEPA</td>
<td>Outdoor air 4.4*</td>
<td>8.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Used HEPA</td>
<td>Recirc. air 18.8</td>
<td>9.1 ± 0.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Δ</td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>New HEPA</td>
<td>Outdoor air 4.4*</td>
<td>9.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Δ</td>
<td>Recirc. air 18.8</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>No HEPA</td>
<td>Outdoor air 6.5*</td>
<td>11.3 ± 0.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Used HEPA</td>
<td>Recirc. air 16.7</td>
<td>12.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Δ</td>
<td></td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

* The deviation of ventilation rates between measurements was less than 3%.
** ± SD

Compared to the condition without a filter, the presence of the used HEPA filter in the system increased the ozone removal rate by 0.7 h⁻¹ at the lower air change rate (4.4 h⁻¹), and by 0.9 h⁻¹ at the higher air change rate (6.5 h⁻¹). Only a single measurement was carried out for a new HEPA filter; the removal rate was 1.4 h⁻¹ at an outdoor air change rate of 4.4 h⁻¹.
Table 3. Ozone removal efficiencies, based on upstream and downstream ozone measurements, for used and new HEPA filters in the recirculation duct

<table>
<thead>
<tr>
<th>Condition</th>
<th>Removal efficiency [%]</th>
<th>Used HEPA</th>
<th>New HEPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4 h⁻¹ outdoor air</td>
<td>5.7 ± 0.8</td>
<td>4.7 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>18.8 h⁻¹ recirc. air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 m s⁻¹ face velocity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8 h⁻¹ outdoor air</td>
<td>3.3 ± 1.8</td>
<td>2.5 ± 1.7</td>
<td></td>
</tr>
<tr>
<td>14.4 h⁻¹ recirc. air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 m s⁻¹ face velocity</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ozone removal efficiencies were determined from ozone measurements made immediately upstream and downstream of the filters (Table 3). These measured removal efficiencies were in the range of 3 to 6%.

The subjective results shown in Table 4 clearly indicate the negative effect of the used HEPA filter on sensory evaluations. The perceived air quality (PAQ) was −0.18 when recirculated air passed through the used HEPA filter compared with +0.06 when no HEPA filter was present (p<0.03), i.e. the used HEPA caused the air quality to be judged as significantly less acceptable. Furthermore, the odor intensity was stronger compared to the condition without a HEPA filter (p<0.006).

Table 4. Effect of HEPA filter on IAQ

<table>
<thead>
<tr>
<th>Condition</th>
<th>Airflow [h⁻¹]</th>
<th>Cabin ozone [ppb]</th>
<th>Acceptability*</th>
<th>Odor intensity**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
<td>Mean</td>
<td>95% c.i.</td>
</tr>
<tr>
<td>No HEPA</td>
<td>4.4</td>
<td>52</td>
<td>2.6</td>
<td>-0.11...0.23</td>
</tr>
<tr>
<td>Used HEPA</td>
<td>4.4</td>
<td>55</td>
<td>1.4</td>
<td>-0.18...0.01</td>
</tr>
</tbody>
</table>

* scale:-1 to +1; -1: clearly unacceptable, +1: clearly acceptable
** scale: 0 to 50; 0: no odor, 50: overpowering odor
The effect of aircraft seats

The effect of aircraft seats on the measured ozone removal rate can be seen from the results presented in Table 5. In the presence of the used HEPA filter at the high air change rate, the ozone removal rate was 3.1 h\(^{-1}\) larger with seats present than with seats absent. The same comparison at lower air change rates indicates a contribution of 2.7 h\(^{-1}\) from the aircraft seats. The difference between the removal rates at high and low outdoor air change rates is most probably due to unaccounted leakage in the system that occurred at high outdoor rates.

**Table 5.** Effect of seats

<table>
<thead>
<tr>
<th>Condition</th>
<th>Airflow [h(^{-1})]</th>
<th>Ozone removal rate [h(^{-1})]</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total**</td>
<td>Total – Ach.</td>
</tr>
<tr>
<td>Used HEPA w seats</td>
<td>Outdoor air 4.4*</td>
<td>9.1 ± 0.6</td>
<td>4.7</td>
</tr>
<tr>
<td>Used HEPA w/o seats</td>
<td>Recirc. air 18.8</td>
<td>6.4 ± 0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Δ</td>
<td></td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>Used HEPA w seats</td>
<td>Outdoor air 8.8*</td>
<td>13.6 ± 1.8</td>
<td>4.8</td>
</tr>
<tr>
<td>Used HEPA w/o seats</td>
<td>Recirc. 14.4</td>
<td>10.5 ± 0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Δ</td>
<td></td>
<td></td>
<td>3.1</td>
</tr>
</tbody>
</table>

* The deviation of ventilation rates between measurements was less than 3%.
** ± SD

The effect of soiled T-shirts

The ozone removal rate in both continuous and repeated experimental designs increased in the presence of soiled T-shirts compared to the condition without T-shirts (Table 6). These data indicate that the 17 T-shirts contribute roughly 3.5 to 5 h\(^{-1}\) to the ozone removal rate.
### Table 6. Effect of soiled T-shirts

<table>
<thead>
<tr>
<th>Condition</th>
<th>Airflow [h⁻¹]</th>
<th>Ozone removal rate [h⁻¹]</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empty</td>
<td>Outdoor air 3*</td>
<td>9.3</td>
<td>6.3</td>
</tr>
<tr>
<td>With T-shirts</td>
<td>Recirc. 20.2</td>
<td>14.4</td>
<td>11.4</td>
</tr>
<tr>
<td>Δ</td>
<td>Used HEPA</td>
<td>5.1</td>
<td>1</td>
</tr>
<tr>
<td>Empty</td>
<td>Outdoor air 6.5*</td>
<td>11.3</td>
<td>4.8</td>
</tr>
<tr>
<td>With T-shirts</td>
<td>Recirc. 16.7</td>
<td>14.9</td>
<td>8.4</td>
</tr>
<tr>
<td>Δ</td>
<td>No HEPA</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>

* The deviation of ventilation rates between measurements was less than 3%.

** ± SD

The condition with repeated ozone exposure in the presence of soiled T-shirts and absence of HEPA filters was the only experiment in which the ultra fine particle concentration increased significantly above background levels. The increase was most pronounced during the first three ozonation periods (Figure 3).

![Figure 3](image-url)

**Figure 3.** Particle concentrations measured in the repeated ozone exposure experiment.
The effect of people

Four experiments, two at low and two at high airflow rates, were conducted with human participants in the simulated airplane cabin. The results presented in Table 7 show that the presence of people increased the ozone removal rate in the cabin by 6.2 and 7.3 h\(^{-1}\) at low and high outdoor airflow rates, respectively. Again, we judge that the difference between the removal rates at high and low outdoor air changes is most probably due to unaccounted for leakage that occurred at high outdoor rates.

**Table 7. Effect of people**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Airflow [h(^{-1})]</th>
<th>Ozone removal rate [h(^{-1})]</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total**</td>
<td>Total – Ach.</td>
</tr>
<tr>
<td>Empty</td>
<td>Outdoor air</td>
<td>9.1 ± 0.6</td>
<td>4.7</td>
</tr>
<tr>
<td>With people Δ</td>
<td>Recirc. 18.8</td>
<td>15.3 ± 0.1</td>
<td>10.9</td>
</tr>
<tr>
<td>Empty</td>
<td>Outdoor air</td>
<td>13.6 ± 1.8</td>
<td>4.8</td>
</tr>
<tr>
<td>With people Δ</td>
<td>Recirc. 14.4</td>
<td>21.0 ± 1.3</td>
<td>12.2</td>
</tr>
</tbody>
</table>

* The deviation of ventilation rates between measurements was less than 3%.
** ± SD

The effect of aging

The influence of prolonged ozone exposure on the surface removal rate (“aging”) was examined in the experiment with constant ozone generation over a five-hour period (Figure 4). Given the outdoor air exchange rate of 8.8 h\(^{-1}\), a pseudo steady-state condition should have been attained within the first hour, and during the final 4 hours of the experiment, the ozone concentration should have remained constant if the ozone removal rate within the cabin was constant. However, it is apparent in Figure 4 that the concentration of ozone in both the
pollution chamber and the aircraft cabin continued to slowly increase during this period. Using a mass balance model and the ozone concentrations in the pollution chamber and cabin, the ozone removal rates were calculated for the final 3.5 hours of this experiment (open triangles in Figure 4). The ozone removal rate decreased throughout this period. This is clearly evident if the average value of the ozone removal rate calculated for the first half of the 3.5 hour period (3.8 h\(^{-1}\)) is contrasted with that during the second half of the period (3.6 h\(^{-1}\)). The trendline shown on the figure indicates that the ozone removal rate decreased by roughly 3% per hour during this experiment.

**Figure 4.** The calculated ozone removal rates (triangles and right y-axis) derived from the measured ozone concentrations in the pollution chamber (diamonds and left y-axis) and aircraft cabin (squares and left y-axis). See text for details.
DISCUSSION

HEPA filters

Due to a tight schedule regarding the use of the simulated aircraft cabin, we were only able to conduct one experiment without a HEPA filter in the system and one experiment with a new HEPA filter in place of the loaded HEPA filter. All of the other experiments were conducted with the loaded HEPA filter in the system. The resulting data is less than ideal for determining the fractional contribution of the loaded HEPA filter or a new HEPA filter to overall ozone removal. However, as reported in Table 3, we were also able to make direct measurements of the ozone removal efficiencies of both the loaded and new HEPA filters at low and high air exchange rates. The removal efficiencies in Table 3 translate to ozone removal rates of 0.5 – 1.1 h\(^{-1}\) for the loaded HEPA filter and 0.4 to 0.9 h\(^{-1}\) for the new HEPA filter. Hence, these direct measurements of ozone removal efficiencies for the loaded HEPA filter and the new HEPA filter are consistent with the ozone removal rates determined by comparing overall ozone removal rates of the system with no HEPA, a new HEPA and a loaded HEPA filter (Table 2).

The effects of used and new HEPA filters on the overall ozone removal rate were found to be similar in magnitude. In the case of the new HEPA filter, ozone may be reacting with tackifiers and binders that are associated with the new filtration media (Bekö et al., 2005a). As the filter ages and captured particles cover the surface of the media, ozone is better able to react with organics associated with the captured material. The measured ozone removal efficiency (2.5 to 6\%) of the used HEPA filter is comparable to values reported in other studies. Hyttinen et al. (2003) reported ozone removal efficiencies in the range of 8-26\% for
nine used supply air filters, while Bekö et al. (2005a) reported 12% for samples from a loaded EU7 filter. Both of these studies were conducted using face velocities in the range of 0.1-0.2 m s\(^{-1}\), almost an order of magnitude smaller than the face velocities in the current investigation (Table 3).

The perceived air quality was significantly poorer with the used HEPA filter in the system compared to no HEPA filter in the system. This is consistent with results from numerous other studies indicating that a loaded ventilation filter adversely impacts the quality of the air that passes through it (Clausen et al, 2004 and references therein). This effect may be amplified by oxidation processes occurring on the surface of the loaded HEPA filter (Bekö et al., 2005a).

