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Roles of the human occupant in indoor chemistry

Abstract Over the last decade, influences of the human occupant on indoor chemistry have been investigated in environments ranging from simulated aircraft cabins to actual classrooms. We have learned that ozone reacts rapidly with constituents of skin surface lipids on exposed skin, hair, and clothing, substantially reducing indoor ozone concentrations but increasing airborne levels of mono- and bifunctional compounds that contain carbonyl, carboxyl, or α-hydroxy ketone groups. Moreover, occupants transfer skin oils to and shed skin flakes (desquamation) onto indoor surfaces. Evidence for the presence of skin flakes/oils has been found in airborne particles, settled dust, and wipes of indoor surfaces. These occupant residues are also anticipated to scavenge ozone and produce byproducts. Under typical conditions, occupancy is anticipated to decrease the net level of oxidants in indoor air. When occupants scavenge ozone, the level of SOA derived from ozone/terpene chemistry decreases; the fraction of SVOCs in the gas-phase increases, and the fraction associated with airborne particles decreases. Occupants also remove organic compounds, including certain chemically active species, via bodily intake. Studies reviewed in this paper demonstrate the pronounced influences of humans on chemistry within the spaces they inhabit and the consequences of these influences on their subsequent chemical exposures.

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Key words: Criegee mechanism; Desquamation; Fatty acids; Ozone; Skin lipids; Squalene.

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Practical Implications
For practical and sometimes ethical reasons, experiments probing indoor chemistry have often been conducted in unoccupied simulated or actual indoor environments. However, this can result in findings that may differ substantially from those that would be obtained in an occupied setting. Going forward, when conducting investigations of chemical transformations that occur in human habitats, it is important to be mindful of the potential role of the occupant and to design experiments accordingly.

Introduction

Occupants impact indoor chemistry through activities such as cooking, smoking, and cleaning. Occupants also impact indoor chemistry through the simple presence of their bodies. While it is well known that bioeffluents can be malodorous and degrade indoor air quality (Yaglou et al., 1936), it is less well known that bodily emissions can react with indoor pollutants. This has only become apparent over the last decade and is the focus of the present review – the influence of the human body, via its skin-oil constituents and other reactive bioeffluents, on chemical reactions among indoor pollutants. Most of the chemical reactions examined in this review involve ozone. We anticipate that the presence of human occupants alters other chemical reactions. However, to date, the processes involving occupants and ozone have been the most studied.

Early papers on indoor chemistry (Weschler and Shields, 1997) and indoor ozone (Weschler, 2000) failed to mention the influence of the human body on either chemistry or ozone concentrations. This omission reflected the fact that most of the early studies of ozone and ozone-initiated chemical transformations were performed in unoccupied chambers or unoccupied indoor environments. The intent was to have well-controlled settings, undisturbed by humans and their activities. This approach also allowed for a wider latitude of experimental conditions, while sidestepping ethical issues regarding the chemicals that subjects might be exposed to.

Early indications of the impact of occupants on indoor chemistry came from a study conducted at Harvard evaluating passive samplers for measuring indoor ozone (Liu et al., 1994) and a study at the Technical University of Denmark examining correlations

between indoor ozone concentrations and emission rates of oxygenated organics with and without occupants in a room (Bakó-Biró et al., 2005). A striking feature of the second study was the lower level of ozone, all else being equal, when occupants were present compared to when they were absent. These studies will be discussed in greater detail in what follows, as will numerous other studies that have clearly shown the impact of occupants on indoor ozone levels and on the products of ozone-initiated chemistry. This includes studies of what occupants leave behind – skin flakes and skin oils – on exposed surfaces and on their clothing. When occupancy or its aftermath alters ozone levels, it indirectly alters levels of products generated from ozone-initiated chemistry. These changes produce their own cascade of effects and will also be briefly discussed.

Human occupants, through the reactive chemicals that they emit, have a large influence on the atmospheric chemistry that occurs around them, ultimately impacting their own chemical exposures and their health.

Skin oils, skin flakes, and body effluents

Ozone-reactive constituents of human skin oil

The human body is covered with skin surface lipids that are a combination of sebum secreted by sebaceous glands and lesser amounts of lipids from the stratum corneum. The chemicals that constitute skin surface lipids can be broadly classified as triacyl glycerols (~25%), unesterfied fatty acids (~25%), wax esters (~22%), squalene (~10%), mono- and diacyl glycerols (~10%), and lesser amounts of sterol esters, sterols, phospholipids, and other species (Nicolaides, 1974). A number of these constituents possess carbon-carbon double bonds and readily react with ozone. On a molar basis, squalene is responsible for roughly 50% of the unsaturated carbon bonds in skin surface lipids, while unsaturated acyl groups present in the fatty acids, wax esters, and mono-, di-, and triacyl glycerols are responsible for the other 50% (Pandrangi and Morrison, 2008). Hence, squalene with its six double bonds and surface concentration of ~10–15 $\mu g/cm^2$ is the most important individual constituent in terms of ozone consumption. Unsaturated fatty acids, with a total surface level of ~11–17 $\mu g/cm^2$ and one or two double bonds, are next in importance (Table 1). Figure 1 shows the structure of squalene and some of the major unsaturated fatty acids. Although cholesterol is present at ~3–4 $\mu g/cm^2$ and possesses a double bond, it reacts with ozone relatively slowly. The probability that ozone reacts with cholesterol upon collision (2.6×10^{-6} to 2.9×10^{-6}, Dreyfus et al., 2005; Gumulka and Smith, 1983) is two orders of magnitude smaller than that with squalene (2×10^{-4} to 5×10^{-4}).

Table 1 Major unsaturated fatty acids found in skin surface lipids, percentage of total lipids, and selected aldehydic products generated by reaction with ozone[a]

Unsaturated fatty acid	Formula	% of skin surface lipids	Aldehydic product(s)
cis-Hexadec-6-enoic	$C_{16:1\Delta6}$	5.4	n-Decanal
cis-Octadec-8-enoic	$C_{18:1\Delta8}$	2.2	n-Decanal
cis-14-Methylpentadec-6-enoic	iso-$C_{16:1\Delta6}$	1.0	8-Methylnonanal
cis-Octadec-6-enoic	$C_{18:1\Delta6}$	0.47	n-Dodecanal
cis-Octadec-9-enoic (Oleic)	$C_{18:1\Delta9}$	0.47	n-Nonanal
cis-Heptadec-6-enoic	$C_{17:1\Delta6}$	0.33	n-Undecanal
Octadeca-5,8-dienoic	$C_{18:2\Delta5,8}$	0.28	n-Decanal, 3-Tridecenal
cis-Tetradec-6-enoic	$C_{14:1\Delta6}$	0.27	n-Octanal
cis-Heptadec-8-enoic	$C_{17:1\Delta8}$	0.21	n-Nonanal
cis-14-Methylhexadec-6-enoic	anteiso-$C_{17:1\Delta6}$	0.20	8-Methyldecanal
cis-16-Methylheptadec-8-enoic	iso-$C_{18:1\Delta8}$	0.20	8-Methylnonanal
Octadeca-9,12-dienoic (Linoleic)	$C_{18:2\Delta9,12}$	0.13	n-Hexanal, 3-Nonenal
cis-Eicos-10-enoic	$C_{20:1\Delta10}$	0.13	n-Decanal
cis-Eicos-7,10-dienoic	$C_{20:2\Delta7,10}$	0.13	n-Hexanal, 3-Nonenal

[a]Partially adapted from information presented in Nicolaides (1974).

Hence, cholesterol does not contribute substantially to ozone consumption. Vitamin E and ubiquinone are present at low levels (~0.01–0.02 $\mu g/cm^2$), and there are even lesser amounts of other ozone-reactive species including vitamin A, β-carotene, lycopene, ascorbic acid, glutathione, and uric acid.

The fractional contribution and surface levels for skin lipids presented in the previous paragraph are averages. These values change as a human ages. For example, the amounts of omega-7 unsaturated fatty acids (unsaturation at the 7th bond from the terminal methyl group) have been found to increase with increasing age (Haze et al., 2001; Nazzaro-Porro et al., 1979).

Ozone/squalene reaction

Ozone reacts with squalene to produce products with a range of volatility. These products can be predicted reasonably well using the Criegee mechanism of ozone reacting with a double bond to generate biradicals that subsequently proceed via multiple pathways to stable oxidation products (Finlayson-Pitts and Pitts, 2000). Table 2, derived from Wisthaler and Weschler (2010), lists some of the primary and secondary products generated from ozone's reactions with squalene. The more volatile primary products (i.e., those formed from the direct ozone/squalene reaction) include acetone, 6-methyl-5-hepten-2-one (6-MHO) and geranyl acetone (Fruekilde et al., 1998). Some of these primary products contain double bonds and can react further with ozone to produce secondary products. The major gas-phase secondary product is 4-oxo-pentanal (4-OPA), derived from the primary products 6-MHO, geranyl acetone, C27-pentaenal, and C22-tetraenal. Other important gas-phase secondary products include

