

This is a repository copy of *Indoor Chemistry*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/129820/>

Version: Accepted Version

Article:

Carlaw, Nicola orcid.org/0000-0002-5290-4779 and Weschler, Charles J. (2018) Indoor Chemistry. *Environmental Science and Technology*. pp. 2419-2428. ISSN 1520-5851

<https://doi.org/10.1021/acs.est.7b06387>

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Introduction

The concentration of an indoor air pollutant is a function of numerous processes including indoor emissions, exchange with outdoors, deposition to indoor surfaces, removal by filtration and “indoor chemistry”. As commonly used today, “indoor chemistry” denotes the chemical and physical transformations that occur in indoor environments. These differ from those that control outdoor atmospheric chemistry for several reasons, including absence of direct sunlight and rain, less extreme temperature fluctuations, much larger surface-to-volume ratios (about three orders of magnitude), and much higher concentrations of organic compounds (roughly an order of magnitude). For instance, consider the fate of a pollutant common to both environments – ozone (O_3) – in a typical suburban residence, compared to outdoors, downwind of a major city, using conditions described in Carslaw¹. Outdoors there is a 97% chance the O_3 molecule will react with nitric oxide (NO), versus ~ 1% chance it will react with an unsaturated volatile organic compound (VOC), ~ 1% chance it will deposit to a surface, and ~ 1% chance it will be photolyzed. In contrast, for typical indoor conditions, the same molecule has a slightly more than 40% chance of reacting with NO, slightly less than 40% chance of surface deposition, a 20% chance of being removed through air exchange, and a 1% chance of reacting with unsaturated VOCs (ozone photolysis is usually negligible indoors).

There have been previous reviews and extended editorials on indoor air chemistry²⁻¹⁰. The present article will be a popular account with a focus on recent findings, in particular those that relate to reactive chemicals indoors. We define reactive chemicals as being those that drive indoor air chemistry or play an important role as reactants. Many different types of reactions occur indoors (e.g., oxidation, hydrolysis, acid/base, photolysis, decomposition, dehalogenation),

both in the gas phase and on surfaces. We will focus on oxidation, photolysis and hydrolysis, as well as the important role of human occupants.

Sources of reactive chemicals indoors

There are many sources of reactive chemicals in indoor air, including outdoor air. Pollutants such as O₃, nitrogen oxides (NO_x), particulate matter (PM) and organics enter with the ventilation air or air that infiltrates through window frames, doors and other openings in the building envelope. The chemicals introduced with outdoor air depend on the location and leakiness of the building. For example, higher indoor concentrations of traffic generated pollutants will be found in homes nearer to busy roads and/or with higher ventilation/infiltration rates.

There are also many indoor sources of reactive chemicals:

- cleaning agents and air fresheners (e.g., terpenes, sodium hypochlorite, ammonia, acetic acid)
- electronic equipment such as photocopiers and laser printers (O₃)
- smoking
- combustion appliances, cooking and heating (e.g., nitrogen dioxide (NO₂), nitric oxide (NO), nitrous acid (HONO), acrolein, polycyclic aromatic hydrocarbons (PAHs))
- home improvement measures such as painting
- building materials including wood, PVC pipes and cable insulation
- furnishings including carpets, other floor coverings and wall coverings
- pesticides
- humans (e.g., squalene, unsaturated fatty acids, isoprene, NO, ammonia)

- pets
- bacteria and fungi, including mold (e.g., microbial organics)

The indoor sources listed above have been discussed in detail¹¹⁻²². Many are linked to occupant activities such as cooking or smoking. Such activities can often lead to extremely high concentrations of reactive chemicals indoors. Singer et al.²³ reported a concentration of 200 ppb of limonene following cleaning indoors, whilst Abdullahi et al.¹⁷ noted PM_{2.5} concentrations of thousands of $\mu\text{g}/\text{m}^3$ associated with frying or deep-frying meat.

Reactive chemistry is itself a source of chemicals that might not otherwise be present indoors. Examples of the reactive chemicals formed through indoor air chemistry are short-lived radical species such as the hydroxyl (OH), hydroperoxy (HO₂), organic peroxy (where the generic term, RO₂, denotes the sum of all peroxy radicals present) and nitrate (NO₃) radicals, as well as Criegee intermediates, which are formed when ozone reacts with commonly occurring indoor unsaturated VOCs such as terpenes. Other species of note are secondary ozonides, as well as nitrated and oxygenated VOCs (such as organic nitrates, carbonyls, dicarbonyls and hydroxy carbonyls) and secondary organic aerosol (SOA). Many of these species are known or expected to be irritating or even carcinogenic,^{24,25} and there are likely to be even more species present than we are currently able to detect, so-called ‘stealth pollutants’.³ Many reactive chemicals will further react to propagate the chemistry as discussed in the next section.

Indoor gas phase chemistry

The concentration of any pollutant indoors will depend on the balance between its sources and sinks. For reactions among gas-phase pollutants to influence indoor environments, the time scale of the reaction must be competitive with air exchange.²⁶ For instance, the rate

coefficients for ozone reacting with limonene and isoprene at 23°C are 5.1×10^{-6} and 3.0×10^{-7} $\text{ppb}^{-1}\text{s}^{-1}$, respectively.^{27,28} At typical indoor concentrations of 20 ppb ozone, 2 ppb limonene and 2 ppb isoprene, ozone removes limonene at a rate equivalent to 0.4 air changes/h while it removes isoprene at a rate equivalent to only 0.02 air changes/h. The ozone/limonene reaction can therefore compete with moderate air exchange, but not the ozone/isoprene reaction.

Much indoor air chemistry research to date has focused on the reactions between oxidants (O_3 and OH radicals) and VOCs, which generate thousands of complex and often multi-functional products in the gas-phase. The main route to OH formation indoors is through reaction of O_3 with alkenes and monoterpenes, whereas O_3 photolysis is the most important process outdoors. For a number of years, and in the absence of any measurements, models predicted that the OH concentration indoors was likely to be $\sim 10^5$ molecule cm^{-3} (~ 0.01 ppt),^{29,30,1} typical for outdoors at nighttime or in the winter when light levels are low. Recent OH measurements indoors have confirmed the predicted background concentrations, but also demonstrated that much higher indoor OH concentrations are possible in the presence of high HONO concentrations close to sunlit windows³¹ or during cleaning activities.³²

Once formed, OH can react with terpenes and any other organics present, often at similar rates to those observed outdoors (Figure 1). However, OH oxidation of monoterpenes is more important indoors reflecting their high indoor concentrations. Clearly, there is the potential for significant chemical processing indoors.

Finally, the NO_3 radical has been postulated to be important indoors given the lower light levels (NO_3 is rapidly photolyzed in sunlight) and frequent co-occurrence of O_3 and NO_2 .³³ Predicted concentrations through modelling studies tend to be low: Carslaw¹ estimated a concentration below 0.03 ppt. Although residual NO_3 concentrations may be low indoors, they

can still impact indoor chemistry as seen in Figure 1 where reactions of NO_3 with monoterpenes lead to formation of RO_2 radicals.