**Aircraft seats and other surfaces**

As indicated in Table 5, the contribution of the seats to the overall ozone removal rate was in the range of 2.7 to 3.1 h\(^{-1}\). With the seats removed, the overall ozone removal rate was between 1.7 and 2.0 h\(^{-1}\). Given that the loaded HEPA filter contributed approximately 0.7 to 0.9 h\(^{-1}\), the other surfaces in the cabin and ventilation system contributed between 0.8 and 1.3 h\(^{-1}\) to the ozone removal rate. We anticipate, based on previous studies examining interactions between ozone and carpet (Weschler et al., 1992; Morrison and Nazaroff, 2000; Morrison and Nazaroff, 2002b), that the carpet within the cabin was primarily responsible for scavenging by “other surfaces”.
Soiled T-shirts

Seventeen soiled T-shirts contributed 3.6 to 5.1 h\(^{-1}\) to the overall ozone removal rate (Table 6), while sixteen people contributed between 6.2 and 7.3 h\(^{-1}\) to the overall ozone removal rate (Table 7). Our previous study (Wisthaler et al., 2005) of the effects of ozone-initiated chemistry on the chemical composition of cabin air examined fresh T-shirts as well as soiled T-shirts. We found that fresh T-shirts, in the presence of ozone, had little effect on the chemicals present in the cabin, indicating that it is primarily the skin oils transferred to the soiled T-shirts that were responsible for the ozone removal. The fact that the soiled T-shirts remove ozone at a rate almost as fast as people themselves illustrates the relatively large contribution that readily transferred human skin oils make to the ozone removal process.

People as ozone sinks

When people are present in the simulated cabin, they contribute between 6.2 and 7.3 h\(^{-1}\) to the overall rate of ozone removal. It is worth attempting to estimate how much of this could be due to surface chemistry and how much could be due to respiration by the human subjects. The breathing rate for sedentary adult females averages 0.48 m\(^3\) h\(^{-1}\) (US EPA, 1997). It is reasonable to assume that all of the ozone inhaled is removed (Thorp, 1950). Hence 16 human subjects would remove 7.7 m\(^3\) h\(^{-1}\). Given that the total volume of the simulated cabin plus recirculation system is 31 m\(^3\), breathing by the sixteen human subjects would be equivalent to an ozone removal rate of 0.25 h\(^{-1}\). Hence, respiration makes only a small contribution (~ 4%) to the removal of ozone by the female subjects in the simulated cabin.
To put ozone removal by passengers in perspective, it is useful to convert the values in Table 7 to ozone deposition velocities (Nazaroff et al., 1993) and compare these with other deposition velocities reported in the literature. We first convert the values in Table 7 to effective Clean Air Delivery Rates (CADR) by multiplying by the volume of the system (31 m$^3$) and dividing by the number of passengers (16), to yield effective CADRs of 12 to 14 m$^3$ h$^{-1}$ per person. We then divide by the surface area of an average person to arrive at the deposition velocity. Using the DuBois formula (ISO, 1990), we estimate that the average female subject has a total skin surface area of ~1.7 m$^2$. Hence, the deposition velocity associated with people in the simulated cabin was between 0.20 and 0.22 cm s$^{-1}$. This is close to what would be anticipated as the upper limit for such a value, based on mass transport considerations (see Figure 1 of Morrison and Nazaroff, 2002b). Based on the total surface area of the cabin seats (24.6 m$^3$) and an estimated total surface area of the T-shirts (16.2 m$^2$), ozone deposition velocities were also calculated for the seats and T-shirts. For the aircraft seats the deposition velocity was between 0.10 and 0.11 cm s$^{-1}$ and for the T-shirts between 0.19 and 0.27 cm s$^{-1}$. It is noteworthy that the deposition velocity for the T-shirts is also at, or beyond, the upper limit of such values, given mass transport constraints. Perhaps the calculated “deposition velocity” for T-shirts and people includes gas phase chemistry with volatile, unsaturated oxidation products (e.g., 6-methyl-5-heptene-2-one) emitted from people and T-shirts, and derived from ozone/skin oil reactions. Further studies are planned to examine this issue.
Comparisons of ozone sinks and effects of aging

Figure 5 presents the relative contribution of HEPA filters, other surfaces, seats and people to ozone removal in the simulated aircraft cabin. Of these sinks, people make the largest relative contribution, almost 60%.

Figure 5. Relative contribution (%) of various sinks to ozone removal in the simulated aircraft cabin. Median values have been used in preparing figure; the range of values were 0.7 to 0.9 h\(^{-1}\) for HEPA filters, 2.7 to 3.1 h\(^{-1}\) for seats, 0.8 to 1.3 h\(^{-1}\) for other surfaces and 6.2 to 7.3 h\(^{-1}\) for people.

The next largest contribution comes from the aircraft seats, approximately 25%. These seats had been in actual service for several years. It is likely that they are soiled with the skin oils of the passengers who occupied them throughout their service life and these residual oils are likely to contribute to ozone removal by the seats. In our previous study (Wisthaler et al., 2005) we saw chemical evidence in support of this hypothesis. The contribution from the HEPA filter is about 7%. The other surfaces in the cabin, excluding the seats and HEPA filter, contribute 10%, a relatively small fraction of the total.
With people present, the measured ozone retention ratios (0.15 to 0.21) were much lower than levels reported in the literature. Without people, the measured ratios (0.33 to 0.52) were closer to literature values. As noted in the Introduction, Nastrom et al. (1980) measured average retention ratios of 0.45 on a Boeing 747-100 and 0.85 on a 747SP. Since these were revenue generating flights, passengers were presumably present, but there is no information on their numbers. The authors state: “There may be factors other than those listed which influence the retention ratio from flight to flight, or even within a flight, such as load factor or flight duration …, but these are not considered here.” Hence, it appears that the influence of passengers on the retention ratio was not systematically examined in this prior study.

It is interesting that the above quote also states that the effect of flight duration on the retention ratio was not considered. The present experiments have shown that ozone removal by surfaces within the simulated cabin does decrease over time (~ 3% per hour). Similar observations have been reported in the literature for both carpets (Morrison and Nazaroff, 2002a) and building filters (Bekö et al., 2005a). Presumably, pollutants present on the various surfaces are gradually consumed by reaction with ozone. “Aged” surfaces can regain some of their ozone scavenging potential if they are not exposed to ozone for several hours or days. During such recovery periods, reactive materials within the bulk of various aircraft cabin materials diffuse to the surface, becoming available for future reaction with ozone.

**Particle generation**

Particle concentrations in the cabin air were measured with a condensation nuclei counter during the majority of the experiments listed in Table 1. For most of these experiments there was no observable increase in particle concentration when ozone was introduced to the
aircraft cabin. However, for many of these experiments a HEPA filter was present in the recirculation system. Given the large fraction of recirculated air (14 to 20 h⁻¹), HEPA filtration removes Secondary Organic Aerosols (SOA) at a rate that would make it difficult to observe moderate particle growth. Only a few experiments were conducted without a HEPA filter in the system. Even without a HEPA filter, particle growth was not observed for most of these experiments. This indicates that reactions of ozone with cabin surfaces do not produce SOA at a rate that can compete with removal by air exchange (4.4 to 6.5 h⁻¹ in the experiments without a HEPA filter). Although the oxidation products generated by ozone-initiated reactions with cabin surfaces are expected to include low volatility species, it is likely that such species remain on the cabin surfaces rather than desorbing and subsequently condensing on existing airborne particles.

Figure 3 shows the only experiment in which SOA formation was observed – cyclical introduction of ozone into the cabin when it contained soiled T-shirts, but no HEPA filter. Note in Figure 3 that the particle concentration was actually higher in the second ozone cycle than in the first cycle. During the first cycle, ozone may have reacted with higher molecular weight unsaturated compounds (e.g., squalene) present in the skin oil on the T-shirts to generate smaller molecular weight products that still contained unsaturated bonds. During the second cycle, gas phase reactions between ozone and the more volatile unsaturated products may then have been responsible for the observed increase in particle concentration. By the fourth and fifth cycle, the increase in particle concentration was small; the precursors were probably depleted. Further experiments are necessary to confirm or refute these conjectures. No experiments without a HEPA filter were performed when people were in the cabin. Hence, we do not know if an increase in particle concentration would be observed if ozone was added
to the cabin in the presence of people but with no filter in the return air. The T-shirt experiment suggests that an increase would be observed.

CONCLUSIONS

Taken together, these measurements provide a more complete picture of the parameters that remove ozone as it is transported from outside the aircraft to the breathing zone of passengers and crew. Ozone removal is desirable in terms of reducing the exposure of passengers and crew to ozone, but ozone removal by surfaces is not without consequences. To a large extent, this removal of ozone is due to reactions with organic compounds on the surfaces. The more volatile oxidation products can subsequently desorb from the surfaces and become part of the mix of chemicals within the cabin to which passengers and crew are exposed. Detailed chemical analyses conducted in this same simulated cabin (Wisthaler et al., 2005) indicate that the oxidation products include saturated and unsaturated aldehydes and squalene oxidation products. In the cited study many of the resulting aldehydes were present at concentrations above their odor thresholds. Formaldehyde and acrolein were present at concentrations high enough to cause chronic health concerns (OEHHA, 2005).

Retention ratios measured in this study are lower than the default value used by the FAA in deciding whether or not ozone-removing devices should be used on aircraft. However, this should not be construed as an extra “margin of protection”. For the reasons outlined above, a low retention ratio indicates significant surface chemistry and, potentially, significant exposures to the consequent oxidation products that desorb from surfaces. The ozone removal associated with people produces products to which other passengers are exposed. From the T-
shirt experiments we know that these products include the squalene oxidation products acetone, 6-methyl-5-heptene-2-one and 4-oxopentanal. We do not know the nature of the major products generated from clothing. Regardless, since the chemistry involves the passengers and crew themselves, the only way to minimize people’s exposure to both ozone and the products of ozone-initiated chemistry is to minimize the concentration of ozone in the cabin. This fact underscores the need for efficient filtration of ambient ozone from the air supply system of an aircraft.

ACKNOWLEDGEMENTS

We thank William W. Nazaroff for suggesting that the results in Table 7 be translated to Clean Air Delivery Rates and deposition velocities and for general observations related to ozone transport from bulk air to the surface of human subjects. We thank Julita Zarzycka, Danuta Myśków, Paweł Wargocki, Kiril Naydenov and Jørn Toftum of the Technical University of Denmark, each of whom contributed to the completion of this project. Finally, we thank the subjects who patiently participated in these experiments.

This work has been supported by the Danish Technical Research Council (STVF) as part of the research program of the International Centre for Indoor Environment and Energy at the Technical University of Denmark and, through a sub-contract for the Airliner Cabin Environmental Research (ACER) Center of Excellence set up and funded by the U.S. Federal Aviation Administration.
REFERENCES

ACGIH (American Conference of Governmental Industrial Hygienists), 2000. TLV’s and BEI’s, 2000. Threshold Limit for Chemical Substances and Physical Agents and Biological Exposure Indices. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.