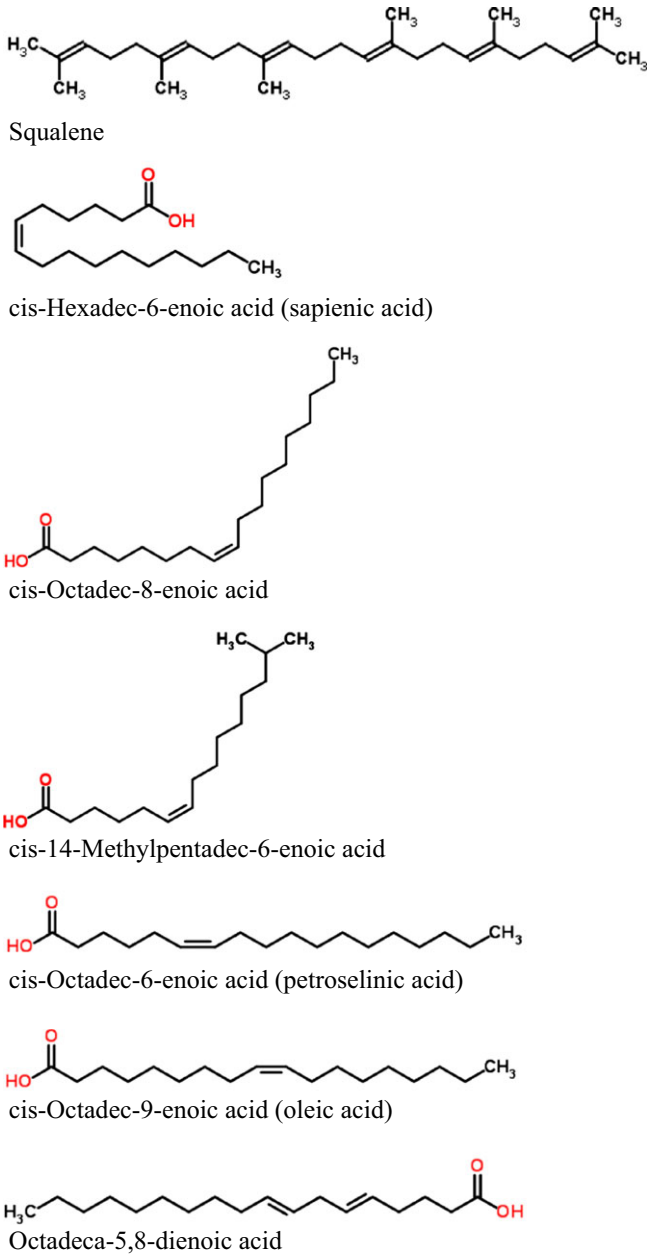

Fig. 1 Structures of squalene and some of the more abundant unsaturated fatty acids in skin surface lipids

4-methyl-8-oxo-4-nonenal (4-MON), 4-methyl-4-octene-1,8-dial (4-MOD), and 1,4-butanedial. In addition to these more volatile products, found primarily in the gas-phase, there are less volatile primary and secondary products found primarily in the condensed phase (e.g., on skin, hair, or clothing surfaces; associated with airborne particles; in surface films). These include aldehydes and organic acids with 27, 22, or 17 carbon atoms and five, four, or three double bonds, respectively. Given the number of double bonds in these less volatile products, they themselves readily react with ozone to generate still more products.

Based on the Criegee mechanism, the ozone/squalene reaction is also anticipated to produce hydrogen peroxide, organic peroxides, and short-lived highly reactive products including hydroxyl, hydroperoxyl, and alkyl peroxyl radicals. These radicals will, themselves, react with squalene and primary and secondary products producing additional carbonyls, dicarbonyls, and hydroxycarbonyls. Fu et al. (2013) observe enhanced hydrophilicity and redox activity during squalene's exposure to ozone, presumably a result of both stable and short-lived oxidation products. They speculate that the hydrophilicity of the squalene oxidation products increases their transdermal penetration and that the combination of increased redox activity and dermal permeability increases the risk these products pose to human health.

Some of the primary and secondary ozone/squalene products can condense on existing particles or nucleate to form new particles. In a series of chamber experiments, Wang and Waring (2014) have examined the formation of secondary organic aerosols (SOA) as a consequence of the reaction of ozone with squalene sorbed to a glass surface. Experimental ozone concentrations ranged from 57 to 500 ppb, and the relative humidity was maintained at either 21% or 51%. In each experiment, the squalene level on the 255 cm^2 glass surface was 3.9×10^{16} molecules/cm^2. The 37-l stainless steel chamber did not contain seed particles and was ventilated at a high air exchange rate (5.4 per hour), limiting the influence of subsequent gas-phase chemistry. A scanning electrical mobility sizer monitored airborne particles between 10 and 900 nm diameter. The mean ozone to squalene deposition velocity was 0.23 cm/s at 21% RH and 0.17 cm/s at 51% RH. The authors inferred that transport resistance was primarily responsible for these values and was significantly larger than reaction resistance. In all but one of thirteen experiments, nucleation occurred followed by an increase in the number and mass concentrations of SOA until steady state was achieved. The SOA mass concentration ranged from 0.01 to 4.2 $\mu g/m^3$, while the number concentration ranged from 180 to 5700 particles/cm^3 with geometric mean diameters ranging from 30 to 74 nm. The amount of SOA produced and the mean particle diameters tended to be larger at higher ozone concentrations. It is difficult to extrapolate the results from these experiments to typical indoor conditions given the high air exchange rate and relatively high ozone concentrations. However, the amount of SOA generated in these experiments was relatively small compared to that generated from similar levels of ozone reacting with moderate levels of either surface-sorbed (Waring and Siegel, 2013) or gas-phase limonene (Weschler and Shields, 1999).

The rate at which ozone reacts with squalene on surfaces has been the subject of at least three studies. Wells et al. (2008) found a reaction probability of $4.5 \pm 1.4 \times 10^{-4}$ for 50 ppb of ozone reacting with

Table 2 Major products generated from ozone's reaction with squalene; the shaded products are less volatile and, in addition to squalene, are precursors for the unshaded products[a]

Product	Formed directly (primary) or indirectly (secondary)	Yield on glass wool[b]
Propan-2-one (acetone)	Primary and secondary	17%[c]
6-Methyl-5-hepten-2-one (6-MHO)	Primary and secondary	14.5%[c]
6,10-Dimethylundeca-5,9-dien-2-one (geranyl acetone)	Primary and secondary	13.5%[c]
1-Hydroxypropan-2-one (hydroxy acetone)	Primary and secondary	
1-Hydroxy-6-methyl-5-hepten-2-one (hydroxy-6MHO)	Primary and secondary	
4-Oxo-pentanal (4-OPA)	Secondary	3.2%[d]
4-Methyl-8-oxo-4-nonenal (4-MON)	Secondary	3.5%[d]
4-Methyl-4-octene-1,8-dial (4-MOD)	Secondary	2.8%[d]
1,4-Butanedial (succinic dialdehyde)	Secondary	2.7%[d]
5-Hydroxy-4-oxopentanal	Secondary	
4-Oxo-pentanoic acid (levulinic acid)	Secondary	
4-Oxo-butanoic acid	Secondary	
4,8,13,17,21-Pentamethyl-docosa-4,8,12,16,20-pentaenal (C27-pentaenal)	Primary	
4,9,13,17-Tetramethyl-octadeca-4,8,12,16-tetraenal (C22-tetraenal)	Primary and secondary	
5,9,13-Trimethyltetradeca-4,8,12-trienal (C17-trienal)	Primary and secondary	
4,8,13,17,21-Pentamethyl-docosa-4,8,12,16,20-pentaenoic acid (C27-pentaenoic acid)	Primary	
4,9,13,17-Tetramethyl-octadeca-4,8,12,16-tetraenoic acid (C22-tetraenoic acid)	Primary and secondary	
5,9,13-Trimethyltetradeca-4,8,12-trienoic acid (C17-trienoic acid)	Primary and secondary	
1-Hydroxy-6,10-dimethylundeca-5,9-dien-2-one (OH-geranyl acetone)	Primary and secondary	

[a]Adapted from Tables 1 and 3, and S1 in Wisthaler and Weschler (2010), where structures for the listed compounds can be found.
[b]Primarily surface chemistry.
[c]Initial yields.
[d]End or experiment, but not at steady state.

squalene on a glass plate with a surface coverage of 1.2×10^{13} molecules/cm^2. Petrick and Dubowski (2009) measured a pseudo first-order rate constant of 1.22×10^{-5} s^{-1} for this reaction at an ozone concentration of 40 ppb and estimated a reaction probability that was approximately 45 times smaller than the value reported by Wells et al. They speculate that the latter value may have included ozone's reaction with unsaturated gas-phase products of ozone/squalene chemistry. As the relative humidity in the Petrick and Dubowski experiments increased, the ratio of aldehydic to ketonic products increased. Furthermore, when NO_2 and NO were present during the reaction, nitrated oxidation products were observed. More recently, Fu et al. (2013), using attenuated total reflection-infrared spectroscopy (ATR-IR), have measured ozone/squalene rate constants that are in approximate agreement with that reported by Wells et al. Based on decreases in the absorbance of squalene's C=C band at 1668 cm^{-1}, they measured an *initial* pseudo first-order rate constant of $(2.8 \pm 0.3) \times 10^{-4}$ s^{-1}; based on the appearance of the C=O band at 1668 cm^{-1}, the value was $(8.8 \pm 0.8) \times 10^{-4}$ s^{-1}. From these rate constants, Fu et al. calculated reaction probabilities of $(1.7 \pm 0.2) \times 10^{-4}$ and $(5.1 \pm 0.7) \times 10^{-4}$, respectively. They judge that that ozone/squalene rate values obtained by monitoring the C=C band are more accurate than those obtained using the C=O band. Regardless, the salient point is that ozone's reaction with squalene on exposed skin, hair, clothing, and other surfaces is very fast and that the deposition velocity of ozone to surfaces coated with squalene will be close to transport limited.

Ozone/unsaturated fatty acid reactions

As shown in Table 1, the most abundant unsaturated fatty acid is *cis*-hexadec-6-enoic acid (5–6% of skin surface lipids by wt). One of the products of its reaction with ozone is decanal. Other precursors for decanal in skin oil include *cis*-octadec-8-enoic acid (~2.2% by wt), *cis*-14-methylpentadec-6-enoic acid (~1% by wt), and octadeca-5,8-dienoic acid (~0.3 by wt). In each case, the reaction that produces decanal also produces an aldehydic carboxylic acid. Table 1 lists the major aldehydic products formed when ozone reacts with the tabulated unsaturated fatty acids. Some of the fatty acids in skin oil contain two or more double bonds and react to form unsaturated aldehydes such as isomers of nonenal. Unsaturated aldehydes are noteworthy for their low odor thresholds (e.g., ~0.1 ppb for 2-nonenal; Buttery et al., 1988). There are numerous other products formed during these reactions. In the well-studied case of oleic acid, additional products include nonanoic acid, 9-oxononanoic acid, 9-oxooctadecanoic acid, and azelaic acid (Hearn and Smith, 2004), while in the case of linoleic acid, they include acrolein (Medina-Navarro et al., 1999) and α-acyloxyalkyl hydroperoxide (Zeng et al., 2013).

As was the case for squalene, reactions of ozone with unsaturated fatty acids are also anticipated to produce hydrogen peroxide, organic peroxides, and short-lived,

highly reactive species such as hydroxyl radicals, hydroperoxyl radicals, and alkyl peroxyl radicals.