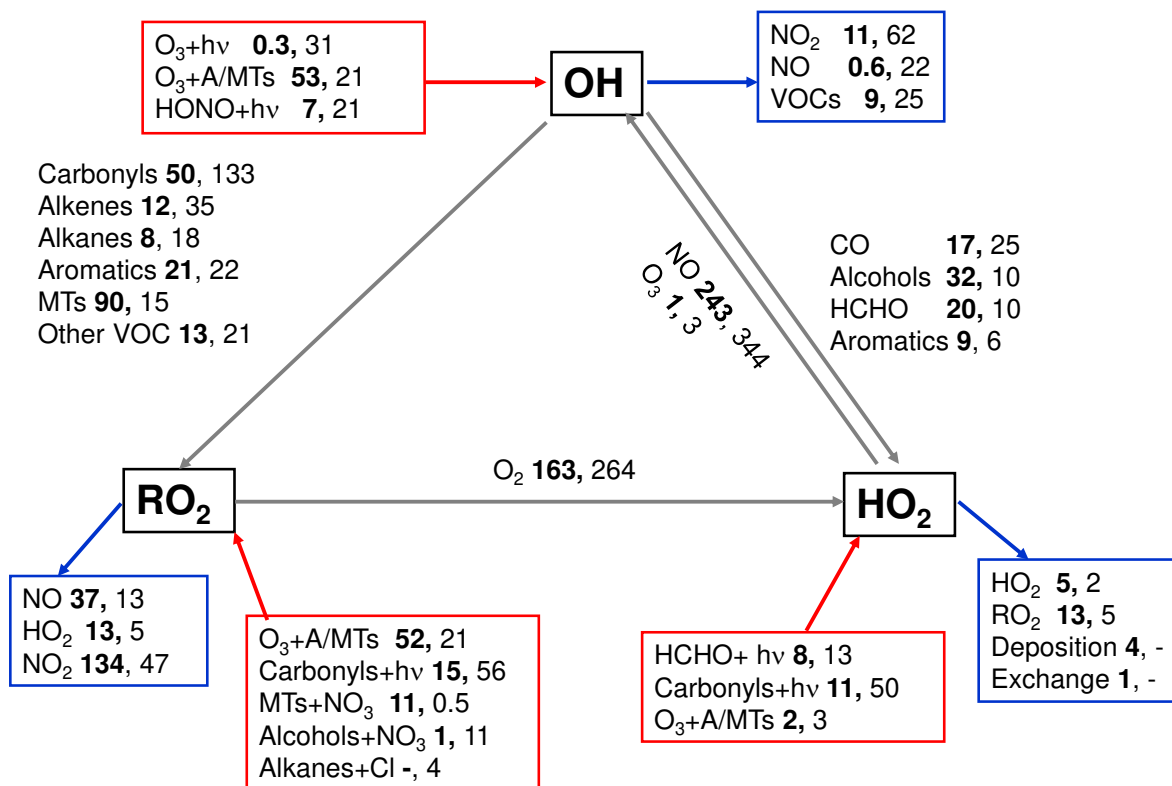


Figure 1. A comparison of rates for key reactions indoors (bold text) and outdoors (normal text) for conditions described in Carslaw¹ and in units of $10^5 \text{ molecule cm}^{-3} \text{ s}^{-1}$. The red boxes denote radical initiation processes, blue boxes radical termination and grey arrows, propagation between radicals. The term '+ hv' denotes a photolysis reaction, while MT denotes monoterpenes and A denotes alkenes.

Indoor Surface Chemistry

Indoor surface reactions tend to occur at interfaces, including air/particle and air/surface films.⁴ The time constraints that the air exchange rate imposes on indoor gas-phase reactions do not apply to surface reactions, with the exception of those involving airborne particles. This lack of time constraint, coupled with high surface-to-volume ratios (typically 2 to 4 m^2/m^3), means that chemistry on surfaces is more important indoors than outdoors. Although new surfaces have

distinct properties, they soil fairly quickly. Under typical indoor conditions, five layers of semi-volatile organic compounds (SVOCs) accumulate on impermeable surfaces in one to three months.³⁴⁻³⁷ After this period, the reactivity of many indoor surfaces changes little over time, reflecting their ongoing acquisition of reactive compounds derived from skin oils, skin flakes, deposited airborne particles, cooking, and cleaning.³⁸

Reactions between ozone and indoor surfaces have been extensively studied. Early investigations with carpets revealed reductions in the concentration of unsaturated organic species and concomitant production of oxidized products, especially aldehydes (Figure 2).^{39, 40} Modeling studies have indicated that the production of these relatively long chain aldehydes, through surface reactions on various materials, also leads to the enhanced formation of nitrated organic material such as peroxyacetyl nitrates.⁴¹

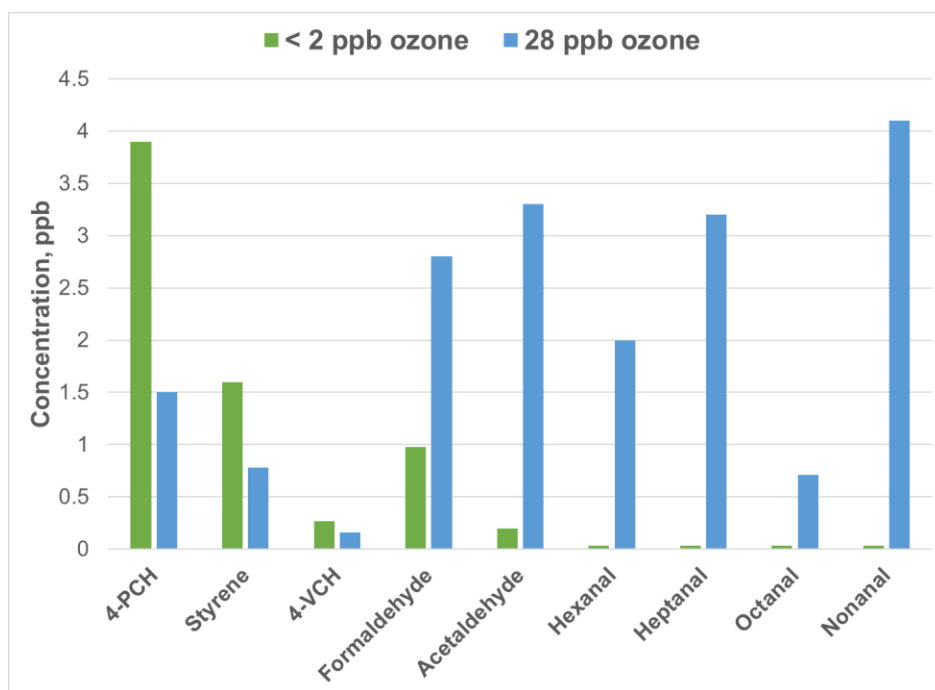


Figure 2. Gas phase concentrations of selected compounds in a 20 m³ chamber containing a new carpet and ventilated at 1 h⁻¹ in the absence or presence of ozone.³⁹ 4-phenylcyclohexene (4-PCH), styrene and 4-vinylcyclohexene (4-VCH) are unsaturated emissions that react with ozone, while the aldehydes are products of ozone-initiated reactions with these and other organics present in the carpet.

The ozone-reactivity of certain terpenoids (e.g., Δ^3 -carene) is significantly enhanced on surfaces compared to the gas phase.⁴²⁻⁴⁴ This has a larger impact for lower volatility terpenoids such as α -terpeniol⁴⁵ and dihydromyrcenol,⁴⁶ which have a greater affinity for surfaces than their more volatile terpene cousins. Benzo[a]pyrene (BaP) is one of many PAHs produced during cooking, smoking and other combustion activities. In the gas phase there is negligible reaction between BaP and ozone, but when BaP is sorbed to glass it reacts with ozone to produce both mono- and diol-epoxides.⁴⁷

As noted in the next section, photolysis of HONO indoors can be a meaningful source of hydroxyl radicals in certain situations. It has long been known that NO_2 reacts with water on indoor surfaces to produce HONO,^{48, 49} and has recently been observed that light can enhance indoor HONO production from interfacial reactions between NO_2 and household chemicals.⁵⁰ HONO, in turn, can react with nicotine sorbed on indoor surfaces to produce carcinogenic tobacco-specific nitrosamines (TSNAs).⁵¹

Wong et al.⁵² found that mopping of a floor with a bleach solution (97% water) resulted in elevated concentrations of both HOCl and Cl_2 despite a high air exchange rate ($\sim 13 \text{ h}^{-1}$). HOCl decayed significantly faster than the air exchange rate, indicating its participation in indoor surface chemistry. ClNO_2 , NCl_3 and NHCl_2 were also identified in the air; NHCl_2 may result from HOCl reacting with amines on indoor surfaces.

Indoor photochemistry

A common misconception about the indoor environment is that the absence of direct sunlight means the absence of indoor photolysis reactions. However, there are many ways that light can propagate through indoor environments: directly through open windows and doors, through windows with some attenuation and through the use of indoor lighting. Consequently,

photolysis still occurs indoors, just more slowly than outdoors. Reactions requiring higher energy light such as O₃ photolysis, are attenuated more indoors relative to outdoors than those reactions requiring less energy, such as HCHO photolysis to produce HO₂ (see Figure 1).