PAPER 4: PRODUCTS OF OZONE INITIATED CHEMISTRY IN A SIMULATED AIRCRAFT ENVIRONMENT
Products of Ozone-Initiated Chemistry in a Simulated Aircraft Environment

ARMIN WISTHALER,1,4 GYÖRGY TAMÁS,1 DAVID P. WYON,1 PETER STROHM-JEISEN,1 DAVID SPACE,5 JONATHAN B. BEAUCHAMP,2 ARMIN HANSEL,1 TILMANN D. MARK,1 AND CHARLES J. WESCHLER1,3,4

International Centre for Indoor Environment and Energy, Technical University of Denmark (DTU), DK-2800 Kgs. Lyngby, Denmark. Institute of Ion Physics, University of Innsbruck, Innsbruck, Austria. Boeing Commercial Airplane Group, P. O. Box 3707, MC 02-WH, Seattle, Washington 98124, Environmental and Occupational Health Sciences Institute, University of Medicine and Dentistry of New Jersey (UMDNJ), and Rutgers University, 170 Frelinghuysen Rd., Piscataway, New Jersey 08854

We used proton-transfer-reaction mass spectrometry (PTR-MS) to examine the products formed when ozone reacted with the materials in a simulated aircraft cabin, including a loaded high-efficiency particulate air (HEPA) filter in the return air system. Four conditions were examined: cabin plus ozone, cabin plus ozonized solvent, cabin plus ozonized solvent plus ozone, and no ozonized solvent. The addition of ozone to the cabinet without T-shirts, or at concentrations typically encountered during commercial air travel, increased the mixing ratio (v/v) of detected pollutants from 35 ppb to 80 ppb. Most of this increase was due to the production of saturated and unsaturated aldehydes and tentatively identified low-molecular-weight carboxylic acids. The addition of ozonized T-shirts, with or without ozone present, increased the mixing ratio of pollutants in the cabin air only slightly, whereas the combination of ozonized T-shirts and ozone increased the mixing ratio of detected pollutants to 100 ppb, with more than 20 ppb originating from squalene oxidation products [acetonitrile, 4-oxopentenal, and 5-methyl-5-heptenal-2-one]. For the two conditions with ozone present, the more-abundant oxidation products included acetonitrile/propionaldehyde (8–20 ppb), formaldehyde (8–10 ppb), nonenal (≈6 ppb), 4-oxopentenal (3–7 ppb), acetic acid (≈7 ppb), formic acid (≈3 ppb), and 6-methyl-5-heptenal-2-one (0.5–2.5 ppb), as well as compounds tentatively identified as acrolein (0.6–1 ppb) and crotonaldehyde (0.6–0.8 ppb). The odor thresholds of certain products were exceeded. With an outdoor air exchange of 3 h−1 and a recirculation rate of 20 h−1, the measured ozone surface removal rate constant was 6.3 h−1 when T-shirts were not present, compared to 11.4 h−1 when T-shirts were present.

Introduction

At the typical cruising altitudes of commercial aircraft, the mixing ratio of ozone in the air outside the cabin is significantly higher than that found in the most polluted cities in the world. Ozone levels vary with altitude, latitude, and time of year. During late winter and early spring at altitudes of >10 000 m and latitudes above 45°, ozone levels in the range of 500–800 ppb are common (1). Even at lower altitudes and in different seasons, ozone mixing ratios are often >200 ppb. It is this air, with its associated ozone, that is used to ventilate the aircraft cabin. Only about half of the wide body commercial aircraft and ~10% of the narrow body aircraft are equipped with catalytic oxides to remove ozone from the ventilation air (2). Even without such devices, ozone levels inside the cabin are lower than those outside the plane. This is due to the destruction of ozone as it passes through the engine compressors, bleed air system, and air-conditioning packs, as well as scavenging of ozone by surfaces in the air delivery/recirculation system and within the cabin. Ozone levels inside aircraft without catalysts are typically 45%–80% of those outside (3). Given the high outdoor ozone levels, levels within the cabin can approach and exceed 100 ppb. Measurements of ozone levels on aircraft in the late 1970s (3) and 1980s (4) helped to promote regulatory action (i.e., Federal Aviation Authority FAR 25.832 and FAR 121.578). Since then, only a limited number of measurements have been made. These were reviewed in a 2002 report by the National Research Council entitled “The Airliner Cabin Environment and the Health of Passengers and Crew” (5). This report concluded that “…unacceptably high O₃ concentrations can occur in passenger cabins of commercial aircraft in the absence of effective controls.” Since that report, at least two notable studies have been published. Spengler et al. (6) used passive samplers to measure time-integrated ozone levels on 106 flight segments. These authors examined two different time intervals in their studies: from takeoff to landing, and a 3-h period at cruising altitude, when ozone levels were expected to be highest. Some of these aircraft contained catalytic ozone converters to remove ozone from the airstream. Nonetheless, the average for 145 time-integrated measurements of ozone on these flights was 80 ppb (with a standard deviation of 130 ppb); 20% of the measurements exceeded 100 ppb and 11% exceeded 120 ppb. Spicer et al. (7), using a real-time ozone monitor, measured ozone levels continuously on four flights within the continental United States. On all four flights, the authors found that ozone levels increased from takeoff when the cruising altitude had been reached. At the cruising altitude, ozone levels averaged 31–106 ppb.

Several acute and chronic health concerns are associated with direct exposure to ozone. In addition, ozone can react with other pollutants in the air to generate products that are known irritants and of potential health concern (6–24). Although ozone-initiated chemistry has been studied in indoor settings (11, 25–27 and references therein), there are no published reports examining ozone-initiated chemistry within aircraft. The aim of the present study was to examine the products formed when ozone, at concentrations typical of those encountered at cruising altitudes, is present in a simulated commercial aircraft cabin. The simulated cabin...
FIGURE 1. Schematic of the simulated aircraft cabin's ventilation system. See text for details.

Methods

Description of Simulated Aircraft Cabin. The study was conducted within a simulated aircraft cabin containing 21 seats (3 rows of 7 seats each). As illustrated in Figure 1, it was installed inside an existing climate chamber that is capable of providing two separately controlled air supply streams. Supply air entered through standard aircraft plenums from two longitudinal slots in the ceiling. The cabin width was 4.9 m, the length was 3.2 m, the cross-sectional area was 8.9 m², and the volume was 28.5 m³. The shape, volume, appearance, and radiant temperature distribution of an aircraft cabin were simulated by attaching aluminum sheets to a metal framework in such a way that the ventilated volume and the air circulation patterns were the same as in a three-row section of an aircraft cabin. Emissions to the cabin air occurred from the materials and fittings specified in this paragraph. Used aircraft seats were obtained from a supplier of aftermarket parts. The carpet had been in use in a passenger aircraft for the duration of its normal service life. The total surface area of the carpet was 15.6 m², whereas that of the airplane seats was 24.5 m². Six panels from a used aircraft cabin interior, with windows, were used in the walls. A HEPA filter that had been in a passenger aircraft for 18 months (its maximum recommended service life) was included in the air recirculation system. Two-thirds of its cross-sectional area was blocked off, so that the area through which the recirculated air passed was in correct proportion to the length of the cabin section.

One controlled air stream was used to maintain the temperature of the air surrounding the unit in the climate chamber. This was adjusted until the inside wall surface temperature was 15°C, as in an aircraft at altitude. Cooling the cabin walls increased the heating load to a level where the supply air inlet temperatures were realistic. Thus, there was a realistic radiant temperature field in the cabin and the pattern of air circulation included the thermal downdrafts that are a characteristic feature of aircraft cabins. The other controlled air stream supplied cold, dry outside air to the simulated cabin via the ceiling plenum. Dehumidification was used but was applied only to the outdoor air. The total supply airflow, including recirculated air, was always 200 L/s (equivalent to 23 h⁻¹), of which 24 L/s (3 h⁻¹) was outdoor air. The value for the outdoor air flow rate was lower than specified by FAR 25.831 (80 L/s at altitude if this cabin had 17 occupants). Experiments were conducted at ground-level barometric pressure. The pressure condition in the simulated cabin was 0.6 Pa higher than that in the outer chamber, to avoid contamination of the cabin air with air that might infiltrate in an uncontrolled manner.

Experimental Conditions. On successive summer days, four different conditions were established in the simulated aircraft cabin: day 1, cabin air (baseline); day 2, cabin air plus ozone (generators on at 10:00 and off at 16:00); day 3, cabin air plus 17 soiled T-shirts (introduced at 10:00); and day 4, cabin air plus 17 soiled T-shirts plus ozone (ozone generators on at 10:00 and off at 16:00). The soiled T-shirts came from male subjects who had been asked to wear fresh T-shirts during the previous night and come to the cabin without showering. The T-shirts were turned inside out and stretched over the seatbacks immediately after the subjects had taken them off. The cabin was ventilated overnight between conditions. Table 1 summarizes the conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>T-shirts</th>
<th>Temperature, °C</th>
<th>Relative Humidity, RH [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>23.2</td>
<td>7.2</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>23.2</td>
<td>7.1</td>
</tr>
<tr>
<td>3</td>
<td>+</td>
<td>23.5</td>
<td>7.0</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>25.8</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Generation and Measurement of Ozone. Four ultraviolet (UV) ozone generators were placed on the floor in the space between the seats at a distance of ~2 m from each corner along the diagonals of the cabin. Given the high rate of air supply (200 L/s), relative to the cabin volume, the mixing time is anticipated to be short (~5 min). The ozone generation rate was controlled by changing the fractions of the UV lamps that were exposed and was the same on days 2 and 4. The ozone mixing ratio in the cabin air was continuously measured with a UV photometric analyzer operating at 254 nm (Dasibi model 1003-AFl). This instrument has a range of 0–500 ppb, a sensitivity of 1 ppb, and a precision of 1 ppb or ±1%, whichever is greater. The sampling point of the ozone instrument was close to the central location of the cabin at a height of 1.2 m.

Proton-Transfer Reaction Mass Spectrometry Measurements. The analytical technique used in this study was
proton-transfer-reaction mass spectrometry (PTR-MS), which is a chemical ionization (CI) technique based on proton-transfer reactions from H$_3$O$^+$ ions to gaseous organic analytes with a higher proton affinity than water (28, 29). A commercial instrument (PTRMS-FTd-s, Ionicon Analytic GmbH) was used for the measurements and operated at a reduced E/N value of ~110 Td (1 Td = 10$^{-17}$ cm$^3$ V molecule$^{-1}$) to limit the fragmentation of linear saturated aldehydes (30) and linear unsaturated aldehydes that occurs at the more commonly used E/N value (120–140 Td). (Here, E is the electric field across the drift tube and N is the gas number density.) The implications of nonstandard PTR–MS operation are described in detail by De Gouw et al. (31) and Hewitt et al. (29). Because of low humidity levels in the analyte air (relative humidity < 7%), see Table 1), the hydration of ions, which usually complicates PTR–MS data gained at low E/N values, was not significant.