Desquamation (shedding skin flakes) and contact transfer

Humans shed their entire outer layer of skin every 2–4 weeks (Baker and Kligman, 1967). The resulting skin flakes are referred to as 'squames' and the process is called 'desquamation'. A typical squame is approximately 40 × 30 × 2 μm and has a mass of ~2.5 ng. An adult sheds roughly 1000 cells/cm^2/h or ~5 × 10^8 cells/day. This equates to 30–90 mg of skin flakes/h (Gowadia and Settles, 2001; Milstone, 2004).

As a consequence of desquamation, coupled with resuspension, human squames are anticipated to be present in indoor airborne particles, settled dust, and on exposed indoor surfaces, especially horizontal surfaces. These squames contain skin surface lipids; the squalene content of skin flakes is ~1% by weight (Clark and Shirley, 1973), and the other ozone-reactive constituents of skin oils are expected to scale accordingly. This means that, at least initially, the skin flakes can react with ozone and other oxidants generating the range of products discussed above. Additionally, humans transfer their skin oils to surfaces that they touch or otherwise contact. Hence, ozone-reactive constituents of skin oils are also anticipated to be present in organic films on indoor surfaces, such as those on windows characterized by Liu et al. (2003).

In a classic study, which appeared in *Nature*, Clark and Shirley (1973) measured the squalene content of size-fractionated airborne particles collected in different indoor environments to infer the percent contribution of skin flakes to these particles. Table 2 of Weschler et al., 2011 shows the squalene content of the particles collected by Clark and Shirley, back-calculated from data presented in their paper. The measured mass fractions of squalene ranged from 40 to 100 μg/g for airborne particles collected in a residence and a laboratory corridor to 1000 μg/g for particles collected in London's crowded underground (subway) system. The mass fractions of squalene in these airborne particles varied by only a factor of two over the size ranges collected. This latter observation is consistent with squalene being present in the particles as a consequence of the incorporation of skin flakes rather than as a consequence of a gas-to-particle partitioning process. Clark (1974) followed up with a study of airborne particles from a rural house and its garden. Using a stereomicroscope, he identified many of the indoor particles as desquamated skin. Consistent with this identification, approximately 75% of the 2- to 6-μm-diameter indoor particles contained proteins compared with only about 32% of the corresponding outdoor particles.

Fox et al. (2003) collected dust samples from classrooms and analyzed them for muramic acid and 3-hydroxy fatty acids. They found much higher levels of these compounds in occupied compared to unoccupied classrooms, indicating that the children were the primary source. Follow-up monitoring in two additional schools confirmed these findings (Fox et al., 2005). In the second study, larger sized particles (>2 μm) were found to be primarily responsible for elevated levels of muramic and 3-hydroxy fatty acids during occupancy. The authors hypothesized that skin flakes were likely the cause. In a related study, Fox et al. (2008) conducted protein analysis of airborne particles collected from classrooms using stand-alone air cleaners. Human K10 epithelial keratin was identified as the most abundant protein in the samples, confirming that shed human skin contributes to airborne particles.

Squalene and cholesterol were analyzed in samples of settled dust collected from 500 children's bedrooms, as well as from the 151 day care centers they attended in the city of Odense, Denmark (Weschler et al., 2011). For both locations, the mass fractions of squalene in dust samples roughly fit a log-normal distribution, with the geometric mean concentration in the bedrooms (32 μg/g) about three times larger than that in the day care centers (11.5 μg/g). Squalene was the 3rd most abundant organic identified in the bedroom dust and the 6th most abundant in the day care dust. The mass fractions of cholesterol in the dust samples did not fit a log-normal distribution as well as squalene. Furthermore, the median value of the ratio of squalene to cholesterol in the bedroom and day care dust samples was substantially smaller than that found in skin surface lipids. Together, these observations suggested other sources of cholesterol, besides desquamation, at these indoor locations (e.g., cooking) and/or perhaps more rapid depletion of squalene than cholesterol from the dust as a consequence of reactions with ozone and other indoor oxidants.

Gene sequence analysis indirectly supports the presence of skin flakes, and hence their associated skin lipids in airborne particles, in settled dust and on various indoor surfaces. Flores et al. (2011) sampled ten different surfaces in twelve public toilets; these included doors to the toilet and stalls, the floors around the sinks and toilets, faucet handles, soap dispensers, toilet handles, and toilet seats. They used gene sequence analysis to classify the sources of the bacteria on these surfaces (e.g., soil, water, mouth, urine, gut, skin). The dominant contributor was human skin; only on toilet surfaces did another source (gut-associated taxa) make a contribution comparable with skin. Complementing these surface studies, airborne particles were sampled in a university classroom and in the supply air for the classroom during occupied and unoccupied periods, as well as in outdoor air (Hospodsky et al., 2012; Qian et al., 2012). Dust samples were taken from the ventilation duct filter and the floor of the classroom. Gene sequence analysis indicated that bacteria associated

with human skin, hair, and nostrils constituted ~20% of the bacteria in the indoor air, supply air, and floor dust samples. Floor dust contained relatively more human-derived bacteria than did the airborne particles, on a per mass basis, and PM10 contained relatively more than PM2.5. Experiments that controlled for resuspension of settled dust indicated that desquamation directly contributes to indoor airborne particles. Under normal conditions, resuspension of skin flakes in settled dust is also an important source of airborne particles. The researchers used mass balance modeling to derive emission rates per occupant for biological particles in the occupied classroom. For bacteria, emission rates per person-hour were 3.7×10^7 genome copies with 18% of the emissions from taxa closely associated with the human skin microbiome. By inference, the results reported in Hospodsky et al. and Qian et al. indicate that human occupancy substantially contributes to ozone-reactive compounds in airborne particles and settled dust. Further evidence of the impact of occupancy on indoor environments comes from the Home Microbiome Project (Lax et al., 2014). As part of this study, surfaces within the homes of seven U.S. families and the skin of the occupants were sampled for bacterial communities over a 6-week period. Humans were more likely to be microbial sources than physical surfaces. Actinobacteria and Proteobacteria, both major species found within the microbial community of the human skin, were the major taxanomic units derived from humans, consistent with extensive skin shedding and skin surface contact in these occupied residences.

The above-cited studies indicate that exposed surfaces in indoor environments occupied by humans are soiled with skin flakes and skin oil. This contributes to a certain commonality among surfaces in occupied environments. When a room is new and has not been occupied, the various surfaces – glass, wood, vinyl, latex paint, cotton, wool, and synthetic fiber – differ from one another chemically. However, over time these surfaces soil. The chemicals that are first encountered by ozone when it diffuses to such a soiled surface are the chemical constituents of the soiling agents, not the chemicals associated with the underlying material. In this way, the ozone-reactive constituents of skin flakes and skin oil may play a role in determining the surface-removal rate constant for ozone in occupied indoor settings. This may partially explain why the deposition velocities measured for ozone in different occupied indoor environments are so similar to one another, typically falling in the range of 0.025–0.040 cm/s (see Table 4 in Nazaroff et al., 1993 and Table 3 in Weschler, 2000), even though the deposition velocity of ozone to the clean surface of individual materials commonly found in a room spans more than three orders of magnitude (Grontoft and Raychaudhuri, 2004; Kleno et al., 2001; Sabersky et al., 1973).

A surface soiled with skin oil may have a larger capacity to sorb certain gas-phase organic compounds than when it is clean, especially an impermeable surface such as glass or stainless steel. This has practical implications. For example, Morrison et al. (2015) have measured an average methamphetamine partition coefficient of approximately 30 μg meth/100 cm^2/ppb meth in air, for a PTFE filter surface coated with skin oil at 30% RH. The authors point out that the concentration of methamphetamine in air would have to be less than 0.003 ppb for a surface with such a partition coefficient to meet a remediation standard of 0.1 μg meth/100 cm^2. They also note that the measured partition coefficients to skin oil from different subjects varied over two orders of magnitude and suggest that, at least in the case of methamphetamine, partitioning is quite sensitive to the composition of the skin oil.

Exhaled breath and personal care products

The previous paragraphs have focused on the reactive constituents of skin surface lipids. Exhaled human breath also contains reactive chemicals. Table 3 lists some of the more important reactive species found in exhaled breath and their rate constants for reactions with ozone, hydroxyl radicals, and nitrate radicals. These include endogenously generated isoprene and nitric oxide. Based on a weighted average of eight studies and over a hundred subjects, the concentration of isoprene in exhaled breath is approximately 210 ppb or 590 μg/m^3, (Fenske and Paulson, 1999). At a breathing rate of 0.7 m^3/h, this corresponds to an emission rate of ~400 μg/h. In a 30 m^3 room ventilated at 1 h^{-1}, a single occupant is predicted to raise the isoprene level by 5 ppb. Despite its relatively high concentration in occupied settings, isoprene is not anticipated to have much effect on indoor ozone levels. The gas-phase reaction between isoprene and ozone has a second-order rate constant of 3.2×10^{-7} ppb^{-1} s^{-1} (NIST, 2013). This means that at commonly occurring levels of ozone and isoprene, the reaction is slow relative to typical air exchange rates and hence has little impact on the composition of indoor air. On the other hand, both the nitrate radical and hydroxyl radical react with isoprene fast enough to easily compete with air exchange rates (Table 3) and impact indoor air. The major products of these reactions include formaldehyde, methyl vinyl ketone, and methacrolein (Atkinson and Arey, 2003).