Kowal et al.⁵³ took a variety of lighting types used in residences and measured the distance-dependent and wavelength-resolved photon fluxes. They also measured the flux of sunlight directly in front of a window. They found significant variation between light sources, both in terms of intensity, but also wavelength dependence. Highest peak intensities were found from fluorescent tubes, whilst the LED light source had zero emission below 400 nm.

The impact of different indoor lighting sources on predicted OH concentrations indoors has been explored using models.^{1, 54} Figure 3 shows OH concentrations predicted by the Carslaw model¹ for the different light sources tested in Kowal et al.,⁵³ as well as in darkness. It indicates a significant variation in the predicted OH concentration depending on indoor lighting type: using an uncovered fluorescent tube indoors is likely to lead to significantly more chemical processing than using an LED. Note also the non-zero concentration of OH predicted in the dark and the ubiquity of this important oxidant indoors.

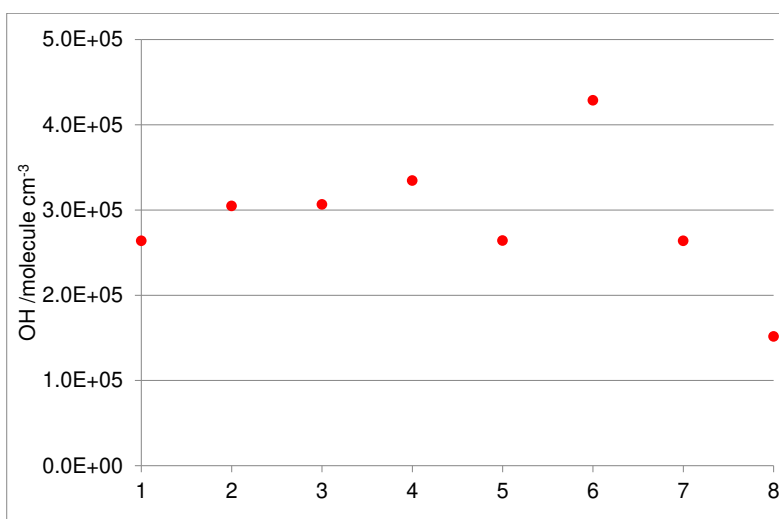


Figure 3. Impact of different light sources on predicted OH concentrations indoors under different lighting conditions: 1 (LED), 2 (halogen), 3 (incandescent), 4 (compact fluorescent), 5 (covered fluorescent), 6 (uncovered fluorescent), 7 (attenuated sunlight only) and 8 (dark).

The importance of indoor lighting was further illustrated in the bleach/mopping study mentioned in the previous section.⁵² Modelling indicated that photolysis of HOCl and Cl₂ was a potential source of chlorine and hydroxyl radicals. Hence, bleach solutions oxidize not only chemicals on the treated surfaces, but chemicals throughout the room.

Finally, recent research has demonstrated photoinduced chemistry in nonanoic acid coated aqueous surface films, resulting in the formation of a range of saturated and unsaturated aldehydes in the gas phase and more highly oxygenated products in the condensed phase.^{55, 56} Aqueous surface films are ubiquitous indoors, as are carboxylic acids from humans and their activities.²¹ Similar processes are likely happening indoors and could be a potentially important source of oxidized organics.

Indoor secondary organic aerosols

Concentrations of terpenes and terpene alcohols tend to be much higher indoors than out, reflecting the ubiquitous use of scented agents in everything from personal care products to cleaning agents and “air fresheners”. Ozone, transported from outdoors or generated indoors, reacts with these terpenoids, generating products with a range of volatilities. The less volatile condense on existing particles or nucleate, producing SOA. When initially produced, SOA are typically ultrafine particles (UFP, < 100 nm diameter),⁵⁷ but grow with time into larger, but still relatively small particles (300 – 700 nm). These processes can generate substantial levels of SOA in indoor environments.^{23, 57-67}

The production of SOA varies with ozone concentration and can be episodic, such as during the use of a scented cleaning product,²³ or it can be relatively continuous, as occurs with the use of plug-in air fresheners.^{68, 69} Although commonly initiated by ozone, SOA production is

augmented by hydroxyl radicals generated by the reaction of ozone with the double bonds in terpenoids (and other) precursors.^{23, 61, 63} Nitrate radicals can also influence SOA production as illustrated by experiments investigating ozone reacting with α -pinene in the presence of different concentrations of NO; the highest SOA yield was measured under the condition anticipated to produce the highest nitrate radical concentration.⁶⁷

Surface chemistry can be a source of SOA, as demonstrated for ozone reacting with surface sorbed d-limonene⁷⁰ and squalene.⁷¹ In these cases, production rates for SOA from ozone-initiated surface chemistry were much smaller than those for certain ozone/terpenoid reactions in the gas phase. However, additional investigation of such processes for alkenes with volatilities between those of limonene and squalene is warranted.

Waring⁷² has used modeling, with inputs represented as distributions within a Monte Carlo framework, to estimate the contribution of SOA formed indoors to the overall indoor burden of airborne particles. On average, SOA from indoor chemistry contributes only a small fraction to the total mass of indoor fine-mode particles (6% with a probability of 50%). However, in 10% of the modeled situations the contribution is > 30%. These high SOA scenarios have elevated levels of ozone and terpenes, especially limonene, coupled with low air exchange rates. Under such conditions (e.g. cleaning), modelling studies have suggested that the composition of SOA may include a significant fraction of peroxide and organic nitrogen species.^{73, 74} These model predictions would benefit from evaluation via measurements of the composition of SOA derived from different mixtures of indoor gas phase pollutants.

Another source of SOA is thermal desorption of SVOCs from surfaces to which they have sorbed.^{36, 75, 76} Upon heating of items such as cooking utensils, stovetops, clothes irons, and radiators, accumulated organic compounds desorb from the surface. As the plume of air

containing these organics rises and cools, many of the organics supersaturate and nucleate forming SOA.

Role of partitioning in indoor chemistry

SVOCs partition between the gas phase and other indoor compartments, including airborne particles, settled dust, exposed surfaces and even the skin, hair and clothing of occupants.^{37, 77-84} Inorganic gases also partition between the gas phase and airborne particles,⁸⁵⁻⁸⁷ as well as into dust and aqueous surface films.

Plasticizers, flame retardants, UV-filters and other additives migrate from the products that originally contained them to other indoor compartments.⁸⁸⁻⁹³ As the concentration of airborne particles increases, the fraction of SVOCs in the particle phase increases, while that in the gas phase decreases. Temperature further influences the partitioning of SVOCs among the various indoor compartments.⁸⁹

When aerosols are transported indoors from outdoors, their volatile constituents re-equilibrate with the surrounding air. This redistribution can be driven by gas-phase concentration differences or temperature differences between outdoor and indoor environments. For instance, loss of PAHs has been demonstrated when indoor particles are compared to co-sampled outdoor particles.^{86,94} Outdoor-to-indoor transport can also result in particle sorption of SVOCs whose indoor concentrations are much higher than their outdoor concentrations,⁸⁷ as is often the case for phthalate ester plasticizers or brominated flame retardants.

Losses of ammonium nitrate have also been reported during outdoor-to-indoor transport of aerosols⁸⁵⁻⁸⁷. Ammonium and nitrate ions in aerosols are coupled to gas-phase ammonia and

nitric acid in the surrounding air. The loss of ammonium nitrate from the aerosols influences their water content and pH, as well as the solubility of transition metals in the aerosols.

Organic films on indoor surfaces are well documented,^{34, 35, 92, 93, 95, 96} and are a consequence of partitioning. There is more time, in some cases as long as the interval between cleaning, for an SVOC to react when sorbed to a surface film than when in the gas phase. Partitioning to indoor surfaces, especially for SVOCs with $\log K_{oa}$ between 10 and 13,³⁷ provides a large reservoir of SVOCs for both surface and gas-phase chemistry. When the original source is removed, this reservoir persists for days, months, or even years^{97, 98} depending on the properties of the sorbed SVOCs.

Impact of moisture on indoor chemistry

Moisture likely plays a significant role in indoor chemistry. As a reference point, at a relative humidity of 65%, aqueous surface films are common, and water is a substantial fraction (~30%) of airborne particles.⁹⁹ The presence and thickness of aqueous surface films and the water content of airborne particles changes with changing relative humidity, as does the amount of water sorbed to porous materials.^{99, 100} Both inorganic (e.g., nitric, hydrochloric) and organic (e.g., formic, acetic, lactic) acids partition between the gas phase and water on surfaces/in airborne particles. The same is true for inorganic (e.g., ammonia) and organic (e.g., nicotine, amines) bases.