Mass scans were performed in the mass-to-charge (m/e) range of 20–200 at a dwell time of 1 s per m/e, resulting in a time resolution of 3 min per spectrum. Ion signals were corrected for mass discrimination and instrumental background, and the protonated formaldehyde signal (m/e = 31) was corrected for a five-fold sensitivity loss (see below). The sum of the corrected ion signals is denoted as the “total VOC signal.” CI pathways of a series of target compounds including linear saturated aldehydes, linear unsaturated aldehydes, linear carboxylic acids, and squalene oxidation products (4-oxopentanal, 6-methyl-5-hepten-2-one) were investigated as part of this study or taken from the literature (32-34).

The PTR–MS instrument was calibrated on site using a dynamically diluted oxygenate standard (Apel–Riemer Environmental, Inc., Denver, CO) containing 1 ppm of methanol, ethanol, acetaldehyde, acetone, and 2-butanone, respectively. It has been shown experimentally and theoretically that the variability of PTR–MS calibration factors for oxygenated hydrocarbons (with the exception of formaldehyde) is on the order of ±15% (35) to ±30% (29, 29). A similar accuracy is expected for the data reported in this study. PTR–MS has a reduced sensitivity to formaldehyde, because of the loss of protonated formaldehyde ions by the reaction with H$_2$O, as discussed in detail by Hansel et al. (36), Steinbacher et al. (37) found a five-fold loss in sensitivity for formaldehyde under dry conditions. A similar value was observed in a previous aircraft cabin experiment (conducted at the same facility as the present study but unpublished) when a cross-calibration between the PTR–MS instrument and a gas chromatography–mass spectrometry (GC–MS) system was performed. The accuracy of reported formaldehyde values is estimated to be ±40%.

A three-way inlet system was configured to sample air from the cabin recirculation system upstream and downstream of the HEPA filter and from outside the ventilation ducts (Figure 1). Air was continuously drawn from the outlet ventilation duct upstream and downstream of the HEPA filter at a flow rate of 300 mL/min via two silica-coated capillaries (inner diameter of 1.02 mm, with lengths of 100 and 150 cm). Sample air from upstream or downstream of the HEPA filter was alternately fed (9 min for each channel) to the PTR–MS instrument via a Teflon solenoid valve. A third sampling port was placed outside the ventilation duct, to exclude possible artifacts from changing volatile organic compound (VOC) levels in the surrounding air. In addition, every 5th, the sample flow was diverted through a VOC scrubber (platinum-coated quartz wool, temperature of $T = 350$ °C) to determine the PTR–MS background signal; these were stable throughout the four days of measurements and were subtracted from the measured signals.

**Aldehyde Artifacts.** There can be both positive and negative artifacts when measuring the mixing ratios of aldehydes in ozone-containing air using conventional techniques such as sorbent or canister sampling (28–30 and references therein). O$_3$ can react with unsaturated hydrocarbons on sorbents or in canisters to form aldehydes (positive artifacts), and it can react with carbonyl hydrazones, in the case of diethylphenylnitroazole (DEPNI) cartridges (negative artifacts). Given that PTR–MS analysis does not require preconcentration, a significant source of artifacts can be ruled out. However, heterogeneous oxidation of reactive compounds in the inlet of the PTR–MS instrument may result in aldehyde artifacts (40). In the present study, the inlet was made of clean prebaked Silcosteel tubing, with the exception of two Teflon solenoid valves. In addition, the residence time in the inlet system was kept as short as possible (~150 ms for air sampled upstream of the HEPA filter), to minimize ozone–inlet surface interactions. A similar inlet configuration used in a previous study (A. Wisthaler, unpublished results) resulted in no detectable aldehyde artifacts (detection limit of 20 ppb) at an ozone mixing ratio of 25 ppb. Aldehyde artifacts, if present at all, are not expected to exceed 20–30 ppb for the individual species reported.

**Results.** As noted previously, for each of the four simulated conditions, the mixing ratio of chemicals were continuously monitored in real-time, using PTR–MS. Figure 2 shows the mixing ratios for ozone and the sum of the organic chemicals detected in the simulated cabin throughout these four days. In the absence of ozone generation, the overall mixing ratio in the cabin air was quite low (typically < 5 ppb). The ozone level in the cabin began to increase within minutes of turning on the ozone generators. The PTR–MS signal began to increase at approximately the same time (see days 2 and 4 in Figure 2). The ozone mixing ratio was smaller on day 4, when soiled T-shirts were present, than on day 2 when the cabin was empty. Conversely, the total PTR–MS signal reached a higher value on day 4 than on day 2.

**Sum of Signals Detected with PTR–MS: Four Conditions.** In reporting the PTR–MS results, this paper will focus on a subset of results obtained during each of the four conditions. For the two conditions when the ozone generators were in operation, the integration periods were 11:00 to 15:40 (day 2) and 11:30 to 16:00 (day 4). During the first of these ozone conditions, with no soiled T-shirts in the cabin, the ozone mixing ratio was 85 ppb at the beginning and 110 ppb at the conclusion, and had a mean value of 93 ppb for the integration period. During the second of these ozone conditions, with soiled T-shirts in the cabin, the O$_3$ mixing ratio was 85 ppb at the beginning and 75 ppb at the conclusion, and had a mean value of 66 ppb. Figure 3 shows the mixing ratios for the sum of the chemicals detected by PTR–MS during the selected integration periods.

For condition 1 (no added ozone), the compounds detected by PTR–MS had a total mixing ratio of 36 ppb. The compounds present at >1 ppb included the following: formaldehyde, methanol, 2-propanol, ethylene glycol (<7 ppb, largest signal), formic acid/ethanol (isobaric species not distinguishable by PTR–MS), acetone, and acetic acid. These compounds account for 26 ppb (73%) of the total detected VOC signal. Of the remaining 10 ppb, benzene and alkyl benzenes account for 1.3 ppb. The rest cannot be unambiguously identified. For the sum of all acyclic monoalkanes and dienes (excluding ethylene, which cannot be detected by PTR–MS), the upper limit is 3 ppb. The upper limit for the sum of the monoterpenes is 300 ppb.

For condition 2 (ozone added to the cabin air), the total VOC signal increased to 80 ppb. Of the individual ion signals, only m/e = 137, the monoterpane signal, decreased (~20%). With the exception of m/e = 93 (methanol), 46 (organic nitrates), and weak ion signals that are indicative of squalene
FIGURE 2. Total mixing ratio (in units of ppb) recorded with PTR–MS instrument from day 1 through day 4. The ozone mixing ratio (in units of ppb) during this period is also shown.

FIGURE 3. Total mixing ratio (in units of ppb) from PTR–MS measurements for the selected integration periods.

<table>
<thead>
<tr>
<th>TABLE 2. Ion Signals (&gt;0.05 ppb) Associated with Major Homologous Series Detected in This Study*</th>
</tr>
</thead>
<tbody>
<tr>
<td>homologous series</td>
</tr>
<tr>
<td>saturated aldehydes</td>
</tr>
<tr>
<td>(C₁–C₁₁)</td>
</tr>
<tr>
<td>unsaturated aldehydes</td>
</tr>
<tr>
<td>(C₂–C₈)</td>
</tr>
<tr>
<td>carboxylic acids (C₁–C₇)</td>
</tr>
</tbody>
</table>

*Contributions from the N₂ signal have not been included. Ions in parentheses are dehydration products. *See Supporting Information for potential interferences.

Oxidation products (see below), the observed increasing ion signals can be attributed to three homologous series: saturated aldehydes, unsaturated aldehydes, and, tentatively, carboxylic acids (Table 2). These identifications are based on previous studies of related systems (8, 41, 42). However, the likelihood that more than one VOC contributes to the observed signal for a particular ion mass must be considered. A detailed discussion on compound identification and possible interferences is given as Supporting Information.

For condition 3 (the absence of added ozone but the presence of soiled T-shirts), the compounds detected via PTR–MS had a total signal of 37 ppb. Only the ion signal at m/z = 59 (acetone/propanal) showed an increase (~0.2 ppb) when the T-shirts were added to the chamber. The total background signal was slightly higher, presumably reflecting a small contribution from the desorption of products formed in the previous "cabin/ozone" experiment.

For condition 4 (soiled T-shirts present and ozone added to the cabin air), the compounds detected via PTR–MS had a total signal of 107 ppb, this is 27 ppb higher than that measured when ozone was present but soiled T-shirts were absent. Seven ion signals showed a relative increase of >0.5 ppb: m/z = 51 (formaldehyde); m/z = 59 (acetone/propanal); m/z = 75 (tentatively identified as propionic acid); m/z = 101 (4-oxopentanal), m/z = 109, 127 (6-methyl-5-heptene-
TABLE 3. Relative Abundance of Species Observed during Conditions When Ozone Was Present in the Simulated Aircraft Cabin

<table>
<thead>
<tr>
<th>chemical or chemical class</th>
<th>Relative Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>saturated aldehydes</td>
<td>55–60</td>
</tr>
<tr>
<td>unsaturated aldehydes</td>
<td>5</td>
</tr>
<tr>
<td>carboxylic acids</td>
<td>13</td>
</tr>
<tr>
<td>squalene oxidation products</td>
<td>15–24</td>
</tr>
<tr>
<td>methanol</td>
<td>~1</td>
</tr>
<tr>
<td>organic nitrites/paroxacyclitnates</td>
<td>~1</td>
</tr>
</tbody>
</table>

2-one/ocetal, and m/z 157 (decanal). These seven ion signals account for 80% of the observed increase relative to the cabin/O2 condition and can be largely explained by the O3-squalene reaction (see below). Acetone and propionaldehyde are isobaric and cannot be distinguished by PTR–MS; the same is true for 6-methyl-5-heptene-2-one and octanal. For the cabin + T-shirts + O3 condition, we assumed a propionaldehyde mixing ratio of 2 ± 1 ppb and an octanal mixing ratio of 0.35 ± 0.15 ppb, based on expectations from the respective homologous series. Table 3 compares the relative abundance of species observed during the two conditions when ozone was present in the simulated aircraft cabin (i.e., cabin + O3, and cabin + T-shirts + O3).

More Detailed Comparisons among the Four Conditions. In the following paragraphs, we will make comparisons among different classes of compounds that contribute to the total signals shown in Figure 5: saturated aldehydes, unsaturated aldehydes, carboxylic acids, squalene oxidation products, and organic nitrites. For the cabin or baseline, the ratios of cabin + T-shirts + no-ozone conditions, the values in the figures to follow should be taken as upper limits, because other unidentified chemicals may contribute to the signal at the m/z 157 characteristic of the compounds. However, for the conditions in which ozone was present, the mixing ratio increases are ascribed, with greater certainty, to the identified products of the resulting oxidative chemistry.