The amount of nitric oxide (NO) exhaled by a human occupant varies with the individual's health status. With upper respiratory tract infections, asthma, and certain other conditions, levels of exhaled NO rise. Normal levels in exhaled breath are in the range of 10–40 ppb, with a geometric mean of 18 ppb reported in a random sampling of healthy adults aged 25–75 (Travers et al., 2007). Hence, in a 30 m^3 room venti-

Table 3 Gas-phase compounds identified in exhaled breath or body emissions, typical concentrations, and second-order rate constants for reactions between these species and ozone (O_3), hydroxyl radicals (OH·), and nitrate radicals (NO_3·)

Compound	Formula	Conc.[a]	Rate constant[b]		
			ppb^{-1} s^{-1}		
		ppb	O_3	OH·	NO_3·
Isoprene	$CH_2=C(CH_3)CH=CH_2$	210[c]	3.2×10^{-7}	2.5	0.017
1-Ethene	$CH_2=CH_2$	23[c]	3.9×10^{-8}	0.20	5.2×10^{-6}
1-Butene	$CH_2=CHCH_2CH_3$	63[c]	2.4×10^{-7}	0.77	3.1×10^{-4}
1-Pentene	$CH_2=CHCH_2\ CH_2CH_3$	21[c]	2.5×10^{-7}	0.67	1.7×10^{-3}
Limonene	$C_{10}H_{16}$	–	5.0×10^{-6}	4.2	0.30
6-MHO	$(CH_3)_2C=CHCH_2CH_2C(O)CH_3$	–	9.7×10^{-6}	4.0[d]	0.17[d]
Geranyl acetone	$(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCH_2CH_2COCH_3$	–	1.9×10^{-6} [e]	–	–
Nitric oxide	NO	18[f]	4.4×10^{-4}	0.81	0.64
Dimethyl sulfide	$(CH_3)_2S$	13[c]	2.5×10^{-8}	0.13	0.027

[a]Concentration in exhaled breath.
[b]Rate constants at 25°C; from NIST (2013) unless otherwise noted.
[c]Fenske and Paulson (1999).
[d]Smith et al. (1996).
[e]Pollman et al. (2005).
[f]Travers et al. (2007).

lated at 1 h^{-1}, a single occupant is predicted to raise the NO level by 0.5 ppb. Nitric oxide reacts rapidly with ozone – three orders of magnitude faster than isoprene (Table 3) – generating nitrogen dioxide (NO_2). Given the relatively small incremental increase that exhaled breath contributes to indoor NO levels, oxidation of NO from human occupants makes only a small contribution to indoor levels of NO_2 and removal of indoor ozone.

Ethylene, 1-butene, and 1-pentene have been reported in exhaled breath at average levels of 23, 63, and 21 ppb, respectively (Fenske and Paulson, 1999). None of these unsaturated linear alkenes reacts with ozone at a rate that is fast enough to compete with typical air exchange rates (Table 3).

In addition to chemicals that are naturally present, exogenous chemicals are found in exhaled breath, emanating from the human body. Wallace et al. (1996) have reviewed the use of breath samples to evaluate human exposure to volatile organic pollutants in indoor settings. From the U.S. EPA's TEAM study, it is apparent that humans exposed to chemicals in one setting can exhale those chemicals in another setting (Wallace, 1987). Smoking and diet are other sources of various exhaled chemicals. Additionally, residues from the use of personal care products such as soaps, shampoos, perfumes, and colognes can desorb from an individual for hours after the use of such products. Limonene has been identified as one of the most abundant compounds in breath samples (Sanchez and Sacks, 2006) and from human bodies in an enclosed environment (Mochalski et al., 2014). Presumably, its sources are diet (flavoring agents) and scented personal care products (Corsi et al., 2007; Robbins, 2002; Singer et al., 2006). An exhaustive description of exogenous, reactive chemicals emitted by human occupants is beyond the scope of the present review. The salient point is that the human body can be a source of reactive chemicals that it does not generate endogenously.

Occupant-influenced chemical transformations

Ozone and humans

Early hints of ozone's reaction with skin surface lipids came from studies conducted by Liu et al. (1994) designed to evaluate the indoor use of passive ozone monitors on human subjects. As part of this effort, the investigators conducted chamber studies in which sampling lines from real-time UV ozone analyzers collected air adjacent to subjects' eyeglass frames. Measurements made at the eyeglass location were approximately 3% lower than in the core of the chamber. The authors concluded that this may be due to instrument error, ozone removal on subject surfaces, or dilution from subject's breath. They also conducted an experiment with a single subject in which the inlet of the sampling line was placed at different locations around the body while the ozone level in the chamber was maintained at 81 ppb. Ozone levels measured on the eyeglass frame averaged 79 ppb; on the shoulder, 69 ppb; and on the chest, 50 ppb. Rotating the sample inlet influenced the measurements, with the level on the shoulder dropping to 60 ppb and the level on the chest increasing to 59 ppb. In a related series of studies, the investigators attached passive samples to a subject's shirt or to a polystyrene backing plate on the shirt. Measured ozone levels were 19 ppb lower (mean difference) for samplers attached to the shirt compared to samplers attached to the backing plate.

Bakó-Biró et al. (2005) measured the surface-removal rate for ozone in a 108 m^3 low-polluting office at the Technical University of Denmark (DTU) during unoccupied and occupied (six female subjects) conditions. These measurements were repeated five times with different groups of subjects and were conducted at two different air exchange rates (1 and 3 h^{-1}). Based on a total of twenty experiments, the average ozone surface-removal rate constant was 1.4 h^{-1} larger when the room was occupied vs. unoccupied. From this increase, we can estimate a deposition velocity, v_d, to the surfaces of the occupants [incremental increase in rate constant for ozone removal × volume of the system (108 m^3) divided by the summed surface area of the occupants (6 × 1.7 m^2)]. The resulting value for v_d is 0.41 cm/s, which is consistent with values measured in later studies (Table 4). As described in Bakó-Biró's PhD thesis (2004), 6-MHO was detected in the air of the occupied office but not the unoccupied office (1.0 $\mu g/m^3$ at an air exchange rate of 1 h^{-1}). At the time of the study, the source of the 6-MHO was not known. We now realize that it was derived from ozone reacting with squalene present on the surfaces of the occupants.

The next study providing direct information on ozone/occupant reactions was conducted in a simulated section of a Boeing 767 at DTU in the presence or absence of 16 young female subjects (Tamas et al., 2006; Weschler et al., 2007). The experiments were duplicated with two groups of subjects; each group was exposed to four conditions: low ozone, low air exchange (4.4 h^{-1}); high ozone, low air exchange; low ozone, high air exchange (8.8 h^{-1}); and high ozone, high air exchange. Proton-transfer-reaction mass spectrometry (PTR-MS) was used to monitor organic compounds in the cabin air during the simulated flights. On the morning of a day in which ozone was scheduled to be used in an experiment, the ozone generators were turned on in a small pre-chamber through which outdoor air flowed on its way to the cabin. The ozone generators were operated until steady-state ozone levels were achieved in both the pre-chamber and the cabin itself; they were then turned off. Immediately after the passengers and crew entered the aircraft at 13:00, the ozone generators were turned back on. Figure 2 shows a typical set of ozone traces from such an experiment. Although the ozone concentration in the pre-chamber is the same in the morning and in the afternoon (~220 ppb), the ozone concentration in the simulated cabin is lower in the afternoon (~80 ppb) than in the morning (~130 ppb). The only difference between the cabin conditions in the morning and afternoon was occupancy by 16 human subjects. At the lower air exchange rate, the average rate constant for ozone removal was 6.2 h^{-1} larger when the cabin was occupied compared to unoccupied; at the higher air exchange, the average rate constant was 7.4 h^{-1} larger when the cabin was occupied compared to unoccupied (Tamas et al., 2006). Based on these increases in the rate constant for ozone removal, the average deposition velocities to the surface of an occupant in these experiments were 0.20 cm/s at the lower air exchange rate and 0.23 cm/s at the higher air exchange rate (Table 4). Occupants were responsible for an average of 58% of the ozone removal in the occupied cabin. Only ~4% of this value was due to respiration; the remaining ~54% was due to ozone reactions on exposed skin, hair, and clothing (Tamas et al., 2006).

A number of gas-phase products indicative of ozone's reactions with constituents of skin oil were

Table 4 Summary from selected studies reporting measured deposition velocities and/or reaction probabilities for ozone and human occupants or ozone and clothing (clean or soiled with skin oil)

Material	Ref	Deposition velocity, cm/s	Reaction probability, [–]
Human occupants	Bakó-Biró et al. (2005)	0.41	
Human occupants	Tamas et al. (2006)	0.20, 0.23	
Human occupants	Wisthaler and Weschler (2010)	0.4 to 0.5	
Human occupants	Fadeyi et al. (2013)	0.40 to 0.62	
Human occupants	Fischer et al. (2013)	0.46	
Human hair, 1st 5 min of exposure to O_3	Pandrangi and Morrison (2008)	~0.19 to 0.31[a]	0.5×10^{-4} to 4×10^{-4}
Human hair, 23rd hour of exposure to O_3	Pandrangi and Morrison (2008)	–	0.1×10^{-4}
Soiled T-shirts	Tamas et al. (2006)	0.19, 0.27	
Laundered cotton	Coleman et al. (2008)	0.30	0.8×10^{-4}
Soiled cotton	Coleman et al. (2008)	0.41	2.2×10^{-4}
Laundered wool	Coleman et al. (2008)	0.10	0.15×10^{-4}
Soiled wool	Coleman et al. (2008)	0.37	2.1×10^{-4}
Laundered polyester	Coleman et al. (2008)	0.11	0.16×10^{-4}
Soiled polyester	Coleman et al. (2008)	0.46	2.7×10^{-4}
Laundered T-shirt	Rai et al. (2014)	0.13	
Soiled T-shirt	Rai et al. (2014)	0.15 to 0.29	
Squalene on glass	Wang and Waring (2014)	0.15 to 0.27; 0.2 mean	

[a]Based on typical air movement adjacent to the human surface. The deposition velocity is very sensitive to this parameter.