A number of chemicals found in materials and products used indoors are susceptible to base-catalyzed hydrolysis. These include phthalate, adipate and sebacate esters used as plasticizers; organophosphate esters used as plasticizers, flame retardants, and pesticides; p-hydroxybenzoic acid esters (parabens) used as antioxidants; bisphenol A diglycidyl ether

(BADGE) used in personal care products and coatings; and acrylate-based copolymers used in adhesives. Hydrolysis reactions tend to be too slow to be important in the gas phase, but can occur on surfaces (e.g., emission of 2-ethylhexanol when PVC flooring plasticized with di(2-ethylhexyl) phthalate (DEHP) and its associated adhesives is placed on moist concrete.^{101, 102}). Wang et al.¹⁰³ have reported the presence of hydrolysis products of parabens and BADGE in 158 dust samples collected from the U.S., China, Korea, and Japan, indicating the ubiquity of this process. Nonetheless, hydrolysis reactions in indoor settings remain relatively unexplored.

As the relative humidity increases, the tendency for polar compounds to sorb to indoor surfaces increases, in turn increasing the probability for their reaction on surfaces (e.g. α -terpeniol on glass, PVC or paint).⁴⁵ Short-lived, highly reactive intermediates may react via different pathways under relatively dry conditions compared to relatively moist conditions, resulting in different product distributions. This is expected to be the case for Criegee intermediates formed in the reaction between ozone and squalene on surfaces.¹⁰⁴

Duncan et al.¹⁰⁵ recently measured water soluble organic gases (WSOGs) indoors and outdoors at thirteen homes; the average concentration was 15 times higher indoors than out. The authors speculate that aqueous processing of these abundant WSOGs under damp indoor conditions can increase the indoor concentrations of oxidized and potentially irritating chemicals.

Microbes can be a source of reactive chemicals indoors, and microbial growth requires moisture. This is a complex topic beyond the scope of the present article. However, a recent publication by Adams et al.¹⁰⁶ provides an excellent introduction.

Impact of occupants on indoor chemistry

Human occupants emit skin oils and shed their skin flakes, rich in skin oil, at an astonishing rate. A typical adult emits sebum at ~ 500 mg/h¹⁰⁷ and sheds skin flakes at 30-90 mg/h.^{108, 109} Skin oil constituents with double bonds react rapidly with ozone and nitrate radicals. The molar fraction of unsaturated species in skin oil is slightly more than 0.9,¹¹⁰ and includes squalene ($\sim 10\%$ by weight) and mono- and di-unsaturated fatty acids ($\sim 12\%$ by weight). Skin oils are transferred to any surface that humans contact, while skin flakes deposit mainly on horizontal surfaces. Ozone can react with unsaturated skin lipids on these surfaces, as well as on exposed skin, hair, and clothing of the occupants themselves. As a result, the ozone concentration in a 30 m³ room with two occupants is roughly half the value it would be if the room were unoccupied.¹¹¹

Numerous gas-phase products are generated by ozone/skin oil oxidation chemistry, including acetone, 6-methyl-5-heptene-2-one (6-MHO), geranyl acetone, and 4-oxopentanal (4-OPA).^{111, 112} These reactions also produce less volatile chemicals that remain on skin, clothing or surfaces, including levulinic, succinic, adipic and suberic acids.¹¹³ Oxidation rates are rapid, implying that these less volatile products are almost always present on skin and surfaces soiled with skin oil and skin flakes.

Breath is also a significant source of reactive chemicals indoors, including isoprene, nitric oxide (NO) and ammonia.¹¹⁴⁻¹¹⁶ In the case of isoprene, typical whole-body emission rates, which are dominated by breath emissions, are roughly in the range of 160 - 170 $\mu\text{g/h}$ (adults) and 90 -100 $\mu\text{g/h}$ (children).^{19, 22} Although isoprene reacts slowly with ozone, it reacts more quickly with hydroxyl and nitrate radicals, forming methacrolein and methyl vinyl ketone amongst other products.

Ammonia is emitted from occupants' skin as well as breath.^{116, 117} For an adult, emission rates tend to be centered around 300 µg/h, but there are large variations with age, diet, oral hygiene and smoking habits.^{118, 119} Ammonia from occupants influences the pH of indoor airborne particles, as well as acid-base chemistry on indoor surfaces.

A fascinating recent observation was reproducible changes in airborne chemicals emitted by cinema-going audiences depending on the genre of films they watched.¹²⁰ Suspense and comedy films elicited the strongest response, and the authors speculate that such behavior may constitute an alert (suspense)/stand-down (comedy) response that may have proved advantageous in evolutionary terms assuming such signals can be perceived by others.

Impact of buildings on indoor chemistry

There is no such thing as a typical building. For example, within the United States there are 118.2 million housing units, 80% in urban areas and 20% in rural areas; 36% are in “very cold” or “cold” climates, 19% in “hot-humid areas”; 32% were built after 1990 and 18% were built before 1950; 28% of the units are built from brick, 15% from wood; the most common number of rooms is 6, but this ranges from 1 to > 9.¹²¹ Buildings are diverse, and it is vital to understand the impacts that variations in building construction, location and operation can have on indoor air chemistry.

A key issue affecting indoor air chemistry is the building ventilation rate. Mechanically ventilated buildings often employ heating, ventilation and air conditioning (HVAC) systems and it is necessary to understand when the system is running, the air exchange rate, the fraction of recirculated air, whether the fraction of outdoor air used for ventilation is fixed or variable, humidification/dehumidification, filtration efficiencies and temperature set-points throughout the

day.¹²² Even in naturally ventilated buildings, it is necessary to measure air exchange rates, temperature and relative humidity to properly understand the chemistry. Although room air is commonly assumed to be well mixed, for extremely fast reactions (e.g., hydroxyl radical reacting with organics) with locally produced reactants, the time required for mixing is an important parameter.⁸

Another consideration is the chemistry that occurs in “hidden” building spaces (e.g., wall cavities, basements, crawl spaces, attics) and/or how this can influence the chemistry in occupied spaces. For instance, Du et al.¹²³ found that for a study of 74 US residences, the basement was a source of VOCs that were found in the living space. Given linked air flow between different parts of a building, out of sight does not necessarily mean out of mind.

Modeling indoor chemistry

Indoor chemistry has been modeled for more than three decades.¹²⁴ We have mentioned some of the applications of modeling throughout this review. It is an overarching activity, incorporating results from the different topics discussed above. It can extend findings from a small number of indoor settings to a larger universe of buildings. Increasingly, indoor air models are being used to evaluate findings, identify gaps and limitations in knowledge, and design experimental programs.⁸ The indoor chemical box model mentioned earlier^{1, 73} contains around 5000 species and 20,000 reactions. Measurements are available for perhaps only 100-200 indoor species; model predictions provide insights that would be absent otherwise.

Models are currently limited due to uncertainties regarding the parameterization of surface interactions, the propagation of light through indoor environments, and the concentrations of a suite of secondary pollutants formed through indoor chemical reactions.⁸ The new CIE program is providing the impetus to address some of these issues through coordinated

laboratory, experimental and modelling studies. We anticipate that in a future review many of these limitations will have been addressed.

Vision

We are currently at a crossroads for indoor air chemistry. Over the past several years there has been increasingly coordinated collaboration among scientists – atmospheric chemists, building physicists, chemical engineers, mechanical engineers, and other specialists -- working at the disciplinary boundaries of this field. State-of-the-art instrumentation and novel derivatization techniques are making accessible what had been nearly impossible measurements. Recent findings answer some questions and raise many more. Where is all this going?