1. Saturated Aldehydes. As shown in Figure 4, saturated aldehydes were major contributors to the total PTR–MS signals measured within the simulated aircraft cabin. Propionaldehyde was not included in this figure, because we cannot distinguish its signal from that of acetone; this signal is reported below as the sum of acetone and propionaldehyde. For both conditions without ozone, the formaldehyde level was ~3 ppb, while levels of higher-molecular-weight aldehydes were <1 ppb. The addition of O3 to the cabin air resulted in significant increases for saturated aldehydes up to undecanal. Formaldehyde levels increased by more than a factor of 3, exceeding 10 ppb for the cabin + T-shirts + O3 condition. Some of the other aldehydes increased by even larger factors. Particularly striking were the increases for heptanal, octanal, nonanal, and decanal. The nonanal level increased 5.5 ppb for both O3 conditions. In the case of butanal, octanal, and decanal, the increase with the addition of O3 was more pronounced when T-shirts were present.

2. Unsaturated Aldehydes. Mono-unsaturated aldehydes with 3–9 C atoms were another group of compounds whose mixing ratios increased significantly when O3 was present, although their resultant levels were approximately an order of magnitude lower than those of their saturated analogues (see Figure 5). PTR–MS indicates that a mono-unsaturated aldehyde with a certain number of C atoms was present, but it cannot identify the specific isomer(s) responsible for a given signal. In the case of propionaldehyde (i.e., acrolein), only one isomer is possible; for butanal, the most likely isomer is 2-butenal (i.e., crotonaldehyde). For higher-molecular-weight species, there are many more possibilities and even chemically informed guesses are difficult. O3 is not shown in Figure 5, because of the interference of 6-methyl-5-heptene-2-one (see below).

Examining the specific results, the acrolein presence increased from ~0.1 ppb for the baseline cabin condition to >0.5 ppb for the cabin + O3 condition, and was 1 ppb for the cabin + T-shirts + O3 condition. (Tetenal may contribute slightly to the acrolein signal at m/z 57.) The level of crotonaldehyde was comparable to that of acrolein for the cabin + O3 condition (0.6 ppb) and somewhat lower (0.8 ppb) than that of acrolein for the cabin + T-shirts + O3 condition. Pentanal, hexanal, heptanal, and nonanal each displayed large mixing ratio increases when ozone was present in the cabin.

3. Carboxylic Acids (Tentative Identification). The level of what is nominally identified as acetic acid increased from ~2–3 ppb in the absence of O3 to ~7 ppb in the presence of O3. T-shirts did not influence this O3-induced increase. On the other hand, the O3-induced increase in the mixing ratios of propanoic and butanoic acids were larger when T-shirts were present (see Figure 6).

4. Squalene Oxidation Products. Squalene (C30H50) is an unsaturated hydrocarbon that is a major component of human skin lipid (43). It reacts with ozone to produce several oxidation products, including acetone, 6-methyl-5-heptene-2-one, 4-oxopentanal, and geranyl acetone (34; also see Figure 6, p 232 in ref 44). Acetone is common in indoor settings; it is emitted by various materials and is produced via the oxidation of numerous precursors. Conversely, 6-methyl-5-heptene-2-one and 4-oxopentanal are less commonly reported indoors; this likely reflects the fact that they are not routinely measured, rather than the conception that they do not commonly occur. Their presence is indicative of squalene oxidation in a given setting. Figure 7 shows the mixing ratios of acetone/propanal, 6-methyl-5-heptene-2-one, and 4-oxopentanal for the four conditions examined in this study. (As noted previously, PTR–MS cannot distinguish acetone from propionaldehyde.) Geranyl acetone was not detected. In the absence of ozone, with or without soiled T-shirts, the level of acetone/propanal was ~1 ppb, and the levels of 6-methyl-5-heptene-2-one and 4-oxopentanal were below their detection limits.

5. Organic Nitrites. As explained in the Supporting Information, the signal measured via PTR–MS at m/z 46 is reported as "organic nitrites" (i.e., the total contribution from organic nitrates and peroxycarbonitrates; see Figure 8). For the cabin (baseline) and cabin + T-shirts conditions, the total mixing ratio of organic nitrites was <0.2 ppb. The mixing ratio increased in the presence of ozone (0.5 ppb) and was still larger when T-shirts and ozone were present together (0.9 ppb). Hence, chemicals associated with the soiled T-shirts reacted with ozone to produce an extm 0.4 ppb of organic nitrites.

Removal of Ozone by Surfaces within Cabin. When the O3 generators were turned off on days 2 and 4, the ozone mixing ratio within the simulated cabin decayed in a first-order fashion (Figure 9). The decay constant for the cabin + ozone condition (day 2) was 0.3 hr⁻¹, whereas that for the cabin + T-shirts + ozone condition was 14.4 hr⁻¹. This decay constant reflects two major sinks: air exchange and removal.
by surfaces within the cabin. Given that the air exchange rate was 3.0 h⁻¹ for both conditions, the decay constant attributable to surface removal was 6.3 h⁻¹ for the cabin + ozone condition and 11.4 h⁻¹ for the cabin + T-shirts + ozone condition. The larger decay constant associated with the latter condition is consistent with surface reactions between ozone and human biofluids sorbed on the T-shirts that had been placed over the seatbacks in the cabin.

The reactivity of surfaces for ozone uptake diminishes in time (see results and discussion by Morrison and Nazaroff (41, 42)). This aging of surfaces, with respect to ozone uptake, is apparent in Figure 2 on days 2 and 4, with aging being more pronounced on day 2 than on day 4. Given the initial, final, and average ozone concentrations during the period of ozone generation on day 2, we calculate that the ozone decay constant attributable to surface removal was 9 h⁻¹ at the beginning of the period (11:00), was 6.3 h⁻¹ at the end of the period (13:40), and averaged 6 h⁻¹ during the period. Analogously, we calculate that, on day 4, the ozone decay constant attributable to surface removal was 13.6 h⁻¹ at the beginning of the period (11:30), was 11.4 h⁻¹ at the end of the period (16:00), and averaged 13.4 h⁻¹ during the period.

Discussion

Gas Phase versus Surface Chemistry: Ozone Removal and Product Emissions. In these studies, the air within the cabin was exchanged with outdoor air three times an hour (3.0 h⁻¹), which sets a constraint on the time available for gas-phase chemistry to occur (45). Furthermore, the upper limit for the sum of monoterpenes in the cabin air prior to the introduction of O₂ was 300 ppt, and this was the only compound class that decreased in concentration during ozonation. The resulting decrease (~60 ppb) was too low to account for significant amounts of oxidation products. Hence, chemical reactions in the gas phase are assumed to have contributed very little to the oxidation products identified in the simulated cabin air during the two conditions in which ozone was present. Instead, these oxidation products are deduced to be a consequence of O₂-initiated reactions with organic species on the surfaces within the aircraft cabin. Several studies have examined the reaction of ozone with unsaturated fatty acids and lipids at air/liquid or air/wall interfaces (34, 46–50), and several studies have specifically examined ozone interactions with new and aged carpets (6,
Taken together, these studies demonstrate the potential of ozone-initiated surface chemistry to influence the gas phase concentrations of selected oxidation products significantly, especially saturated and unsaturated aldehydes. Such reactions and subsequent emissions occur at rates sufficient to support meaningful product concentrations at the air exchange rates used in the present study.

Given that the rate at which ozone was removed by surfaces within the cabin was measured for both the baseline and T-shirt conditions, and that the air exchange rate is also known, it is a simple matter to compare the ozone removal rate with the rate at which oxidized products enter the cabin air. During the period from 11:00 to 15:40 on day 2, when no T-shirts were in the cabin, ozone was removed by surfaces at an average rate of 740 ppb/h (i.e., the product of the mean ozone mixing ratio, 88 ppb, and the average surface removal rate constant, 8 h⁻¹). During this same period, the products of ozone-initiated oxidation entered the cabin air at an average rate of 130 ppb/h (i.e., the product of the air exchange rate constant, 3 h⁻¹, and the difference between the mixing ratio of pollutants in the cabin air with and without ozone).

41, 42, 51]. In other words, for every molecule of O₃ removed by the surfaces within the aircraft, 0.18 molecules of oxidized product entered the cabin air.

Analogously, during the period from 11:30 to 16:00 on day 4, when worn T-shirts were in the cabin, ozone was removed by surfaces at an average rate of 686 ppb/h (i.e., the mean ozone mixing ratio, 69 ppb, times the average surface removal rate constant, 13.4 h⁻¹). During this same period, the products of ozone-initiated oxidation were entering the cabin air at an average rate of 210 ppb/h (i.e., the air exchange rate constant, 3 h⁻¹, times the difference between the mixing ratio of pollutants in the cabin air with and without ozone, 70 ppb). For every molecule of O₃ removed by the surfaces within the aircraft, 0.24 molecules of oxidized product entered the cabin air. Hence, the presence of the recently worn T-shirts increased the average emission rate of oxidized products, relative to the average ozone removal rate [from 0.18 to 0.24].

On both days that O₃ was in the cabin (days 2 and 4), it was removed by surfaces at a faster rate than the rate at which oxidized products entered the air. Some O₃ may decompose on the surfaces without producing oxidation products. The large difference between O₃-removal and product-emission rates indicates that either the fractional amount of decomposition was large or that oxidized products were accumulating on the cabin surfaces. It is anticipated that some oxidation products are essentially nonvolatile.
Other products, with higher molecular weights and lower vapor pressures than those identified in Figures 4–8, are volatile, but likely to desorb at rates slower than they are being formed. Even some of the smaller molecular-weight products may desorb at rates slower than they are being formed. The surfaces within the simulated cabin presumably accumulated oxidized products that continued to desorb after their production from O₃-initiated chemistry had ceased. This was the observation of Morrison and Nazaroff (42), who found that ozone-exposed carpets continued to emit aldehydes for significant periods after the cessation of their exposure to ozone.

Increased emission rates for specific compounds, because of the presence of ozone, can be calculated from the compound's measured concentrations and the known outdoor-air flow rate. For example, during the period from 11:00 to 13:40 on day 2, the concentration of formaldehyde was 8.4 ppb, compared to the concentration of 2.7 ppb prior to the introduction of ozone, this represents an increase of 5.7 ppb. Given that the flow rate of outdoor air was 24 L/s (86.4 m³/h), the increased emission rate of formaldehyde during this period was 2 × 10⁻⁵ mol/h (600 µg/h). This is a typical increase in ozone concentration seen in indoor environments.

If we assume that most of this increase was due to the oxidation of carbonyl compounds on the carpet and seat surfaces (total textile surface area of 40.2 m²), the area-specific emission rate for formaldehyde was 5 × 10⁻⁷ mol m⁻² h⁻¹ (15 µg m⁻² h⁻¹). For acetaldehyde and nonanal, the calculated area-specific emission rates were 2 × 10⁻⁷ and 4.6 × 10⁻⁷ mol m⁻² h⁻¹ (9.2 and 66 µg m⁻² h⁻¹), respectively. In total, the saturated aldehydes had an area-specific emission rate of 170 µg m⁻² h⁻¹, whereas the unsaturated aldehydes had an area-specific emission rate of 26 µg m⁻² h⁻¹. The combined emission rate for saturated and unsaturated aldehydes was close to 200 µg m⁻² h⁻¹. Morrison and Nazaroff (42) measured area-specific emission rates for aldehydes from four different carpets. They found that the total aldehyde emission rate increased from values in the range of 1–70 µg m⁻² h⁻¹ in the absence of ozone to values in the range of 60–800 µg m⁻² h⁻¹ in the presence of 100 ppb of ozone, increases similar to those measured in the present study.