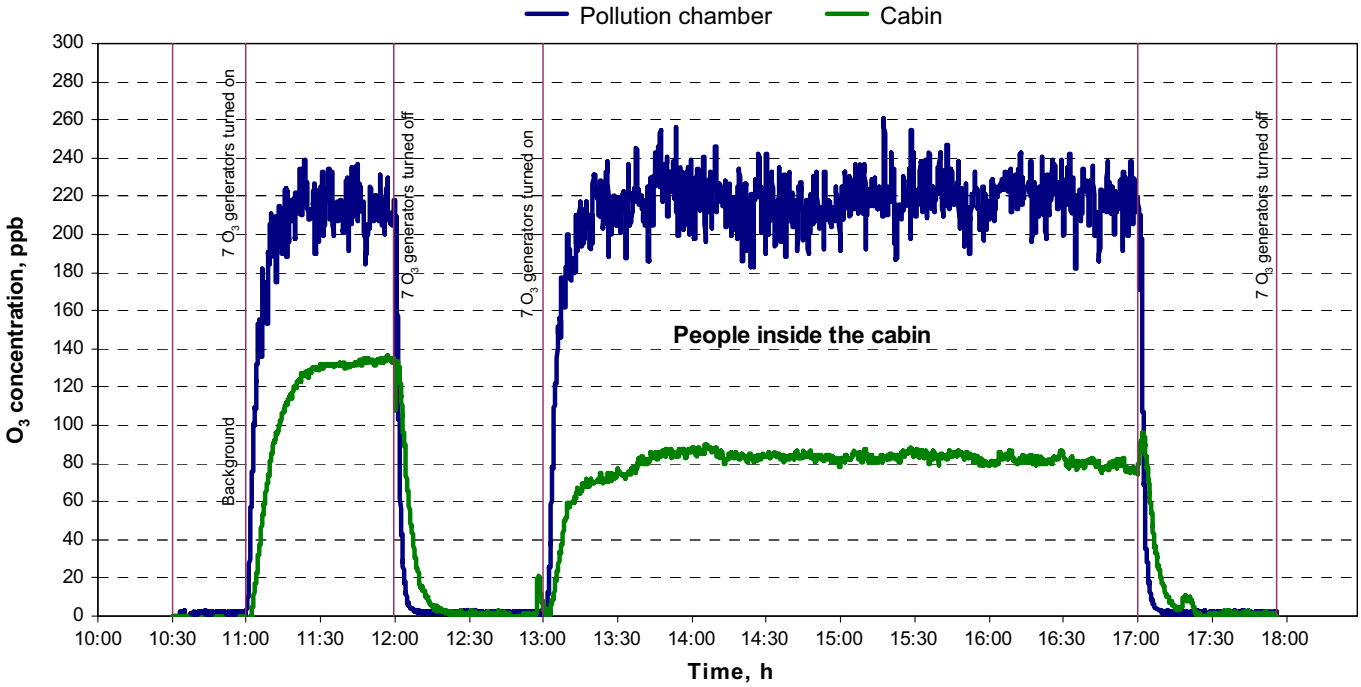

Fig. 2 Ozone levels in the pre-chamber (pollution chamber, upper trace) and simulated aircraft cabin (lower trace) on the day of an ozone experiment. During this example, the air exchange rate was 8.8 h^{-1}

identified in these experiments (Weschler et al., 2007). Those produced with the highest yields were acetone (~10%), nonanal (3–5%), decanal (2–4%), 6-MHO (2–4%), and 4-OPA (2–3%). The acetone emission rate due to ozone/occupant reactions (0.39 mg/h per person) was comparable to its breath emission rate. The continuous PTR-MS measurements indicated that, as anticipated, primary gas-phase products such as 6-MHO reached steady-state concentrations faster than secondary products such as 4-OPA.

Following the experiments in the simulated aircraft cabin, a similar study was conducted at DTU in a simulated 30 m^3 office ventilated at 1 h^{-1} (Wisthaler and Weschler, 2010). Once again, a PTR-MS was used to continuously monitor organic compounds in the air. Two scenarios were investigated. In the first, a steady-state ozone concentration was established in the room before two occupants entered. In the second, two subjects were in the office before ozone was introduced. For scenario 1, Figure 3 (top) shows the levels of ozone, 6-MHO, and 4-OPA from before occupancy until 4.5 h after the occupants entered the room. Prior to occupancy, the steady-state ozone level was 33 ppb and the levels of 6-MHO and 4-OPA were less than 0.2 ppb. As soon as two males entered the office, the level of ozone started to decrease while the level of 6-MHO started to increase. The level of 4-OPA also increased, but not as fast as that of 6-MHO. By 13:00, the 6-MHO had reached a steady-state level of 2.3 ppb, while the level of 4-OPA was still increasing. At 14:30, the 4-OPA level had reached 2.0 ppb, and the ozone level has decreased to 17 ppb, half its initial value.

Figure 3b (bottom) shows the results for scenario 2. Prior to occupancy, the levels of ozone, 6-MHO, and 4-OPA were all low. At 10:00, two males entered the office and the level of 6-MHO increased slightly (to ~0.2 ppb). At 12:00, the ozone generators were turned on. The levels of ozone and 6-MHO did not start to measurably increase until 12:30, while the level of 4-OPA started to increase at 12:45. By 13:30, the ozone level had reached 14 ppb, 6-MHO had reached 1.8 ppb, and 4-OPA had reached 0.7 ppb. At this point, the occupants left. Immediately the ozone level started to increase while that of 6-MHO started to decrease. At the final set of measurements (14:00), the ozone level had reached 21 ppb, 6-MHO had decreased to 1.0 ppb, and 4-OPA had increased to 0.85 ppb. The lag in 4-OPA's response reflects the fact that it is a secondary product.

In these scenarios, the two occupants removed ozone with rate constants between 1.7 and 2.0 h^{-1}, corresponding to deposition velocities between 0.4 and 0.5 cm/s (Table 4). The authors estimate that in a 30 m^3 room at typical ventilation rates, a single human occupant contributes 10–25% to overall O_3 removal.

To better understand these results, experiments were performed in which a small enclosure was placed on the surface of the forehead, cheek, or forearm of one of the investigators, with air from the reactor flowing directly into the PTR-MS (Wisthaler and Weschler, 2010). The air that flowed through the enclosure was

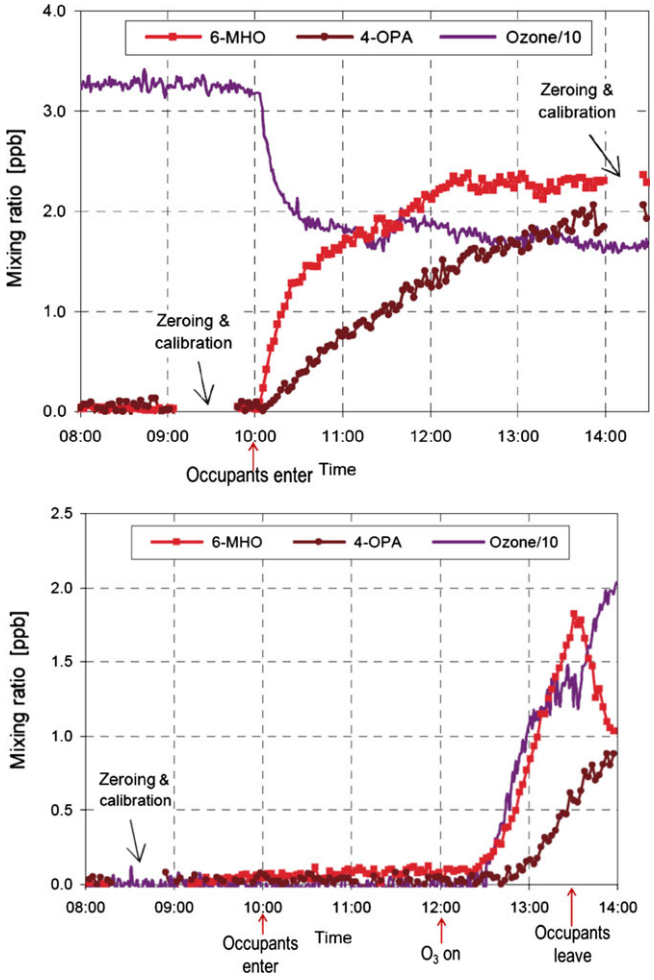

Fig. 3 Levels of ozone, 6-MHO, and 4-OPA in a simulated office during occupied and unoccupied periods. Scenario 1 (top) – steady-state level of ozone established; occupants enter at 10:00; and monitoring ends at 14:30. Scenario 2 (bottom) – monitoring begins at 8:00; occupants enter at 10:00; ozone generators turned on at 12:00; occupants leave at 13:30; and monitoring ends at 14:00. Adapted from Figure 3 of Wisthaler and Weschler (2010)

either clean air or air containing ozone. When the air contained ozone, a number of carbonyls were detected, the more abundant ones being acetone, 6-MHO, decanal, geranyl acetone, and 4-OPA. Using the same ozone levels, the amounts of products were greatest when the enclosure was on the forehead, consistent with higher levels of skin lipids on the forehead than on the cheek or forearm. Significantly, in the absence of ozone, carbonyl emissions from human skin were negligible. This suggests that carbonyl emissions from skin are not a consequence of endogenous processes, but instead result from oxidation processes on the surface of skin.

Using a tubular reactor, Pandrangi and Morrison (2008) investigated the reactions of ozone with human hair that had been either washed with shampoo (and sometimes conditioner) the day of the experiment or unwashed for 2–3 days before. The reactions were monitored for 24 h. During the initial 5 min, the reaction probabilities were in the range of $(0.5–4) \times 10^{-4}$; these values decreased to $<0.4 \times 10^{-5}$ during the 23rd hour (Table 4). Washed hair treated with a conditioner had roughly twice the integrated ozone uptake as washed hair that was not treated. Human hair taken close to the scalp had higher reaction probabilities than that taken further away, consistent with more skin oil on hair closer to the hair follicle. The most abundant carbonyls identified were 6-MHO, geranyl acetone, nonanal, and decanal, and their yields tended to be higher for unwashed vs. washed hair. Based on the measured reaction probabilities coupled with reported rates for sebum emission, the authors concluded that that ozone flux to exposed hair and bare skin is close to transport limited. They proceeded to develop a useful figure for estimating ozone's deposition velocity to the surface of a human as a function of the reaction probability over a range of air movement adjacent to the human surface. For reaction probabilities from $(1–4) \times 10^{-4}$, the deposition velocity to the human surface ranges from 0.18 to 0.83 cm/s and is fairly sensitive to the near surface air movement. Based on these measurements, the authors estimate that in a 30 m^3 room ventilated at 0.3 h^{-1}, a single occupant accounts for roughly 10% of the ozone removal.