An emerging area of research is intensive field campaigns in residences, offices and schools utilizing cutting edge analytical techniques (e.g., proton-transfer-reaction/high resolution mass spectrometry; chemical ionization/high resolution mass spectrometry; cavity ring down spectroscopy; low-pressure laser-induced fluorescence spectroscopy; actinic flux spectroradiometry). Such field campaigns will be complemented by studies in test houses where researchers with different scientific expertise bring together their instruments to make coordinated, simultaneous measurements under manipulated indoor scenarios. Comprehensive measurement campaigns should significantly facilitate model development and aid in the search for chemicals that “must be there” including amines, organic nitrates, peroxides and peroxy radicals. We anticipate more detailed studies of indoor acid/base chemistry, hydrolysis reactions, photochemistry promoted by photosensitizers, and microbe/indoor chemical interactions. Even the role of water in indoor chemistry is relatively understudied, both in the gas-phase and on surfaces, and is beginning to receive increased attention. The impact of human occupancy on the

indoor environment is far more important than initially imagined,^{18-21, 125} and further investigations are likely to uncover additional impacts.

Indoor environments have changed significantly in the last 50 years¹⁶ and will continue to do so. An emerging area of research focuses on low- or zero-energy buildings, which tend to have low ventilation rates and, hence, more time for gas-phase chemistry to occur. With increasing use of ‘green materials’ and products containing manmade nanoparticles, we envision investigations into their emissions/reactions and how their chemical interactions evolve with age. As various regions of the world warm, more buildings will use air-conditioning, which is often accompanied by substantial recirculation of indoor air. Recirculation amplifies certain indoor chemical processes. Climate change is associated not only with increasing heatwaves, but also increases in outdoor pollutant levels that can impact indoor environments¹²⁶. As stated in a National Academy of Sciences’ report: “Climate change may worsen existing indoor environmental problems and introduce new problems”.¹²⁷

We conclude with the fundamental question driving indoor chemistry research: What are the specific chemical reactions that transform relatively benign chemicals into ones that are responsible for malodors, irritancy, material degradation and adverse health outcomes? Given the continuing and dramatic changes in indoor environments, it is more important than ever that we understand indoor chemistry to ensure that building occupants and building contents are protected from unanticipated exposures to harmful chemicals.

Acknowledgements

In 2016, after funding several preliminary studies, the Sloan Foundation announced a ten-year program in *Chemistry of Indoor Environments (CIE)*¹⁰. Although not the subject of the

present article, some early findings from this program have been reported. We thank Dr. Paula J. Olsiewski, Director of the *CIE* program, for her efforts in bringing together a diverse community of scientists to improve understanding of the chemistry taking place indoors.

References

1. Carslaw, N., A new detailed chemical model for indoor air pollution. *Atmos. Environ.* **2007**, *41*, (6), 1164-1179.
2. Weschler, C. J.; Shields, H. C., Potential reactions among indoor pollutants. *Atmos Environ* **1997**, *31*, 3487-3495.
3. Weschler, C. J., Reactions among indoor pollutants: What's new? *The Scientific World* **2001**, *1*, 443-457.
4. Morrison, G., Interfacial chemistry in indoor environments. *Environ. Sci. Technol.* **2008**, *42*, (10), 3494-3499.
5. Weschler, C. J., Chemistry in indoor environments: 20 years of research. *Indoor Air* **2011**, *21*, 205-218.
6. Morrison, G., Recent Advances in Indoor Chemistry. *Curr Sustainable Renewable Energy Rep* **2015**, *2*, (2), 33-40.
7. Nazaroff, W. W.; Goldstein, A. H., Indoor chemistry: research opportunities and challenges. *Indoor Air* **2015**, *25*, (4), 357-61.
8. Morrison, G. C.; Carslaw, N.; Waring, M. S., A modeling enterprise for chemistry of indoor environments (CIE). *Indoor Air* **2017a**, *27*, (6), 1033-1038.
9. Wells, J. R.; Schoemaeker, C.; Carslaw, N.; Waring, M. S.; Ham, J. E.; Nelissen, I.; Wolkoff, P., Reactive indoor air chemistry and health—A workshop summary. *International Journal of Hygiene and Environmental Health* **2017**, *220*, (8), 1222-1229.
10. Alfred P. Sloan Foundation, Chemistry of Indoor Environments, <https://sloan.org/programs/science/chemistry-of-indoor-environments>, last accessed 11/17/2017.
11. Nazaroff, W. W.; Weschler, C. J., Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos. Environ.* **2004**, *38*, 2841-2865.
12. Wang H, Morrison GC. Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes. *Environ. Sci. Technol.* **2006**, *40*, 5263-5268.
13. Seaman, V.Y.; Bennett, D.H.; Cahill, T.M., Indoor acrolein emission and decay rates resulting from domestic cooking events. *Atmos. Environ.* **2007**, *43*(39), 6199-6204.

14. Destailats, H.; Maddalena, R. L.; Singer, B. C.; Hodgson, A. T.; McKone, T. E., Indoor pollutants emitted by office equipment: A review of reported data and information needs. *Atmos. Environ.* **2008**, *42*, (7), 1371-1388.
15. Odabasi, M., Halogenated volatile organic compounds from the use of chlorine-bleach-containing household products. *Environ. Sci. Technol.* **2008**, *42*, 1445-1451.
16. Weschler, C. J., Changes in indoor pollutants since the 1950s. *Atmos. Environ.* **2009**, *43*, 153-169.
17. Abdullahi, K.L.; Delgado-Saborit, J.M.; Harrison, R.M. Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: a review. *Atmos. Environ.* **2013**, *71*, 260-294.
18. Tang, X. C.; Misztal, P. K.; Nazaroff, W. W.; Goldstein, A. H., Siloxanes are the most abundant volatile organic compound emitted from engineering students in a classroom. *Environ. Sci. Technol. Letters* **2015**, *2*, (11), 303-307.
19. Tang, X.; Misztal, P. K.; Nazaroff, W. W.; Goldstein, A. H., Volatile Organic Compound Emissions from Humans Indoors. *Environ. Sci. Technol.* **2016**, *50*, (23), 12686-12694.
20. Liu, S.; Li, R.; Wild, R. J.; Warneke, C.; de Gouw, J. A.; Brown, S. S.; Miller, S. L.; Luongo, J. C.; Jimenez, J. L.; Ziemann, P. J., Contribution of human-related sources to indoor volatile organic compounds in a university classroom. *Indoor Air* **2016**, *26*, (6), 925-938.
21. Liu, S.; Thompson, S. L.; Stark, H.; Ziemann, P. J.; Jimenez, J. L., Gas-Phase carboxylic acids in a university classroom: abundance, variability, and sources. *Environ. Sci. Technol.* **2017**, *51*, (10), 5454-5463.
22. Stöner, C.; Edtbauer, A.; Williams, J., Real-world volatile organic compound emission rates from seated adults and children for use in indoor air studies. *Indoor Air*, 2017 doi: 10.1111/ina.12405
23. Singer, B. C.; Coleman, B. K.; Destailats, H.; Hodgson, A. T.; Lunden, M. M.; Weschler, C. J.; Nazaroff, W. W., Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmos. Environ.* **2006**, *40*, (35), 6696-6710.
24. Weschler, C. J., Ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-initiated chemistry. *Environ. Health Perspect.* **2006**, *114*, 1489-96.
25. Wolkoff, P., External eye symptoms in indoor environments. *Indoor Air* **2017**, *27*, 246-260.
26. Weschler, C. J.; Shields, H. C., The influence of ventilation on reactions among indoor pollutants: Modeling and experimental observations. *Indoor Air* **2000**, *10*, (2), 92-100.
27. Atkinson, R.; Hasegawa, D.; Aschmann, S. M., Rate constants for the gas-phase reactions of O₃ with a series of monoterpenes and related-compounds at 296-K +/-2-K. *Int. J. Chem. Kinet.* **1990**, *22*, 871-887.
28. Greene, C. R.; Atkinson, R., Rate constants for the gas-phase reactions of O₃ with a series of alkenes at 296-K +/-2-K. *Int. J. Chem. Kinet.* **1992**, *24*, 803-811.
29. Weschler, C. J.; Shields, H. C., Production of the hydroxyl radical in indoor air. *Environ. Sci. Technol.* **1996**, *30*, 3250-3258.