Influence of the Environmental Control System. The recirculation loop of the air handling system used for the cabin simulation contains both a HEPA filter and a cooling coil. The PTR-MS analysis measured no major differences in the mixing ratios of pollutants upstream and downstream of the loaded HEPA filter. This was true whether or not ozone was present in the airstream. Hence, if any emission of organic compounds or oxidized organic compounds from the surface of the loaded filters occurred, the emission rates were insufficient to produce detectable mixing ratio differences at the rate at which recirculated air flowed through the filter. There is also the potential for the cooling coil to scavenge some of the less volatile oxidation products produced by ozone-initiated chemistry. This could decrease the mixing ratio of oxidation products in the recirculated air, and, subsequently, in the cabin air. Measurements to evaluate the magnitude of this effect were not conducted. However, we do know that the cooling coil water temperature was well above the dewpoint of the recirculated air, so scavenging via absorption in the condensate was unlikely to occur.

The rate at which the simulated cabin air was replaced with outdoor air (3.0 h⁻¹) is lower than that typically encountered on commercial aircraft. Higher ventilation rates would provide more dilution air for oxidized products emitted from cabin surfaces. However, higher ventilation rates may also increase the emission rates of such compounds (52, 53). In addition, in actual aircraft, a higher air exchange rate means higher O₃ levels within the cabin, as a consequence of increased outdoor-to-indoor transport. (This factor does not apply to the current study where the ozone levels were not determined by outdoor-to-indoor transport but were artificially established to be similar to those reported on a subset of actual flights.) Further studies are needed to examine the influence of varying outdoor air supply rates on the mixing ratio of oxidation products.
Implication of the Results. Anecdotally, a much stronger odor was perceived upon entering the cabin shortly after the ozone conditions than before ozone was introduced. Prior to the introduction of ozone, the concentrations of neither the saturated nor unsaturated aldehydes exceeded their odor thresholds. However, during the two conditions when O₃ was present in the simulated cabin, many of these compounds had mixing ratios similar to or above their odor thresholds (see the table listing odor thresholds (54, 55) for selected saturated and unsaturated aldehydes in the Supporting Information). These included octanal, nonanal, decanal, and, most likely, one or more nonenal isomers. Nonanal’s mixing ratio in the simulated cabin air was 3 times its odor threshold during one period when ozone was present.

Over the course of a typical commercial flight, the O₃ mixing ratio increases from a relatively low level prior to departure to its maximum value sometime after attaining cruising altitude and then decreases sharply as the plane descends and lands (for example, see Figure 26 in ref 5). During the early portion of a flight, as the O₃ mixing ratio within the cabin increases, the mixing ratio of oxidized products is expected to increase (see days 4 and 4 in Figure 2). Although some of the oxidation products may reach mixing ratios higher than their odor thresholds, the approach to and eventual increase above odor thresholds is expected to be gradual enough for passengers within the aircraft to be unable to perceive the odor. The olfactory sense habituates relatively quickly. Conversely, sensory irritation (eyes, throat, nasal passages) may become more pronounced as the duration of exposure increases. Several of the oxidation products identified in this study would be expected to contribute to sensory irritation, including certain aldehydes and carboxylic acids. Both propenal (i.e., acrolein) and 2-butanal (i.e., crotonaldehyde) are known lachrymators. For acrolein, California has established 0.08 ppb as the acute reference exposure level (REL) (protective against mild adverse symptoms) and 0.65 ppb as the chronic REL (56). Formaldehyde has a chronic REL of 2.4 ppb (59). The levels of acrolein (see Supporting Information for potential interferences) and formaldehyde measured during the two conditions when ozone was present in the cabin air exceeded these RELs. Measurements of such oxidation products aboard actual commercial aircraft during periods of elevated ozone mixing ratios are warranted.

Aircraft cabins have a tendency to have low relative humidities during the cruise portion of a flight and this is often assumed to be the reason for complaints related to dryness. However, in addition to relative humidity, factors such as increased concentrations of indoor pollutants are known to cause the perception of dryness (57). The current findings suggest the possibility that another factor may contribute to the perception of dryness: ozone reactions with constituents of skin oils (e.g., squalene and oleic acid) or skin cells (e.g., unsaturated phospholipids).

The mixing ratios of oxidized products were much larger, and that of ozone smaller, when recently worn T-shirts and ozone were present in the simulated cabin than when only ozone was present. This suggests that, in a commercial aircraft, the interaction between ozone and both crew and passengers will be significant, reducing the level of ozone within the cabin, but leading to additional products in the cabin air. Hence, occupant density is an important factor to consider when evaluating ozone mixing ratios and ozone-initiated chemistry in commercial aircraft.

Acknowledgments

The authors acknowledge Fang Lei, who assisted in the operation of the simulated cabin, and Boeing, which provided financial support. The climate chambers at DTU were constructed with a grant from the Danish Research Council for Scientific and Technical Research. SVTF-Jönköping provided resources related to the PRR-MS analyses. Authors A.W. and G.T. made equivalent contributions to this work.

Supporting Information Available

A more-detailed discussion of possible interferences in the interpretation of the PPR-MS results, as well as a table listing thresholds of selected saturated and unsaturated aldehydes (Table S1). In PDF format, are available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


VOL. 39, NO. 13, 2009 | ENVIRONMENTAL SCIENCE & TECHNOLOGY • 4831


(52) Wangs, P.; Wuyon, D. P.; Sundell, J.; Clauser, G.; Fanger, O. The effects of outdoor air supply rate in an office on perceived air quality, sick building syndrome (SBS) symptoms and productivity. Indoor Air 2000, 10, 222–236.


Received for review December 19, 2004. Revised manuscript received April 15, 2005. Accepted May 5, 2005.
Original articles in conference proceedings
PAPER 5: INFLUENCE OF OZONE-LIMONENE REACTIONS ON PERCEIVED AIR QUALITY
INFLUENCE OF OZONE-LIMONENE REACTIONS ON PERCEIVED AIR QUALITY

G Tamás1, C Weschler1,2, J Toftum1 and PO Fanger1

1 International Centre for Indoor Environment and Energy (ICIEE), Technical University of Denmark, 2800-Kgs. Lyngby, Denmark
2 Environmental and Occupational Health Sciences Institute (UMDNJ-RW Johnson Medical School & Rutgers Univ.), Piscataway, NJ 08854 USA

ABSTRACT
The present study was designed to evaluate the perceived air quality in low polluting office environments when ozone and limonene were simultaneously present in the air. The measurements were made in four identical and adjacent 40 m² test offices ventilated with outdoor air at 1.4 h⁻¹ (22°C, 50% relative humidity). Ozone and limonene were introduced into each test office separately or together at different rates to obtain various ratios of pollutant concentrations. After a given condition reached steady state, subjects entered the offices one-by-one and immediately assessed the air quality. The results indicate that, for each condition, the perceived air quality was poorer in the office where ozone and limonene were present together compared to the offices where only ozone or only limonene was present. Particle concentrations and the resulting particle size distributions were monitored prior to and during the sensory evaluations. The total number of particles increased significantly when ozone and limonene were present together, with the magnitude of the increase depending on the relative concentration of the reactants. The largest increase in particle concentrations was observed for particles smaller than 0.5 μm diameter. A correlation was observed between the resulting particle number concentration and the sensory pollution load.

INDEX TERMS
Indoor air chemistry, Ozone, Limonene, Secondary organic aerosols, Perceived air quality

INTRODUCTION
Scented products such as air fresheners, cosmetics and household cleaners are widely used in homes and non-industrial work places to impart pleasant odors and to counteract malodors originating from a variety of indoor sources, including human activities. In addition to their intended benefits, these products emit significant quantities of chemicals that may themselves cause adverse health effects or may initiate reactions to yield harmful secondary products (Nazareno and Weschler, 2003). Of special note are terpenes such as D-limonene and α-pinene whose reactions with ozone are fast enough to compete with normal air change rates (Weschler, 2000). Average indoor levels of 5-15 ppb limonene have been reported in a number of studies (Seifert et al., 1989; Fellin and Olston, 1994), but levels may reach several hundreds of ppb during and immediately after product use (Wainman et al., 2000). Similarly ozone is also commonly found in various indoor settings as a result of outdoor-to-indoor transport or direct emission from indoor sources. Concentrations of 20-40 ppb ozone are commonly reported indoors, but in extreme cases levels can exceed 100 ppb (Weschler et al., 1989; Weschler, 2000). Ozone-D-limonene reactions produce both stable species and reactive free radicals. The free radicals, in turn, react to generate additional species. The oxidation products include a number of organic acids and aldehydes with low odor thresholds. Some of these products are anticipated to be more irritating than their precursors. Both primary and secondary products can exist in the gas phase and in the condensed phase; the distribution between these phases depends on the vapor pressure of the compound. Low vapor pressure products contribute to the growth of secondary organic aerosols (Weschler and Shields, 1999). Although indoor ozone/terpene reactions have been investigated in a number of studies, only a few have evaluated the human sensory effects of ozone/terpene initiated reaction products (Fiedler et al., 2002; Knudsen et al., 2002; Kleno and Wolkoff, 2004). The present experiments were designed to evaluate the impact of ozone limonene reaction products on the perceived air quality under realistic indoor conditions using different relative concentrations of ozone and limonene.

METHODS
Experimental plan
The measurements were carried out in four identical and adjacent non-furnished low polluting offices (Figure 1)

* Corresponding author email: gyt@mek.dtu.dk
ventilated at 1.4 h⁻¹ (± 0.1 h⁻¹). In each room the outdoor air was supplied by an axial fan mounted in the window, connected to a damper followed by an activated charcoal filter to remove ozone. The temperature and humidity were maintained at 22.3°C (± 0.4%) and 51% (± 6%) RH, respectively. Several small fans were used to achieve good mixing inside each room. The polluted air was extracted by another axial fan mounted in each window. The corridor was well ventilated and used as the space where subjects refreshed their olfactory sense between assessments of the air in the rooms.