Rim et al. (2009) used computational fluid dynamics (CFD) to model the reaction between ozone and the human envelope, focusing on the concentrations of ozone and its reaction products in the breathing zone. They found that, as a consequence of the reaction of ozone with the human surface, the concentration of ozone in the breathing zone was 59% to 75% that in air located one meter from the body at air exchange rates less than 3 h^{-1}. At the same time, the concentrations of ozone reaction products were 120% to 250% higher in the breathing zone than in bulk air. At higher air exchange rates, the difference between breathing zone and bulk air concentrations depended on the nature of the air distribution system, with differences being larger when the supply air came from a ceiling diffuser compared to a floor location. The authors validated their CFD model using heated cylinders as surrogates for humans.

Following up on studies made in simulated aircraft cabins, the U.S. Federal Aviation Administration (FAA) funded simultaneous measurements of ozone and selected volatile organic compounds in the cabins of 38 transcontinental U.S. flights and 14 transoceanic flights (Weisel et al., 2013). At cruising altitudes, ozone was measured at 1 min intervals while a single sample of VOCs was collected on a sorbent tube. An ozone scrubber was used upstream of the sorbent tube to avoid ozone reacting with 6-MHO collected on the sorbent. The analytical methods were not capable of detecting 4-OPA. The average and peak ozone values

varied with aircraft type (Boeing 737s, 747s, 757s and 777s) and were highest on 747s with median values of 50 ppb for average and 125 ppb for peak. Considering all flights, median levels of 6-MHO, nonanal, and decanal were 0.73, 1.9, and 1.6 ppb, respectively; peak values were 13, 14, and 12 ppb. A linear regression model that included ozone, percent occupancy, and aircraft type explained 25% of the variability in 6-MHO levels, with both ozone and percent occupancy significant at the 0.05 level. Analogous linear regression models for the C6-C10 aldehydes explained 18–22% of their variability, with ozone significant at the 0.05 level for octanal, nonanal, and decanal.

Wang et al. (2014a) have measured levels of various VOCs on 14 domestic flights in China. Although an ozone scrubber was not used upstream of the sorbent sampler, 6-MHO was identified on all flights with a mean concentration of 8.9 $\mu g/m^3$ (1.7 ppb) and a peak value of 16 $\mu g/m^3$ (3.1 ppb). Decanal was the most abundant saturated aldehyde reported, with a mean concentration of 26 $\mu g/m^3$ (4.1 ppb) and a peak value of 36 $\mu g/m^3$ (5.6 ppb). Interestingly, nonanal levels tended to be lower than those of decanal, with a mean concentration of 19 $\mu g/m^3$ (3.3 ppb) and a peak value of 24 $\mu g/m^3$ (4.1 ppb). In a follow-up paper, Wang et al. (2014b) used positive matrix factorization to identify the major sources of the different VOCs on these flights. They found that the levels of 6-MHO, decanal, and nonanal covaried ('Factor 1'), suggesting that reactions between ozone and constituents of skin surface lipids were the major source of these species on the fourteen flights.

These studies (Wang et al., 2014a,b; Weisel et al., 2013) confirmed a number of observations made in the simulated aircraft cabin at DTU (Tamas et al., 2006; Weschler et al., 2007; Wisthaler et al., 2005). However, on actual aircraft flights analytical limitations and uncontrolled variables make it difficult to probe ozone/occupant interactions as thoroughly as can be achieved in a simulated setting.

Over a 2-week period in a classroom in semi-rural southwestern Sweden, Fischer et al. (2013) monitored ozone and carbon dioxide continuously and VOCs six times a day. Measurements were made during occupied (24 pupils and a teacher) and unoccupied periods of routine school days with no deliberate interventions. This study in an actual classroom-confirmed earlier findings in various simulated settings. Ozone and carbon dioxide levels were strongly anticorrelated. When students left the classroom for lunch, carbon dioxide levels decreased and ozone levels increased. When they returned from lunch, carbon dioxide levels increased and ozone levels decreased. Similar changes occurred at the beginning and end of a class day, as well as at the beginning and end of break periods. Based on measurements made during 26 different occupied periods, the authors calculated an average value of 0.46 cm/s for the deposition velocity of ozone to the surface of a pupil (Table 4). Using Tenax for sampling and thermal desorption/GC/MS for analysis, both 6-MHO and 4-OPA were detected in the air of the occupied classroom, but quantification of 6-MHO was hampered due to possible reaction with ozone during collection on Tenax. The level of 4-OPA increased through a typical school day, reaching a value of approximately 0.7 ppb. The time at which its level in classroom air started to decrease lagged behind the time when the students left for the day. By the following morning, its level had decayed to background levels (~0.2 ppb). The amount of ozone removed by the occupants was 2.6 times larger than the amount removed by inanimate surfaces in the classroom, illustrating the large impact that humans have on ozone levels in a densely occupied room.

A roofless soccer stadium is not a traditional indoor environment, but it can be densely occupied, and the air within a stadium has levels of chemical constituents that can be quite different from those in the surrounding outdoor environment. Veres et al. (2013) have made continuous measurements of ozone, carbon dioxide, and VOCs (using PTR-MS) at the Coface Arena in Mainz, Germany. The measurements, conducted 12 m above ground level in one of the entryways, began a few hours before an evening game that started at 20:30 and was attended by 31, 000 fans. A striking figure in the paper displays the levels of carbon dioxide, ozone, 6-MHO, and decanal from 18:45 until 24:00. As the fans start to enter the stadium, the levels of CO_2, 6-MHO, and decanal increase with approximately the same slope, while the level of ozone starts to fall. By 20:30, the CO_2 level has increased by 80 ppm, 6-MHO has reached 0.8 ppb, decanal has reached 0.3 ppb, and the ozone level has decreased by 10 ppb. As soon as the fans begin to exit at ~22:30, the levels of CO_2, 6-MHO, and decanal begin to decrease, and the level of ozone begins to increase. CO_2 and 6-MHO are down to background levels by 23:30, but the decanal level is still higher than it was before the game. Presumably, decanal, with its lower vapor pressure, sorbs to surfaces within the stadium to a greater extent than 6-MHO and CO_2.

When occupancy alters ozone levels, it also alters the concentration of products derived from reactions of ozone with other indoor pollutants. An example comes from a study by Fadeyi et al. (2013) that examined how secondary organic aerosol (SOA) derived from the ozone/limonene reaction was influenced by occupants in a 240 m^3 simulated classroom at the National University of Singapore. The simulated classroom has an air-handling system that recirculates a fraction of the air; in these experiments, the recirculation rate was 7 h^{-1}, and the exchange rate with outdoor air was 1 h^{-1}. Two scenarios were investigated. The first scenario was without occupants; starting in the morning,

ozone and limonene were emitted at rates that resulted in steady-state levels of approximately 60 and 35 ppb, respectively; after 4 h, the ozone generator was turned off; 45 min later, the limonene emission was shut down and the experiment ended. The second scenario was identical to the first scenario in all respects, but occupancy; 18–20 subjects entered the chamber 45 min after ozone and limonene emissions had begun. During the experiments, ozone levels were measured continuously with a UV photometric analyzer, and size-fractioned airborne particles were measured continuously with a fast mobility particle sizer (FMPS). A total of eight experiments were performed, two with an empty classroom and six with occupants. Experiments were conducted with either new or used filters in the air-handling unit, but this had little influence on the results. As expected, ozone levels in the classroom were substantially lower when it was occupied vs. when it was unoccupied (at steady state, 35–40 ppb occupied vs. ~60 ppb unoccupied). Conversely, the level of SOA was lower when the classroom was occupied vs. when it was unoccupied (at steady state, ~3 $\mu g/m^3$ occupied vs. 5.4–6.3 $\mu g/m^3$ unoccupied). Presumably, most of the SOA was derived from the ozone/limonene reaction. The contribution from the ozone/squalene reaction to SOA under the conditions of the experiment is anticipated to be relatively small (Rai et al., 2013; Wang and Waring, 2014). This study has implications regarding the impact of occupancy on other products derived from ozone-initiated chemistry indoors.

Ozone, clothing, and skin oils

Park and Obendorf (1994) reported that fabric soiled with squalene and exposed to room air in the dark yellowed as a consequence of squalene oxidation and that products included aldehydes and carbonyls. Presumably, the major oxidant in these studies was ozone.

The initial studies of ozone chemistry in the simulated B-767 at DTU were conducted using seventeen T-shirts, worn overnight by male graduate students, as surrogates for human passengers (Tamas et al., 2006; Wisthaler et al., 2005). On successive days, four conditions were examined: cabin without T-shirts or ozone, cabin with ozone but no T-shirts, cabin with T-shirts but no ozone, and cabin with T-shirts and ozone. A PTR-MS was used to continuously monitor the organic compounds in the cabin air over this 4-day period. For otherwise identical conditions, the ozone concentration reached a level of 75 ppb when soiled T-shirts were present compared to 110 ppb with no soiled T-shirts. At the lower air exchange rate (3 h^{-1}), the first-order ozone removal rate constant was 5.1 h^{-1} larger with soiled T-shirts than without. At the higher air exchange rate (6.5 h^{-1}), the ozone removal rate constant was 3.6 h^{-1} larger with soiled T-shirts than without (Tamas et al., 2006). The deposition velocities for the soiled T-shirts were 0.27 and 0.19 cm/s for the two conditions. These values are close to those measured for human subjects in the same cabin (Table 4). Ozone and soiled T-shirts together raised the concentration of detected VOCs to 100 ppb compared to 80 ppb with ozone and no soiled T-shirts (Wisthaler et al., 2005). More than two-thirds of the additional 30 ppb was due to an increase in squalene oxidation products, specifically acetone, 6-MHO, and 4-OPA. Furthermore, the net concentration of organic nitrates, also measured by PTR-MS, was much higher when ozone and soiled T-shirts were in the cabin (0.93 ppb) compared to only ozone (0.46 ppb) or only soiled T-shirts (0.03 ppb).