30. Sarwar G, Corsi R, Kimura Y, Allen D, Weschler CJ. Hydroxyl radicals in indoor environments. *Atmos Environ* **2002**, *36*, 3973–88.
31. Gomez Alvarez, E.; Amedro, D.; Afif, C.; Gligorovski, S.; Schoemaeker, C.; Fittschen, C.; Doussin, J. F.; Wortham, H., Unexpectedly high indoor hydroxyl radical concentrations associated with nitrous acid. *PNAS* **2013**, *110*, 13294-13299.
32. Carslaw, N.; Fletcher, L.; Heard, D.; Ingham, T.; Walker, H., Significant OH production under surface cleaning and air cleaning conditions: Impact on indoor air quality. *Indoor Air*, **2017**, *27*, 1091-1100.
33. Weschler, C. J.; Brauer, M.; Koutrakis, P., Indoor ozone and nitrogen dioxide - a potential pathway to the generation of nitrate radicals, dinitrogen pentoxide, and nitric-acid Indoors. *Environ. Sci. Technol.* **1992**, *26*, (1), 179-184.
34. Liu, Q. T.; Chen, R.; McCarry, B. E.; Diamond, M. L.; Bahavar, B., Characterization of polar organic compounds in the organic film on indoor and outdoor glass windows. *Environ. Sci. Technol.* **2003**, *37*, 2340-9.
35. Huo, C.-Y.; Liu, L.-Y.; Zhang, Z.-F.; Ma, W.-L.; Song, W.-W.; Li, H.-L.; Li, W.-L.; Kannan, K.; Wu, Y.-K.; Han, Y.-M.; Peng, Z.-X.; Li, Y.-F., Phthalate Esters in Indoor Window Films in a Northeastern Chinese Urban Center: Film Growth and Implications for Human Exposure. *Environ. Sci. Technol.* **2016**, *50*, 7743-7751.
36. Wallace, L. A.; Ott, W. R.; Weschler, C. J.; Lai, A. C. K., Desorption of SVOCs from heated surfaces in the form of ultrafine particles. *Environ. Sci. Technol.* **2017**, *51*, 1140-1146.
37. Weschler, C. J.; Nazaroff, W. W., Growth of organic films on indoor surfaces. *Indoor Air* **2017**, *27*, 1101–1112.
38. Wang, H.; Morrison, G., Ozone-surface reactions in five homes: surface reaction probabilities, aldehyde yields, and trends. *Indoor Air* **2010**, *20*, 224-234.
39. Weschler, C. J.; Hodgson, A. T.; Wooley, J. D., Indoor chemistry - ozone, volatile organic-compounds, and carpets. *Environ. Sci. Technol.* **1992**, *26*, (12), 2371-2377.
40. Morrison, G. C.; Nazaroff, W. W., The rate of ozone uptake on carpets: Experimental studies. *Environ. Sci. Technol.* **2000**, *34*, 4963-4968.
41. Kruza, M.; Lewis, A.C.; Morrison, G.C.; Carslaw, N., Impact of surface ozone interactions on indoor air chemistry: a modelling study. *Indoor Air* **2017**, *27*, 1001-1011.
42. Fick, J.; Nilsson, C.; Andersson, B., Formation of oxidation products in a ventilation system. *Atmos. Environ.* **2004**, *38*, 5895-5899.
43. Fick, J.; Pommer, L.; Astrand, A.; Ostin, R.; Nilsson, C.; Andersson, B., Ozonolysis of monoterpenes in mechanical ventilation systems. *Atmos. Environ.* **2005**, *39*, 6315-6325.
44. Springs, M.; Wells, J. R.; Morrison, G. C., Reaction rates of ozone and terpenes adsorbed to model indoor surfaces. *Indoor Air* **2011**, *21*, (4), 319-327.
45. Shu, S.; Morrison, G. C., Surface Reaction Rate and Probability of Ozone and Alpha-Terpeneol on Glass, Polyvinyl Chloride, and Latex Paint Surfaces. *Environ. Sci. Technol.* **2011**, *45*, (10), 4285-4292.

46. Shu, S.; Morrison, G. C., Rate and reaction probability of the surface reaction between ozone and dihydromyrcenol measured in a bench scale reactor and a room-sized chamber. *Atmos. Environ.* **2011**, *47*, 421-427.
47. Zhou, S.; Yeung, L. W. Y.; Forbes, M. W.; Mabury, S.; Abbatt, J. P. D., Epoxide formation from heterogeneous oxidation of benzo[a]pyrene with gas-phase ozone and indoor air. *Environ. Sci. Process. Impact* **2017**, *19*, 1292-1299.
48. Pitts, J. N.; Sanhueza, E.; Atkinson, R.; Carter, W. P. L.; Winer, A. M.; Harris, G. W.; Plum, C. N., An investigation of the dark formation of nitrous acid in environmental chambers. *International Journal of Chemical Kinetics* **1984**, *16*, (7), 919-939.
49. Pitts, J. N.; Biermann, H. W.; Tuazon, E. C.; Green, M.; Long, W. D.; Winer, A. M., Time-resolved identification and measurement of indoor air-pollutants by spectroscopic techniques -nitrous acid, methanol, formaldehyde and formic-acid. *Journal of the Air Pollution Control Association* **1989**, *39*, (10), 1344-1347.
50. Gómez Alvarez, E.; Sörgel, M.; Gligorovski, S.; Bassil, S.; Bartolomei, V.; Coulomb, B.; Zetzsch, C.; Wortham, H., Light-induced nitrous acid (HONO) production from NO₂ heterogeneous reactions on household chemicals. *Atmos. Environ.* **2014**, *95*, 391-399.
51. Sleiman, M.; Gundel, L. A.; Pankow, J. F.; Jacob, P.; Singer, B. C.; Destailats, H., Formation of carcinogens indoors by surface-mediated reactions of nicotine with nitrous acid, leading to potential thirdhand smoke hazards. *PNAS* **2010**, *107*, (15), 6576-6581.
52. Wong, J. P. S.; Carslaw, N.; Zhao, R.; Zhou, S.; Abbatt, J. P. D., Observations and impacts of bleach washing on indoor chlorine chemistry. *Indoor Air*, **2017**, *27*, 1082-1090.
53. Kowal, S. F.; Allen, S. R.; Kahan, T. F., Wavelength-resolved photon fluxes of indoor light sources: implications for HO_x production. *Environ. Sci. Technol.* **2017**, *51*, 10423-10430.
54. Waring, M. S.; Wells, J. R., Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources. *Atmos. Environ.* **2015**, *106*, 382-391.
55. Rossignol, S.; Tinel, L.; Bianco, A.; Passananti, M.; Brigante, M.; Donaldson, D. J.; George, C., Atmospheric photochemistry at a fatty acid-coated air-water interface. *Science* **2016**, *353*, 699-702.
56. Tinel, L.; Rossignol, S.; Bianco, A.; Passananti, M.; Perrier, S.; Wang, X. M.; Brigante, M.; Donaldson, D. J.; George, C., Mechanistic insights on the photosensitized chemistry of a fatty acid at the air/water interface. *Environ. Sci. Technol.* **2016**, *50*, 11041-11048.
57. Rohr, A. C.; Weschler, C. J.; Koutrakis, P.; Spengler, J. D., Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting. *Aerosol Sci. Technol.* **2003**, *37*, 65-78.
58. Weschler, C. J.; Shields, H. C., Indoor ozone/terpene reactions as a source of indoor particles. *Atmos. Environ.* **1999**, *33*, (15), 2301-2312.
59. Sarwar, G.; Corsi, R.; Allen, D.; Weschler, C., The significance of secondary organic aerosol formation and growth in buildings: experimental and computational evidence. *Atmos Environ* **2003**, *37*, (9-10), 1365-1381.