Experimental conditions
One office was always used as a reference exposure where neither ozone nor limonene was introduced. A second office contained different levels of ozone. In a third office different levels of limonene were maintained using a pump, a bubbler and a flow meter to achieve a controlled flow of limonene-saturated air from the bubbler. In the fourth office ozone and limonene were generated at the same rates as ozone in the second and limonene in the third room (Figure 1). Ozone was photochemically generated using a UV lamp contained in a small glass box placed in, and drawing its air from, the test room. Hence, a small fraction (1/30th) of the air in the test rooms in which ozone was generated was exposed to UV light. This may have had a slight amplifying effect on the subsequent chemistry (Yeo and Shibamoto, 1992). Table 1 shows the intended steady-state ozone and limonene concentrations in the offices containing only ozone or only limonene. The first four experimental conditions covered 10-15-30-45 ppb ozone (± 5 ppb max deviation) and 40-50-83-115 ppb limonene. Conditions 5 and 6 were designed to initially yield three times as much product as Conditions 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Ozone (ppb)</th>
<th>Limonene (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>115</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>115</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
<td>83</td>
</tr>
</tbody>
</table>

Subjects and procedure
During the experiments a panel of untrained subjects consisting of approximately twenty staff members and students (age 22-60 years) from the ICIEE assessed the air quality shortly after entering each of the test rooms; this was done using a pseudo-continuous acceptability scale (Clausen, 2000). The evaluation order of the rooms was randomized and there was a one-minute break between each assessment. The experiments were carried out during two weeks in June 2003. On each experimental day a different condition (Table 1) was evaluated. The order in which the conditions were established in the rooms was also randomized. Assessments were conducted after steady-state conditions had been achieved. The mean air acceptability votes were compared using the paired t-test to determine whether the perceived air quality differed significantly between the experimental conditions and/or between the test offices.
Physical measurements

Temperature and RH values were monitored continuously during the experiment. The outdoor air supply rate was measured in each office before each experiment started using the decay method. The ozone concentration in the two offices where ozone was generated was continuously measured with ozone meters (Dasibi 1003-AH and 1003-RE). Particle levels were measured with an N-Trak condensation nuclei counter (0.02-1 μm diameter size range) and a Lissar optical particle counter (0.1-0.2; 0.2-0.3; 0.3-0.4; 0.4-0.5; 0.5-0.7; 0.7-1; 1-2, and > 2 μm diameter size ranges). The number concentrations of particles [part/cm³] were measured directly. Based on the number concentration, and assuming that the particle mass is distributed according to a lognormal distribution, the mass concentrations [μg/m³] were calculated using the geometric mean diameter of the particle size range and 1.2 g/cm³ density (Turpin and Lim, 2001). The steady-state limonene levels were evaluated by GC/MS analysis of two-hour sorbent samples. Real-time TVOC levels were estimated with a B&K 1302 Multigas Monitor using the UA987 filter.

RESULTS

Physical measurements

Figure 2 shows the evolving nature of the particle concentrations for the different size ranges in the room where ozone and limonene were generated together under Condition 1. The results are typical of those observed under the other conditions studied. The largest growth was observed in the 0.02-0.2 μm size range in each condition.

In the offices where either ozone or limonene was present separately or nothing was generated, the background level of particles was relatively low (typically less than 1000 part/cm³, although on a few occasions the level was 10 times higher). Compared to these levels the particle concentrations in the ozone-limonene office increased one to two orders of magnitude, depending on the ozone and limonene concentrations (Table 2). Background TVOC levels were similar in each office (between 3.5 and 5 mg/m³), and did not change when only ozone was added to the test room. On the other hand, for Conditions 1, 2, 5 and 6, TVOC concentrations detectably increased when limonene was added to the rooms. After initiating the addition of limonene, the concentration of ozone in the ozone/limonene offices decreased by 17-45%, depending on the condition.

![Figure 2](image)

Figure 2. Particle concentration in Condition 1 (Ozone 10 ppb, Limonene 115 ppb) prior to and during the sensory assessment in the ozone-limonene room

Table 2 summarizes the ozone, TVOC and total particle concentrations (0.02-1 μm) during the sensory assessments in the offices where ozone and limonene were simultaneously present.

<table>
<thead>
<tr>
<th>Cond.</th>
<th>Ozone (ppb)</th>
<th>TVOC (mg/m³)</th>
<th>Particles (part/cm³)</th>
<th>Particles (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.1 ± 0.3</td>
<td>7.7 ± 0.3</td>
<td>10700 ± 7300</td>
<td>15.5 ± 0.9</td>
</tr>
<tr>
<td>2</td>
<td>7.8 ± 0.5</td>
<td>5.7 ± 0.1</td>
<td>3100 ± 1200</td>
<td>11.1 ± 1.9</td>
</tr>
<tr>
<td>3</td>
<td>21.0 ± 0.6</td>
<td>5.4 ± 0.2</td>
<td>15000 ± 700</td>
<td>14.2 ± 0.9</td>
</tr>
<tr>
<td>4</td>
<td>31.6 ± 1.4</td>
<td>5.9 ± 0.1</td>
<td>50000 ± 4400</td>
<td>11.3 ± 1.0</td>
</tr>
<tr>
<td>5</td>
<td>15.2 ± 0.8</td>
<td>7.0 ± 0.3</td>
<td>96000 ± 5000</td>
<td>21.9 ± 1.0</td>
</tr>
<tr>
<td>6</td>
<td>4.1 ± 0.3</td>
<td>5.5 ± 0.3</td>
<td>138000 ± 7300</td>
<td>21.2 ± 1.4</td>
</tr>
</tbody>
</table>
Subjective measurements
The percent dissatisfied with the perceived air quality in the office where nothing was generated (Office 4 in Fig. 1) averaged 10%. Compared to this level, the quality of the air in the office where only ozone was generated (Office 3 in Fig. 1) was slightly less acceptable, but the difference was only significant (p < 0.05) when the ozone concentration reached 30 or 45 ppb. The presence of limonene (Office 2 in Fig. 1) also negatively affected the air acceptability compared to the office where nothing was generated; it decreased significantly (p < 0.05) at limonene concentrations of 50, 85 and 115 ppb. In the office where ozone and limonene were present together (Office 1 in Fig. 1) the air acceptability radically decreased (p < 0.001) compared to the office where nothing was generated resulting in more than 90% dissatisfied with the perceived air quality under all six experimental conditions.

The sensory pollution load (olf) in the offices was calculated from the sensory assessments and the average outdoor air supply rate (Fanger, 1988; Clausen, 2000). Figure 3 indicates the sensory pollution load (above background levels) in each office for each condition. Similarly to the results seen for the air acceptability, the sensory pollution load was modestly affected by the presence of ozone alone, and affected to a greater extent by the presence of limonene, scaling with the limonene concentration. When ozone and limonene were present together the sensory pollution load was always dramatically higher than that for ozone alone (p < 0.025) or limonene alone (p < 0.05). The sensory pollution load was highest for ozone and limonene together in Conditions 5 and 6.

![Figure 3. The sensory emission rates measured in ozone, limonene and ozone-limonene rooms as a function of the experimental conditions](image)

The sensory pollution load obtained in Office 1 with the different combinations of ozone and limonene concentrations showed a fairly good correlation with the measured particle levels in the size ranges of 0.02-0.1 μm (p < 0.01, R²=0.8) as well as for particles in the size range of 0.1-0.2 μm (p < 0.005, R²=0.8).

DISCUSSION
Elevated concentrations of sub-micron particles were observed even when the ozone and limonene concentrations were at relatively low levels. The simultaneous presence of ozone and limonene also negatively affected the perceived air quality. The most striking condition was that in which the limonene concentration in the absence of ozone did not affect the perceived air quality (40-50 ppb), but the combination of limonene and ozone (32 ppb residual) caused more than 50% to be dissatisfied with the air quality. This indicates that chemical reactions resulting from ozone-terpene chemistry may substantially affect perceived air quality. Knudsen et al. also observed degradation of perceived air quality while exposing people to ozone limonene reaction products but only at a relatively low air change rate (0.3 h⁻¹). In the present study, as more particles were formed, the effects on the perceived air quality increased. Ozone-limonene chemistry produces both gas phase and condensed phase oxidation products; at present we cannot disentangle the sensory effects of these two phases. However, this co-production allows us to predict sensory effects by measuring only one phase, in this case the concentration of airborne particles. The present investigation also showed that the odor of limonene can be detected at lower levels (40-85 ppb) than indicated in certain literature (438 ppb; Devos et al., 1990).

CONCLUSION AND IMPLICATIONS
Ozone has direct, adverse effects on human health (Bell et al., 2004 and references therein). Ozone also initiates reactions that produce potentially irritating products. The current study, using concentrations of ozone and limonene known to occur in indoor settings, demonstrates that the products of ozone-initiated reactions with
limonene negatively affect short term evaluations of perceived air quality. Other studies also report negative effects resulting from exposures to the products of ozone/limonene reactions (Knudsen et al., 2002, Kleino and Wolkoff, 2004). Although the consequences of long term exposures to the products of such chemistry remain to be determined, we deem it prudent to limit indoor ozone levels. Devices that emit ozone at significant rates should not be used indoors. Moreover, ozone-filtration may be beneficial in mechanically ventilated buildings located in regions that repeatedly violate outdoor ozone standards.

ACKNOWLEDGEMENTS

The authors thank all the subjects participating in the experiments for their contribution.

This work has been supported by the Danish Technical Research Council (STVF) as part of the research programme of the International Centre for Indoor Environment and Energy established at the Technical University of Denmark for the period 1998-2007.

REFERENCES


Fanger PO. 1988 Introduction of the olf and the decipal units to quantify air pollution perceived by humans indoors and outdoors Energy and Buildings 12, 1-6

Fellin P. and Olton R. 1994 Assessment of the influence of climatic factors on concentration levels of volatile organic compounds (VOCs) in Canadian homes Atmospheric Environment, Vol. 28, No. 22, pp. 3581-3586


Kleino JG. and Wolkoff P. 2004 Changes in eye blink frequency as a measure of trigeminal stimulation by exposure to limonene oxidation products, isoprene oxidation products and nitrate radicals Int Arch Occup Environ Health, 77: 235-243


Nazaroff WW. and Weschler CJ. 2003 Cleaning products and air fresheners: exposure to primary and secondary air pollutants Atmospheric Environment 38, pp. 2841-2865


Turpin BJ. and Lim HJ. 2001 Species contribution to PM 2.5 mass concentrations: revisiting common assumptions for estimating organic mass Aerosol Science and Technology 35, pp. 602-610


Weschler CJ., Shields H. and Naul D. 1989 Indoor ozone exposures JAPA, 39, pp. 1562-1568

Weschler CJ. and Shields H. 1999 Indoor ozone / terpene reactions as a source of indoor particles Atmospheric Environment, 33, pp. 2301-2312

Yeo HC. and Shibamoto T. 1992 Formation of formaldehyde and malonaldehyde by photooxidation of squalene Lipids 27(1), pp. 50-53
PAPER 6: ULTRA-FINE PARTICLES AS INDICATORS OF THE
GENERATION OF OXIDIZED PRODUCTS ON THE SURFACE OF USED
AIR FILTERS
ULTRA-FINE PARTICLES AS INDICATORS OF THE GENERATION OF OXIDIZED PRODUCTS ON THE SURFACE OF USED AIR FILTERS

G Bekö1,2,4*, G Tamás4, O. Halás1, G. Clausen2, C. J. Weschler3,3

1 Faculty of Civil Engineering, Slovak University of Technology, 813 68 Bratislava, Slovakia
2 International Centre for Indoor Environment and Energy, Technical University of Denmark
2800-Kgs. Lyngby, Denmark
3 EOHSI (UMDNJ-RW Johnson Medical School & Rutgers Univ.), Piscataway, NJ 08854 USA
4 These authors have made equivalent contributions to this work.