Coleman et al. (2008) included clothing soiled with skin oils and freshly laundered clothing in a study of ozone reactions with materials commonly found in aircraft cabins. The fabrics examined were cotton, wool, and polyester. To soil them, a 25-year-old male wore them next to his skin while he slept (~8 h). The authors used a 10.5-l stainless steel chamber to investigate both ozone consumption and byproduct formation. The 3 h average ozone deposition velocities for clean and skin-oil-soiled cotton were 0.30 and 0.41 cm/s, respectively; for clean and soiled wool, the values were 0.10 and 0.37; for clean and soiled polyester, 0.11 and 0.46 cm/s (Table 4). In other words, soiling with skin oils increased the deposition velocities and decreased the extent to which deposition velocities to the fabrics differed from one another. The deposition velocities to the soiled fabrics were more than 80% of the transport-limited values measured by coating the fabrics with potassium iodide (KI). The reaction probability with ozone was as low as 1.5×10^{-5} for freshly laundered clothes and as high as 2.7×10^{-4} for clean clothes. In the absence of ozone, the organic emissions from the fabrics were negligible; in the presence of ozone, the emissions from the soiled fabrics were two to three times larger than those from the clean fabrics. Acetone followed by 6-MHO dominated the emissions from soiled clothes, consistent with ozone's reaction with squalene. The emission of decanal was also elevated for the soiled fabrics compared to the clean fabrics, consistent with ozone's reactions with unsaturated fatty acids found in skin oil. Within a fully occupied B-737 cabin, the authors estimated that the clothing worn by the passengers and soiled with their skin oil would contribute more than 40% to ozone removal.

Rai et al. (2014) investigated the consumption of ozone and generation of VOCs when ozone was introduced into a 5.2 m^3 chamber containing a skin-oil-soiled T-shirt and compared the results to when the chamber was empty or contained a freshly laundered T-shirt. In 12 experiments, they measured deposition velocities of ozone to the soiled T-shirt that ranged between 0.15 and 0.29 cm/s, with an average value of 0.22 cm/s (Table 4). In contrast, the deposition

velocity to the freshly laundered T-shirt was 0.12 cm/s. The deposition velocity measured in an experiment conducted at 12% RH (0.23 cm/s) was similar to that measured in an experiment conducted at 44% RH (0.25 cm/s). An increase in the air exchange rate from 0.5 to 2.7 h^{-1} slightly increased the deposition velocity (0.23 vs. 0.26 cm/s). This impact of air exchange was opposite to that reported by Tamas et al. (2006), but in both cases, the differences may be within the error of the experiments. The researchers identified acetone and 4-OPA as emissions from the soiled T-shirt that were not detected for the laundered T-shirt. They detected neither 6-MHO nor geranyl acetone, presumably because these products would have been oxidized by ozone during the sampling procedure. The average combined molar yield for acetone and 6-MHO, based on ozone consumption, was 0.17. As anticipated, the VOC emissions were higher at higher ozone concentrations. Two experiments were conducted at 22 ppb ozone and demonstrated that, even at this relatively low level, there were significant ozone-initiated VOC emissions.

In the same experiments where they examined VOC emissions from ozone's reaction with a skin-oil-soiled T-shirt, Rai et al. (2013) monitored the generation of submicron particles using an SMPS (detecting particles from 9.7 to 420 nm diameter). The difference in number concentration between chamber inlet and exhaust air was significantly higher when a T-shirt soiled with skin oil was in the chamber than when no T-shirt or a laundered T-shirt was present. However, these differences were modest. At the higher air exchange rate (2.7 h^{-1}), the difference was <50 particles/cm^3; at 0.5 h^{-1}, the difference at the end of the experiment ranged from 500 to 2000 particles/cm^3. The differences were higher at higher ozone levels and when the T-shirts had been worn for a longer period of time. In the 0.5 h^{-1} experiments, when the difference was at its maximum value, the geometric mean diameter was between 31 and 36 nm. At an ozone level of 20 ppb and for a T-shirt worn 6 h, the steady-state difference was ~500 particles/cm^3. The generated particles appeared to be hygroscopic given their increase in size with increasing relative humidity. Although direct comparisons are not possible, the generation of submicron particles measured in these soiled T-shirt experiments is consistent with the generation of SOA measured by Wang and Waring (2014) in the reaction of ozone with squalene on a glass surface (see 'Ozone/squalene reaction').

Ozone, dust, and skin oils

Given that settled dust in occupied settings contains skin flakes and their associated skin oils, we expect such dust to react with and contribute to ozone's removal indoors. The following is an update of an analysis presented in the supporting information of Weschler et al. (2011).

Assume that the reaction probability for O_3 with squalene present in dust, γ', scales linearly with the mass fraction of squalene in the dust (Moise and Rudich, 2002). If the mass fraction of squalene in dust is 36 μg/g (median reported for bedroom dust in Weschler et al., 2011), and we use the reaction probability of 4.5×10^{-4} measured by Wells et al. (2008) for O_3 with pure squalene, then $\gamma' = (3.6 \times 10^{-5})(4.5 \times 10^{-4}) = 1.6 \times 10^{-8}$. Vibenholt et al. (2014) examined reaction of ozone with floor dusts from offices, schools, and homes using a stainless steel FLEC. They measured the rate constant for ozone removal per gram of dust and from this, using the specific surface areas of the dust samples, calculated deposition velocities from 2.7×10^{-4} to 5.8×10^{-4} cm/s. These values correspond to area-averaged reaction of probabilities from 3.0×10^{-8} to 6.4×10^{-8}. (For the relatively high mass-transfer conditions in the FLEC, the reaction probability can be approximated from the deposition velocity using equation 18 in Cano-Ruiz et al. (1993)). These area-averaged reaction probabilities for typical settled dust samples from offices, schools, and homes are only two to four times larger than the value of 1.6×10^{-8} estimated based on the presence of squalene in dust. Furthermore, this analysis has not accounted for the unsaturated carbon bonds present in the fatty acids, wax esters, and glycerols that co-occur with squalene in skin surface lipids. These are present at net levels comparable to those of squalene (Pandrangi and Morrison, 2008) and could possibly double the reaction probability attributed to skin surface lipids present in dust. In summary, it appears that skin flakes shed by occupants contribute in a meaningful way to indoor dust's ozone reactivity.

Although skin flakes are anticipated to meaningfully contribute to the ozone reactivity of settled dust, settled dust makes only a small contribution to ozone's removal by indoor surfaces in typical homes and offices. Ozone's removal by skin oils in settled dust is estimated to be similar to that resulting from gas-phase reactions with commonly occurring indoor terpenes (Weschler et al., 2011).

In the experiments reported in Vibenholt et al. (2014), both unexposed and exposed dust samples were analyzed for organic constituents. Three isomers of octadecenoic acid are present in skin oil and, together, account for more than 3% of skin surface lipids by weight. Significantly, octadecenoic acid was found in the dust samples, and its level was reduced on exposure to ozone. On the other hand, the level of decanal in the dust increased by a factor of three to nine following exposure of the dust to ozone. As previously noted, decanal is an anticipated product from the reaction of ozone with some of the more abundant unsaturated

fatty acids in skin oil (Table 1). The levels of octanal and nonanal were also multiple times larger in the ozone-exposed dust. Both of these aldehydes are oxidation products of unsaturated fatty acids found in skin oil (Table 1), although other precursors are also expected in settled dust. Interestingly, in a different study (Molhave et al., 2005), exposure to a combination of ozone and house dust was found to cause significantly more peak expiratory flow and discomfort symptoms than exposure to either ozone alone or dust alone.

Many of the products anticipated from reactions between ozone and constituents of skin oils have low volatility and would remain on dust as opposed to entering the gas-phase. Although Vibenholt et al. have examined dust for a subset of such constituents, this area warrants further investigation using methods that would permit identification of a wider variety of oxidized compounds.

Indoor/outdoor ratio for ozone: reassessment

Earlier papers (e.g., Weschler et al., 1989; Weschler, 2000) have stated that, under steady-state conditions, the ratio of the indoor to the outdoor concentration for ozone (I/O) can be estimated by a simple expression:

$$\mathrm{I/O} = \frac{\lambda}{\lambda + k_\mathrm{d}}, \tag{1}$$

where is λ the rate at which indoor air is replaced with outdoor air, and k_d is the first-order rate constant for ozone's removal by indoor surfaces. This expression should be modified (Stephens et al., 2012) by a term that accounts for the efficiency with which ozone penetrates a building's envelope (P):

$$\mathrm{I/O} = \frac{P \times \lambda}{\lambda + k_\mathrm{d}}. \tag{2}$$

Stephens et al. have measured values for P ranging from 0.62 to 1.02 in a test house and seven single-family residences. In terms of the flow rate of outdoor air into the space (Q), equation 2 can be rewritten as:

$$\mathrm{I/O} = \frac{P \times Q}{Q + (v_\mathrm{d} \times A_\mathrm{room})}, \tag{3}$$

where v_d is ozone's average deposition velocity to room surfaces, and A_room is the net area of all exposed surfaces in a room. The ratio of room surfaces to room volume (V) relates k_d and v_d:

$$k_\mathrm{d} = v_\mathrm{d} \times A_\mathrm{room}/V. \tag{4}$$

However, we now know that in occupied settings, humans are a major sink for ozone and should be accounted for when calculating I/O. This can be accomplished using the following expression for steady-state conditions:

$$\mathrm{I/O} = \frac{P \times \lambda}{\lambda + k_\mathrm{d} + k_\mathrm{h}}, \tag{5}$$

where k_h is the first-order rate constant for ozone's removal by human surfaces. In terms of Q, this can be stated as:

$$\mathrm{I/O} = \frac{P \times Q}{Q + (v_\mathrm{d} \times A_\mathrm{room}) + (v_\mathrm{h} \times A_\mathrm{human})}, \tag{6}$$

where v_h is ozone's average deposition velocity to a human surface, and A_human is the net area of all occupants in a room. The latter is given by:

$$A_\mathrm{human} = (\mathrm{BSA/occupant}) \times (\#\ \mathrm{occupants}), \tag{7}$$

where BSA is the body surface area, which can be readily calculated using a number of different expressions (Verbraecken et al., 2006). For adults, BSA is typically in the range of 1.7–2.0 m^2. The ratio of the net body surface area of all occupants to room volume relates k_h and v_h:

$$k_\mathrm{h} = v_\mathrm{h} \times A_\mathrm{human}/V. \tag{8}$$

For occupied settings, estimating the indoor/outdoor ratio for ozone without accounting for removal by the occupants can lead to substantial errors, with the error growing larger as the air exchange rate grows smaller.