60. Sarwar, G.; Olson, D. A.; Corsi, R. L.; Weschler, C. J., Indoor fine particles: The role of terpene emissions from consumer products. *J. Air Waste Manag. Assoc.* **2004**, *54*, (3), 367-377.
61. Destailhats, H.; Lunden, M. M.; Singer, B. C.; Coleman, B. K.; Hodgson, A. T.; Weschler, C. J.; Nazaroff, W. W., Indoor secondary pollutants from household product emissions in the presence of ozone: A bench-scale chamber study. *Environ. Sci. Technol.* **2006**, *40*, (14), 4421-4428.
62. Sarwar, G.; Corsi, R., The effects of ozone/limonene reactions on indoor secondary organic aerosols. *Atmos Environ* **2007**, *41*, (5), 959-973.
63. Fan, Z. H.; Weschler, C. J.; Han, I. K.; Zhang, J. F., Co-formation of hydroperoxides and ultra-fine particles during the reactions of ozone with a complex VOC mixture under simulated indoor conditions. *Atmos. Environ.* **2005**, *39*, 5171-5182.
64. Chen, X.; Hopke, P. K., A chamber study of secondary organic aerosol formation by linalool ozonolysis. *Atmos. Environ.* **2009**, *43*, 3935-3940.
65. Chen, X.; Hopke, P. K., Secondary organic aerosol from alpha-pinene ozonolysis in dynamic chamber system. *Indoor Air* **2009**, *19*, 335-345.
66. Chen, X.; Hopke, P. K., A chamber study of secondary organic aerosol formation by limonene ozonolysis. *Indoor Air* **2010**, *20*, 320-328.
67. Liu, Y.; Hopke, P. K., A chamber study of secondary organic aerosol formed by ozonolysis of α -pinene in the presence of nitric oxide. *Journal of Atmospheric Chemistry* **2014**, *71*, (1), 21-32.
68. Norgaard, A. W.; Kudal, J. D.; Kofoed-Sorensen, V.; Koponen, I. K.; Wolkoff, P., Ozone-initiated VOC and particle emissions from a cleaning agent and an air freshener: Risk assessment of acute airway effects. *Environment International* **2014**, *68*, 209-218.
69. Steinemann, A., Ten questions concerning air fresheners and indoor built environments. *Build. Environ.* **2017**, *111*, 279-284.
70. Waring, M. S.; Siegel, J. A., Indoor secondary organic aerosol formation initiated from reactions between ozone and surface-sorbed D-limonene. *Environ. Sci. Technol.* **2013**, *47*, 6341-8.
71. Wang, C. Y.; Waring, M. S., Secondary organic aerosol formation initiated from reactions between ozone and surface-sorbed squalene. *Atmos. Environ.* **2014**, *84*, 222-229.
72. Waring, M. S., Secondary organic aerosol in residences: predicting its fraction of fine particle mass and determinants of formation strength. *Indoor Air* **2014**, *24*, (4), 376-89.
73. Carslaw, N.; Mota, T.; Jenkin, M. E.; Barley, M. H.; McFiggans, G., A significant role for nitrate and peroxide groups on indoor secondary organic aerosol. *Environ. Sci. Technol.* **2012**, *46*, (17), 9290-9298.
74. Carslaw, N., A mechanistic study of limonene oxidation products and pathways following cleaning activities. *Atmos. Environ.* **2013**, *80*, 507-513.

75. Bhangar, S.; Mullen, N. A.; Hering, S. V.; Kreisberg, N. M.; Nazaroff, W. W., Ultrafine particle concentrations and exposures in seven residences in northern California. *Indoor Air* **2011**, *21*, (2), 132-144.
76. Wallace, L. A.; Ott, W. R.; Weschler, Ultrafine particles from electric appliances and cooking pans: experiments suggesting desorption/nucleation of sorbed organics as the primary source. *Indoor Air* **2015**, *25*, 536-546.
77. Weschler, C. J.; Nazaroff, W. W., Semivolatile organic compounds in indoor environments. *Atmos. Environ.* **2008**, *42*, (40), 9018-9040.
78. Weschler, C. J.; Nazaroff, W. W., SVOC exposure indoors: fresh look at dermal pathways. *Indoor Air* **2012**, *22*, 356-377.
79. Morrison, G.; Li, H. W.; Mishra, S.; Buechlein, M., Airborne phthalate partitioning to cotton clothing. *Atmos. Environ.* **2015b**, *115*, 149-152.
80. Morrison, G. C.; Andersen, H. V.; Gunnarsen, L.; Varol, D.; Uhde, E.; Kolarik, B., Partitioning of PCBs from air to clothing materials in a Danish apartment. *Indoor Air* **2017b**, doi: 10.1111/ina.12411
81. Bennett, D. H.; Moran, R. E.; Wu, X.; Tolve, N. S.; Clifton, M. S.; Colón, M.; Weathers, W.; Sjödin, A.; Jones, R.; Hertz-Picciotto, I., Polybrominated diphenyl ether (PBDE) concentrations and resulting exposure in homes in California: relationships among passive air, surface wipe and dust concentrations, and temporal variability. *Indoor Air* **2015**, *25*, 220-229.
82. Saini, A.; Rauert, C.; Simpson, M. J.; Harrad, S.; Diamond, M. L., Characterizing the sorption of polybrominated diphenyl ethers (PBDEs) to cotton and polyester fabrics under controlled conditions. *Sci. Total Environ.* **2016**, *563*, 99-107.
83. Saini, A.; Okeme, J. O.; Mark Parnis, J.; McQueen, R. H.; Diamond, M. L., From air to clothing: characterizing the accumulation of semi-volatile organic compounds to fabrics in indoor environments. *Indoor Air* **2017**, *27*, (3), 631-641.
84. Parker, K.; Morrison, G., Methamphetamine absorption by skin lipids: accumulated mass, partition coefficients, and the influence of fatty acids. *Indoor Air* **2016**, *26*, (4), 634-641.
85. Lunden, M. M.; Revzan, K. L.; Fischer, M. L.; Thatcher, T. L.; Littlejohn, D.; Hering, S. V.; Brown, N. J., The transformation of outdoor ammonium nitrate aerosols in the indoor environment. *Atmos Environ* **2003**, *37*, (39), 5633-5644.
86. Sangiorgi, G.; Ferrero, L.; Ferrini, B. S.; Lo Porto, C.; Perrone, M. G.; Zangrando, R.; Gambaro, A.; Lazzati, Z.; Bolzacchini, E., Indoor airborne particle sources and semi-volatile partitioning effect of outdoor fine PM in offices. *Atmos Environ* **2013**, *65*, 205-214.
87. Johnson, A. M.; Waring, M. S.; DeCarlo, P. F., Real-time transformation of outdoor aerosol components upon transport indoors measured with aerosol mass spectrometry. *Indoor Air* **2017**, *27*, (1), 230-240.
88. Sukiene, V.; Gerecke, A. C.; Park, Y. M.; Zennegg, M.; Bakker, M. I.; Delmaar, C. J. E.; Hungerbuhler, K.; von Goetz, N., Tracking SVOCs' Transfer from products to indoor air and settled dust with deuterium-labeled substances. *Environ. Sci. Technol.* **2016**, *50*, (8), 4296-4303.