ABSTRACT
Ultrafine particle concentrations were measured upstream and downstream of filter samples when the air passing through the filters either did or did not contain ozone. This was done using small-scale test equipment in a low-polluting office with a very low background ozone level. When the airstream contained ozone, the downstream/upstream concentration ratio of ultrafine particles was higher than when the airstream did not contain ozone. It is not anticipated that the filter removes ultrafine particles less efficiently when ozone is present in the airstream. Indeed, the fact that the downstream/upstream ratio was higher when ozone was present indicates the creation/growth of ultrafine particles after the air has passed through the filter. Such an observation is consistent with low volatility oxidation products desorbing from the filter and subsequently partitioning between the gas and the surface of ultrafine particles that have passed through the filter, including particles that were previously too small (< 20 micron diameter) to be detected by the instrument used in these studies.

INDEX TERMS
Ultrafine particles, Ozone, Ventilation filters, Gas/Particle Partitioning

INTRODUCTION
Filters remove particles from ventilation air and thus reduce the rate at which HVAC components soil and lower the concentration of airborne particles to which occupants are exposed. However, particulate filters also introduce sensory pollutants into the air that passes through them. Studies have reported that particle loaded ventilation filters can degrade perceived indoor air quality (Pejtersen et al., 1989; Pusu et al., 1994; Clausen, 2004 and references therein), increase sick building syndrome symptoms (Clausen et al. 2002) and decrease performance (Wargocki et al., 2003). The sensory pollutants emitted by loaded ventilation filters are assumed to be a mixture of organic compounds associated with particles collected on the filters and organic compounds formed on the filter as a consequence of chemical reactions or microbial activity. Oxidation processes, especially those driven by ozone, are expected to be the dominant chemical transformations occurring on filter surfaces. Consistent with this expectation, studies carried out by Hyttinen et al. (2004) and Bekö et al. (2005) indicate that particulate filters remove a fraction of ozone from the air stream; the fraction varies with the service life of the filter and, to some extent, the time since the flow of air through the filter was last interrupted. Although the removal efficiency is approximately 5 to 10% for a filter that has been in continuous operation for an extended period, it can be as high as 50% when an HVAC system is first turned on after several hours of inactivity (Bekö et al. 2003). If an oxidation product generated on the filter surface has a low concentration in the air upstream of the filter, it will desorb into the airstream since its surface concentration is larger than its equilibrium surface concentration.

Reactions between ozone and certain higher molecular weight unsaturated organic compounds (e.g. terpenoids) in the indoor environment are known to significantly increase the mass concentration of secondary organic aerosols (Weschler et al. 2003 and references therein). Oxidation reactions occurring on filter surfaces are assumed to be similar to such ozone-initiated indoor chemistry and may lead to the growth of ultrafine airborne particles downstream of used ventilation filters. The objective of the present study was to see if it was possible to detect an increase in the concentration of ultrafine particles downstream of a used ventilation filter when ozone was present in the airstream compared to when it was not. Such an increase would be further evidence that ozone was reacting with organic compounds on the surface of the filter to generate oxidation products that subsequently desorbed and recondensed on particles immediately downstream of the filter.

* Contact author email: gb@mek.dtu.dk
METHODS

Ultratine airborne particle concentrations upstream and downstream of used filter samples were monitored using a small-scale test rig (Figure 1). Measurements were made with approximately 75 ppb of ozone in the airstream or with less than 3 ppb ozone in the airstream. The test rig was situated in a 40 m² low-polluting office ventilated with outside air at 500 m³·h⁻¹. The air supplied to the office passed through an ozone-removing filter that kept the ozone level below 3 ppb. Filter samples (100 mm diameter) were cut from a 0.6 x 0.6 m² EU7 fiberglass filter, used for a substantial period of time in a suburban area of Copenhagen and subsequently stored for several months. The filter samples were not treated in any way prior to the measurements. A new EU7 filter, intended to ensure the uniformity of supply air upstream of the tested filter sample, was inserted 600 mm upstream of the filter sample in the test rig. Thus, before encountering the evaluated filter sample, the outdoor air had passed through two filters and contained a relatively small number of particles.

![Figure 1. Small-scale test rig used for the measurements.](image)

The measurements were conducted at airflow of 1.0 Ls⁻¹. The experimental conditions are shown in Table 1. Each experiment lasted approximately 1.5 hours. A “+” in the ozone generation column indicates the presence of approximately 75 ppb of ozone in the airstream, while a “-” indicates that there was no ozone added to the airstream. Experiments 1 & 2, 3&4, 5&6, and 7 & 8 are paired filter samples, representing either samples cut from the same bag (Experiments 1 & 2 and Experiments 3 & 4) or the same filter for both the presence and absence of ozone (Experiments 5 & 6 and Experiments 7 & 8). Both the order in which the ozone conditions occurred and the order of the ultratine particle counters in the sampling train were varied.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Filter Sample</th>
<th>Ozone generation</th>
<th>Downstream Sampling Point (cm)</th>
<th>Downstream Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-</td>
<td>150</td>
<td>#1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>+</td>
<td>150</td>
<td>#1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>+</td>
<td>150</td>
<td>#2</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-</td>
<td>150</td>
<td>#2</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>+</td>
<td>30</td>
<td>#1</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>-</td>
<td>30</td>
<td>#1</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>+</td>
<td>30</td>
<td>#2</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>-</td>
<td>30</td>
<td>#2</td>
</tr>
</tbody>
</table>

An ozone generator based on UV irradiation of filtered ambient air was used to supply ozone-containing air to a 200 L glass chamber. In turn, the resulting mixture was delivered directly from the outlet of the glass chamber to the intake of the test rig via flexible duct. The ozone concentration upstream of the filter sample was held constant by a damper situated at the end of the flexible duct. The up- and downstream concentrations of ozone were measured simultaneously using two Dasibi model 1003 UV ozone monitors, while the up- and downstream concentrations of ultratine particle were measured using two P-Trak Ultratine Particle Counters (TSI). Downstream sampling occurred at different points for Experiments 1-4 (~ 150 cm after the filter sample) and
Experiments 5-8 (~30 cm after the filter sample). The upstream sampling point was always 30 cm upstream from the filter.

In a separate set of experiments, particle concentrations were measured in the test rig at various distances (5, 30, 100, 150, and 200 cm) downstream of a filter sample with ~100 ppb of ozone in the air upstream of the filter. The measurement at each position was conducted twice. The recorded value was the average of 50 one-second measurements. The upstream concentration was measured 30 cm before the filter throughout this series of experiments.

RESULTS

Figure 2 presents particle concentrations for Experiment 1 (no ozone) and 2 (~75 ppb ozone upstream), as well as the ozone removal efficiency for Experiment 2. During the measurements, the ozone removal efficiency for Experiment 2 decreased from an initial value of 65% to a final value of 12%. The average downstream to upstream ratio of ultrafine particle concentrations was 60% when the airstream contained ozone whereas it was 54% when it did not. Ratios of the particle concentration downstream to the particle concentration upstream have been calculated for each experiment and are shown as match pairs in Figure 3.

**Figure 2.** Concentrations of 0.02 – 1 μm diameter particles for Experiments 1 and 2 and the corresponding ozone removal efficiency during Experiment 2.

**Figure 3.** Ratios of particle concentrations (Downstream/Upstream) for each experiment.
In the paired measurements, the downstream/upstream ultrafine particle concentration ratios were always higher when ozone was passing through the filter compared with when it was not. However, significantly higher downstream/upstream values were recorded when the downstream sampling point was 30 cm from the filter (Experiments 5-8) compared with 150 cm from the filter (Experiments 1-4). As noted in the Methods section, the dependence of the particle concentration on the distance downstream of the filter was measured in a separate set of experiments. The results from these experiments are shown in Figure 4.

![Graph](image)

**Figure 4.** Relationship between the particle concentration and the location of the sampling point downstream of the filter sample (distances of 5, 30, 100, 150, and 200 cm). Each value is the average of two measurements at each point. The upstream concentration was always measured 30 cm before the filter.

**DISCUSSION**

Particle concentrations upstream and downstream of the filter samples were generally low, reflecting filtration of the outdoor air delivered to the experimental room followed by further filtration as the air passed through the diffuser (itself a filter) upstream of the actual filter sample. These very low particle concentrations immediately upstream of the filter sample made it easier to detect small differences in particle concentrations that might result from altered experimental conditions.

The apparent particle removal efficiencies for the experiments with ozone in the airstream were always lower than those for the matching experiments without ozone in the airstream. However, we do not expect the filter’s ability to remove ultrafine particles to be altered by the presence of ozone. Instead, we interpret this apparent change in removal efficiency to be due to the growth of ultrafine particles downstream of the sample filter (via absorption of low volatility organics). Ultrafine particles are an extremely sensitive marker for changes in the concentrations of low volatility organic compounds in an airstream. Even a small increase in the low vapor-pressure organics desorbing from a filter will manifest itself as an increase in ultrafine secondary organic aerosols. Presumably, when ozone passes through a loaded filter, low vapor-pressure oxidation products desorb from the filter and partition between the gas phase of the airstream and particles in the airstream. Such processes will result in accretion and growth of the particles that have passed through the sample filter. As a consequence, ultrafines that had been too small to be counted by the ultrafine particle counter (smaller than 20 nm in diameter) can grow in diameter up to and beyond the point where they become “countable”. In extreme cases, this process may result in a downstream ultrafine particle count that is actually higher than the corresponding upstream count (e.g., Experiment 5).

The downstream/upstream ratios were significantly higher for Experiments 5-8 compared with Experiments 1-4. The cause appears to be that the downstream sampling point in Experiments 5-8 was 30 cm downstream from the sample filter, while in Experiments 1-4 it was 150 cm downstream from the filter. This is consistent with the results shown in Figure 4, which indicate lower particle concentrations further downstream of the filter. Presumably this reflects loss of particles to the surfaces of the ductwork as the air flows through the test rig.

**CONCLUSION AND IMPLICATIONS**

The results of these experiments provide circumstantial evidence for the formation of oxidation products as the
loaded ventilation filters scavenge ozone. The increase of secondary organic aerosols observed downstream of the filter when ozone is present in the airstream is not, in itself, of great concern. The actual increase in particle mass concentration as a consequence of this chemistry is quite small. Indeed, we would not have been able to measure the increase if the background concentration of particles (the upstream concentration) had not been so low.

The significance of the observation is that it supports the hypothesis that ozone can initiate oxidation processes on the surface of loaded filters. We suspect that these oxidation processes can change the mix of chemicals in the air downstream of a loaded filter and may result in ventilation air that is less acceptable, in terms of sensory perceptions, than the air would have been if such oxidative chemical transformations had not occurred.

ACKNOWLEDGEMENTS
This work has been supported by the Danish Technical Research Council (STVF) as part of the research program of the International Centre for Indoor Environment and Energy, Technical University of Denmark.

REFERENCES
Clausen G. 2004 “Ventilation filters and indoor air quality: a review of research from the International Centre for Indoor Environment and Energy”. Indoor Air, 14, S7, pp 202-207.