Other impacts of occupancy on chemistry

Oxidative capacity of indoor air

The oxidative capacity of indoor air is defined by the sum total of all oxidants present in the air. In addition to ozone, other major indoor oxidants include hydroxyl radicals (OH) and nitrate radicals (NO_3). Ozone/skin lipid chemistry produces both primary (e.g., 6-MHO, geranyl acetone) and secondary (e.g., 4-MOD) species that are expected to impact the indoor levels of these free radical oxidants through gas-phase interactions (Weschler and Wisthaler, 2010; Weschler, 2011). The

levels of OH and NO_3 are not meaningfully affected by reactions with squalene and unsaturated fatty acids on human surfaces or surfaces soiled with skin flakes or skin oils, since surface reactions are slow and of negligible consequence compared with the relevant gas-phase reactions (Weschler and Shields, 1996). The reaction of ozone with 6-MHO produces hydroxyl radicals (OH) with a reported yield of 75% (Smith et al., 1996). The second-order rate constant for the ozone/6-MHO reaction (9.6×10^{-6} ppb^{-1} s^{-1} at 25°C) is almost twice as large as that for ozone's reaction with limonene and thirty times faster than the constant for ozone's reaction with isoprene (Table 3). At indoor concentrations of 1 ppb for 6-MHO and 20 ppb for ozone, OH will be produced at 1.4×10^{-4} ppb s^{-1}. Only the ozone reaction with limonene, at typical indoor levels, produces OH at a faster rate. In occupied indoor settings where there are no major sources of terpenoids, the ozone/6-MHO reaction may be one of the major sources of OH in the air. On the other hand, 6-MHO consumes OH rapidly (Table 3). At a concentration of one ppb, it removes OH with a first-order rate constant (4.0 s^{-1}) that is comparable to any other indoor pollutant at typical indoor levels.

6-MHO also reacts rapidly with nitrate radicals (Table 3). At typical indoor levels, only limonene and phenol remove NO_3 at a faster rate than 6-MHO. The major indoor pathway to nitrate radical formation is via the reaction of ozone with nitrogen dioxide. If humans are present in an indoor setting, ozone levels are lower than they would otherwise be, resulting in lower NO_3 levels. At the same time, ozone/squalene reactions will generate 6-MHO, which, in turn, will rapidly react with NO_3. When a room is occupied, 6-MHO may function as a governor (i.e., limiter) on the indoor concentrations of both NO_3 and OH.

Geranyl acetone is another product of the ozone/squalene reaction that may affect the oxidative capacity of indoor air. Although rate constants have not been measured, geranyl acetone is expected to react rapidly with OH and NO_3 as it is structurally similar to 6-MHO, but contains two unsaturated carbon-carbon bonds rather than one. Furthermore, the reaction of geranyl acetone with OH and NO_3 produces additional 6-MHO. Hence, geranyl acetone is expected to further reduce the concentrations of OH and NO_3 in indoor settings. 4-OPA reacts with both OH and NO_3 radicals, but with smaller second-order rate constants than those for 6-MHO. As a consequence, 4-OPA is only a moderate sink for OH and a negligible sink for NO_3. Although isoprene reacts at only a moderate rate with ozone and NO_3, it reacts with OH almost as fast as 6-MHO. Hence, isoprene in exhaled breath may impact OH levels in an occupied room.

The extent to which occupants alter the oxidative capacity of indoor air depends on the concentration of other compounds that are simultaneously present, especially terpenoids, which can be sources of OH through reaction with ozone and sinks for both OH and NO_3. Under typical conditions, occupancy is anticipated to decrease the net level of oxidants in a room. A great deal could be learned from real-time measurements of OH, NO_3, Criegee intermediates, and other short-lived, highly reactive species in indoor environments where the only difference is 'unoccupied' or 'occupied' (Gligorovski and Weschler, 2013).

Impact on SVOC levels

Numerous SVOCs with unsaturated carbon-carbon bonds are known to participate in indoor chemistry (e.g., terpene alcohols, sesquiterpenes, unsaturated fatty acids). The airborne concentrations of these unsaturated SVOCs can be altered by occupancy. Indeed, the rate at which occupants remove certain chemicals via inhalation, dust ingestion, and dermal absorption can compete with other indoor removal processes (Little et al., 2012). Zhang et al. (2014) have incorporated a human uptake and exposure model into an indoor chemical fate mass balance model. This integrated model has been used to probe how human intake and elimination of a chemical (e.g., biotransformation, renal excretion, fecal egestion, hand washing, bathing) impacts its fate indoors. Compared to the unoccupied condition, including a human occupant in an indoor setting reduces the concentrations of chemicals with low vapor pressures by as much as two orders of magnitude if one assumes that the chemical is only degraded in the gas-phase. Even if degradation of a chemical occurs in other indoor compartments, occupancy may reduce indoor concentrations of certain chemicals by up to 60%. Reducing the concentration of a reactive SVOC reduces product concentrations and, if the other reactant is not present in large excess, also reduces the rate at which the reaction occurs. This is an area that is potentially rich for further exploration.

SVOCs partition between the gas-phase and airborne particles (Weschler and Nazaroff, 2008). The ratio of the concentration of an SVOC in particles (C_p) to an SVOC in the gas-phase (C_g) is given by:

$$\frac{C_p}{C_g} = K_p \times [\mathrm{TSP}], \tag{9}$$

where K_p is the coefficient that describes partitioning between particles and the gas-phase, and [TSP] is the total concentration of airborne particles. In turn, K_p can be estimated from the octanol/air partition coefficient (K_{oa}):

$$K_p = \frac{f_{om\_TSP} \times K_{oa}}{\rho} \tag{10}$$

where f_{om_TSP} is the fraction of organic matter in the airborne particles, and ρ is the density of the airborne particles. Substituting for K_p in equation 9:

$$\frac{C_p}{C_g} = ((f_{om\_TSP} \times K_{oa})/\rho) \times [TSP]. \quad (11)$$

When the concentration of SOA in a room goes down as a consequence of occupancy, as occurred in the study by Fadeyi et al. (2013), f_{om_TSP} decreases and the level of TSP decreases. These changes act in the same direction, resulting in a smaller value for C_p/C_g. To get a sense of the potential impact of this effect, consider the results from the Fadeyi study where occupancy reduced the SOA level by 3 $\mu g/m^3$. Assume that [TSP] = 15 $\mu g/m^3$ and f_{om_TSP} = 0.4 when the classroom containing ozone and limonene was unoccupied vs. [TSP] = 12 $\mu g/m^3$ and f_{om_TSP} = 0.25 when it was occupied. For an SVOC with log K_{oa} = 10.5 (e.g., BDE 47 or PCB 180), the ratio of C_p/C_g would have been 0.19 when the classroom was unoccupied and 0.096 when the room was occupied. In other words, in this hypothetical example, occupancy reduced the ratio of particle-phase to gas-phase SVOC by a factor of two.

Conclusions

As measured in both simulated and actual settings, the impact of occupancy on ozone levels is remarkably large. This is a combination of primary reactions, on human surfaces, between ozone and constituents of skin lipids and secondary reactions, on both human surfaces and in the gas-phase, between ozone and primary products that retain a carbon-carbon double bond (e.g., 6-MHO, geranyl acetone, 4-MOD, 7-hydroxy-5-heptenoic acid). The evidence supporting a role for gas-phase chemistry includes the facts that i) the impact of occupants on ozone removal rates tends to be smaller at higher ventilation rates, which reduce the time available for gas-phase reactions and ii) ozone deposition velocities to human surfaces measured in various experiments (Table 4) tend to be close to transport-limited values. Ozone consumption via reaction with gas-phase primary products would help to explain such large values. Concentrations of secondary products within an occupied room increase more slowly than those of primary products. Hence, the longer the duration of an individual's interaction with ozone in an indoor environment, the greater the exposure to secondary products. Given their multiple oxygen-containing functional groups, secondary products may be more irritating than primary products.

Skin-oil composition changes with age (Haze et al., 2001; Nazzaro-Porro et al., 1979) as does the rate of desquamation. Studies with occupants over a range of ages from infants to elderly would be informative. It would also be useful to have information on the *rate* at which indoor environments change with occupancy, as well as how quickly clothing becomes soiled with skin oils. Some of the ozone scavenging that is measured when an occupant enters a room is due to exposed skin and hair and some is due to the occupant's clothing, but we do not know the relative contribution of each.

We know very little regarding the less volatile products derived from ozone/skin lipid chemistry that remain on the skin. We can predict ozone-derived products based on the Criegee mechanism, but for most of the less volatile products, these predictions still have to be verified by measurements. Similarly, we know little regarding the products of ozone/skin-oil chemistry that accumulate on exposed indoor surfaces or settled dust. It would be valuable to conduct studies of the impact of occupancy, both short term and long term, on the composition of surface chemicals. Such studies could address numerous questions: How do the chemicals on surfaces respond to a daily cycle of occupied/unoccupied? Are surfaces periodically 'recharged' by occupancy? How long must a room be occupied before changes in surface constituents are noticeable? State-ofthe-art techniques such as the "direct analysis in real time" (DART) ion source coupled with mass spectrometry might be used to probe changing surface composition.

There are numerous other research opportunities that address the role of the occupant in the chemistry of the human habitat. Although PTR-MS has been used in simulated indoor environments and at a soccer stadium, it has yet to be used to examine the manner in which VOCs change in response to occupancy in actual settings such as a classroom or office. As of now, the impact of humans on indoor levels of hydroxyl and nitrate radicals is largely speculative. Real-time measurements, using state-of-the-art analytical methods, under both occupied and unoccupied conditions are needed (e.g., laser-induced fluorescence (LIF) measurements of hydroxyl radicals (e.g., Gomez Alvarez et al., 2013); cavity ring-down spectroscopy measurements of nitrate radicals). Aerosol mass spectrometry (AMS) might be used to probe the manner in which the composition of airborne particles changes with occupancy. The potential measurements listed in this paragraph would be especially valuable if they could be performed in concert with one another under occupied and unoccupied conditions. In this way, connections among the various species could be better understood.

Over the past decade, our eyes have been opened to the role of the human occupant in indoor chemistry. We have read the early pages of what promises to be a long and interesting book – interesting, in part, because the subject is us. This unfolding story promises to inform strategies designed to protect our health, our technical devices, and our cultural artifacts.

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