89. Wei, W.; Mandin, C.; Blanchard, O.; Mercier, F.; Pelletier, M.; Le Bot, B.; Glorennec, P.; Ramalho, O., Temperature dependence of the particle/gas partition coefficient: An application to predict indoor gas-phase concentrations of semi-volatile organic compounds. *Sci. Total Environ.* **2016a**, *563*, 506-512.
90. Wei, W.; Mandin, C.; Blanchard, O.; Mercier, F.; Pelletier, M.; Le Bot, B.; Glorennec, P.; Ramalho, O., Distributions of the particle/gas and dust/gas partition coefficients for seventy-two semi-volatile organic compounds in indoor environment. *Chemosphere* **2016b**, *153*, 212-219.
91. Wei, W.; Mandin, C.; Blanchard, O.; Mercier, F.; Pelletier, M.; Le Bot, B.; Glorennec, P.; Ramalho, O., Predicting the gas-phase concentration of semi-volatile organic compounds from airborne particles: Application to a French nationwide survey. *Sci. Total Environ.* **2017**, *576*, 319-325.
92. Venier, M.; Audy, O.; Vojta, S.; Becanova, J.; Romanak, K.; Melymuk, L.; Kratka, M.; Kukucka, P.; Okeme, J.; Saini, A.; Diamond, M. L.; Klanova, J., Brominated flame retardants in the indoor environment - Comparative study of indoor contamination from three countries. *Environment International* **2016**, *94*, 150-160.
93. Melymuk, L.; Bohlin-Nizzetto, P.; Vojta, S.; Kratka, M.; Kukucka, P.; Audy, O.; Pribylova, P.; Klanova, J., Distribution of legacy and emerging semivolatile organic compounds in five indoor matrices in a residential environment. *Chemosphere* **2016**, *153*, 179-186.
94. Naumova, Y. Y.; Offenberg, J. H.; Eisenreich, S. J.; Meng, Q.; Polidori, A.; Turpin, B. J.; Weisel, C. P.; Morandi, M. T.; Colome, S. D.; Stock, T. H.; Winer, A. M.; Alimokhtari, S.; Kwon, J.; Maberti, S.; Shendell, D.; Jones, J.; Farrar, C., Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. *Atmos. Environ.* **2003**, *37*, (5), 703-719.
95. Bi, C.; Liang, Y.; Xu, Y., Fate and Transport of Phthalates in Indoor Environments and the Influence of Temperature: A Case Study in a Test House. *Environ. Sci. Technol.* **2015**, *49*, 9674-9681.
96. Wu, Y.; Eichler, C. M. A.; Leng, W.; Cox, S. S.; Marr, L. C.; Little, J. C., Adsorption of phthalates on impervious indoor surfaces. *Environ. Sci. Technol.* **2017**, *51*, 2907-2913.
97. Lyng, N. L.; Gunnarsen, L.; Andersen, H. V., The effect of ventilation on the indoor air concentration of PCB: An intervention study. *Build. Environ.* **2015**, *94*, 305-312.
98. Kolarik, B.; Andersen, H. V.; Frederiksen, M.; Gunnarsen, L., Laboratory investigation of PCB bake-out from tertiary contaminated concrete for remediation of buildings. *Chemosphere* **2017**, *179*, 101-111.
99. Ho, W.; Hidy, G. M.; Govan, R. M., Microwave measurements of the liquid water content of atmospheric aerosols. *J. Appl. Meteorol.* **1974**, *13*, 871-879.
100. Leygraf, C.; Graedel, T.; *Atmospheric Corrosion*; Wiley-Interscience: New York, 2000.
101. Sjöberg, A.; Ramnäs, O., An experimental parametric study of VOC from flooring systems exposed to alkaline solutions. *Indoor Air* **2007**, *17*, (6), 450-457.
102. Chino, S.; Kato, S.; Seo, J.; Ataka, Y., Study on emission of decomposed chemicals of esters contained in PVC flooring and adhesive. *Build. Environ.* **2009**, *44*, 1337-1342.

103. Wang, L.; Liao, C.; Liu, F.; Wu, Q.; Guo, Y.; Moon, H.-B.; Nakata, H.; Kannan, K., Occurrence and human exposure of p-hydroxybenzoic acid esters (parabens), bisphenol a diglycidyl ether (BADGE), and their hydrolysis products in indoor dust from the United States and three east Asian countries. *Environ. Sci. Technol.* **2012**, *46*, 11584-11593.
104. Zhou, S.; Forbes, M. W.; Abbatt, J. P. D., Kinetics and products from heterogeneous oxidation of squalene with ozone. *Environ. Sci. Technol.* **2016b**, *50*, 11688-11697.
105. Duncan, S. M.; Sexton, K. G.; Turpin, B. J., Oxygenated VOCs, aqueous chemistry, and potential impacts on residential indoor air composition. *Indoor Air* **2017**, DOI: 10.1111/ina.12422.
106. Adams, R. I.; Lymperopoulou, D. S.; Misztal, P. K.; De Cassia Pessotti, R.; Behie, S. W.; Tian, Y.; Goldstein, A. H.; Lindow, S. E.; Nazaroff, W. W.; Taylor, J. W.; Traxler, M. F.; Bruns, T. D., Microbes and associated soluble and volatile chemicals on periodically wet household surfaces. *Microbiome*, **2017**, *5*, 128.
107. Downing, D. T.; Stranieri, A. M.; Strauss, J. S., The effect of accumulated lipids on measurements of sebum secretion in human skin. *J. Invest. Dermatol.* **1982**, *79*, 226-8.
108. Gowadia, H. A.; Settles, G. S., The natural sampling of airborne trace signals from explosives concealed upon the human body. *Journal of Forensic Sciences* **2001**, *46*, 1324-31.
109. Milstone, L. M., Epidermal desquamation. *J Dermatol Sci* **2004**, *36*, (3), 131-40.
110. Pandrangi, L. S.; Morrison, G. C., Ozone interactions with human hair: Ozone uptake rates and product formation. *Atmos. Environ.* **2008**, *42*, (20), 5079-5089.
111. Wisthaler, A.; Weschler, C. J., Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *PNAS* **2010**, *107*, 6568-6575.
112. Weschler, C. J.; Wisthaler, A.; Cowlin, S.; Tamas, G.; Strom-Tejse, P.; Hodgson, A. T.; Destailhats, H.; Herrington, J.; Zhang, J. J.; Nazaroff, W. W., Ozone-initiated chemistry in an occupied simulated aircraft cabin. *Environ. Sci. Technol.* **2007**, *41*, (17), 6177-6184.
113. Zhou, S.; Forbes, M. W.; Katrib, Y.; Abbatt, J. P. D., Rapid oxidation of skin oil by ozone. *Environ. Sci. Technol. Letters* **2016**, *3*, (4), 170-174.
114. Fenske, J. D.; Paulson, S. E., Human breath emissions of VOCs. *J. Air Waste Manag. Assoc.* **1999**, *49*, 594-598.
115. Travers, J.; Marsh, S.; Aldington, S.; Williams, M.; Shirtcliffe, P.; Pritchard, A.; Weatherall, M.; Beasley, R., Reference ranges for exhaled nitric oxide derived from a random community survey of adults. *Am J Respir Crit Care Med* **2007**, *176*, (3), 238-42.
116. Schmidt, F. M.; Vaittinen, O.; Metsälä, M.; Lehto, M.; Forsblom, C.; Groop, P. H.; Halonen, L., Ammonia in breath and emitted from skin. *J. Breath Res.* **2013**, *7*, (1), 017109.
117. Furukawa, S.; Sekine, Y.; Kimura, K.; Umezawa, K.; Asai, S.; Miyachi, H., Simultaneous and multi-point measurement of ammonia emanating from human skin surface for the estimation of whole body dermal emission rate. *J. Chromatogr. B* **2017**, *1053*, 60-64.
118. Norwood, D. M.; Wainman, T.; Liroy, P. J.; Waldman, J. M., Breath ammonia depletion and its relevance to acidic aerosol exposure studies. *Archives of Environmental Health* **1992**, *47*, (4), 309-313.

119. Filipiak W., Ruzsanyi V., Mochalski P., Filipiak A., Bajtarevic A., Ager C., Denz H., Hilbe W., Jammig H., Hackl M., Dzien A. and Amann A., Dependence of exhaled breath composition on exogenous factors, smoking habits and exposure to air pollutants. *J. Breath Res.*, **2012**, 36008.
120. Williams, J.; Stöner, C.; Wicker, J.; Krauter, N.; Derstroff, B.; Bourtsoukidis, E.; Klüpfel, T.; Kramer, S., Cinema audiences reproducibly vary the chemical composition of air during films, by broadcasting scene specific emissions on breath. *Sci Rep.* **2016**, *6*, 25464; doi: 10.1038/srep25464
121. US EIA (Energy Information Administration), Residential Energy Consumption Survey, 2015 at <https://www.eia.gov/consumption/residential/data/2015/#structural>, accessed November 7th, 2017.
122. Rackes, A.; Waring, M. S., Modeling impacts of dynamic ventilation strategies on indoor air quality of offices in six US cities. *Build. Environ.* **2013**, *60*, 243-253.
123. Du, L.; Batterman, S.; Godwin, C.; Rowe, Z.; Chin, J. Y., Air exchange rates and migration of VOCs in basements and residences. *Indoor Air* **2015**, *25*, 598-609.
124. Nazaroff, W. W.; Cass, G. R., Mathematical-Modeling of Chemically Reactive Pollutants in Indoor Air. *Environ. Sci. Technol.* **1986**, *20*, 924-934.
125. Weschler, C. J., Roles of the human occupant in indoor chemistry. *Indoor Air* **2016**, *26*, 6-24.
126. Terry, A. C.; Carslaw, N.; Ashmore, M.; Dimitroulopoulou, S.; Carslaw, D. C., Occupant exposure to indoor air pollutants in modern European offices: An integrated modelling approach. *Atmos. Environ.* **2014**, *82*, 9-16.
127. IOM (Institute of Medicine). 2011. *Climate Change, the Indoor Environment, and Health*. Washington, DC: The National Academies Press.