Indoor Chemistry: Materials, Ventilation Systems, and Occupant Activities

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Summary: Chemical processes taking place in indoor environments can significantly alter the nature and concentrations of pollutants. Exposure to secondary contaminants generated in these reactions needs to be evaluated in association with many aspects of buildings to minimize their impact on occupant health and well-being. Focusing on indoor ozone chemistry, we describe alternatives for improving indoor air quality by controlling chemical changes related to building materials, ventilation systems, and occupant activities.

Keywords: indoor chemistry, building materials, controls

1 Introduction

Indoor chemistry is now recognized as an important factor influencing occupant exposure to air pollutants, including ozone, organic compounds, and particulate matter. Here, we examine how ozone-initiated indoor reactive chemistry is influenced by building materials, ventilation systems and occupant activities. By investigating indoor chemistry in this way, we demonstrate the importance of intelligent decisions by each of the major stakeholders for controlling indoor air chemistry, and thereby improving the healthfulness of buildings.

2 Indoor reactive chemistry

Chemical transformations occur indoors. Such transformations influence the kind and amounts of pollutants to which people are exposed. To ensure healthy environments, those with responsibilities for indoor environmental quality should recognize the potential for chemical transformations and seek to limit their adverse effects.

An analogy exists with motor vehicle emissions into urban air. Primary pollutants are directly emitted from motor vehicles, including unburned and partially oxidized organics from fuel, nitrogen oxides from high-temperature combustion, and carbon monoxide from fuel-rich combustion.

In the atmosphere, primary pollutants may be chemically transformed. Nitrogen oxides and volatile organic compounds combine in the presence of sunlight to form secondary pollutants, among which are ozone, aldehydes, organic acids, and secondary particulate matter. Thus, if one seeks to understand the health risks associated with motor vehicle use, one should not only consider the primary emissions, but also the formation of secondary pollutants.

Evidence is emerging that the same principle applies for indoor environments. Several broad classes of chemical reactions may occur in indoor air. These include oxidation-reduction reactions, acid-base reactions, hydrolysis reactions, and decomposition reactions.

Ozone is an important carrier of oxidative chemical potential. Ozone from ambient air enters buildings along with ventilation. Some products used indoors also may generate ozone. Indoor ozone levels exceeding 20 ppb on a transient basis are not uncommon. Pollutants that react at a meaningful rate with ozone include nitrogen oxides, unsaturated volatile organics, terpenoids, and unsaturated fatty acids and oils. The products of ozone-initiated indoor chemistry are diverse, including free radicals (e.g., \( \text{OH} \)), peroxides (e.g., \( \text{H}_2\text{O}_2 \)), short-lived organics (e.g., ozonides), and stable organics (e.g., carbonyls).

Ozone-initiated indoor air chemistry causes both positive and negative effects. Homogeneous and heterogeneous ozone decomposition reduces human inhalation exposure to this respiratory irritant. On the other hand, the products of ozone-initiated chemistry also have adverse health effects. At present, it is not clear whether the net effects of uncontrolled ozone-initiated chemistry are beneficial or harmful. However, it is feasible to improve indoor air quality through engineering control that is targeted at simultaneously reducing ozone concentrations and limiting the formation of harmful byproducts.

The next three sections explore ozone-induced chemistry associated with building materials and furnishings, building ventilation systems, and occupant activities.
3 Building materials and furnishings

Ozone chemistry associated with building-material surfaces influences indoor air quality by removing ozone and by generating volatile byproducts. Volatile reactants emitted from construction materials and furnishings can also react homogeneously with ozone in air. We focus here on structural materials and furnishings that represent large surface areas in occupied spaces.

Carpet has a high specific surface area and, when present, tends to be among the largest surface sinks of ozone [1]. Weschler et al. found that ozone reacted with new carpet to form a variety of volatile carbonyl compounds [2]. Ozone appears to react with unsaturated fatty acids or their esters, generating formaldehyde and several other volatile aldehydes. For every 100 molecules of ozone consumed, from 5 to 70 molecules of carbonyl compounds are emitted, and of these, 1 to 15 molecules are formaldehyde [3]. Ozone uptake rates on four tested carpet samples varied by about a factor of two, and the carpet with the highest rate generated the most volatile carbonyl species. Older carpets in homes appear to retain their ozone reactivity, but produce far fewer byproducts [4]. It may therefore be feasible to manufacture carpets that can effectively remove ozone while minimizing byproduct formation. Identification of reactive surface coatings is key here and it has been suggested that reactive oils, from the manufacturing or processing of carpets, may be the cause of elevated byproduct emissions [3]. If so, then altered processes or reformulated oils might lead to a reduction in byproduct formation without significantly reducing ozone uptake rates.

With some exceptions, ozone tends to be relatively unreactive on hard flooring. Vinyl flooring is composed of polyvinylchloride, softened with phthalate plasticizers, neither of which is anticipated to react readily with ozone. Smooth plastics generally react weakly with ozone [5]. Similarly, hardwood floors with well-cured coatings should also be relatively unreactive [6]. Conversely, some reactivity is anticipated between ozone and linoleum, which is composed of cork, fillers and linseed oil. The unsaturated fatty acids and esters in linseed oil are subject to oxidation, forming volatile aldehydes and acids [7]. Tile floors appear to consume ozone at rates comparable to carpet [8], but are not expected to generate volatile organic byproducts.

Painted gypsum-board walls are modest sinks for ozone and generate formaldehyde with yields ranging from 0 to 0.28 [9]. Reiss et al. [10] measured ozone reaction probabilities on well-aged paint that were 1 to 2 orders of magnitude lower than for carpets. Although painted wallboard often constitutes most of the specific surface area in the occupied space of a building, aged paint appears to be a weaker overall sink for ozone than carpet [10]. Conversely, unpainted gypsum board exhibits useful indoor air chemistry characteristics, even while it may be undesirable architecturally. In particular, Poppendieck et al. [11] found that unpainted gypsum board is a strong sink for ozone and generates few volatile byproducts.

Although architecturally unusual, exposed brick, concrete and gravel appear to be desirable, along the lines of unpainted gypsum board. Simmons and Colbeck [8] show that aged or new bricks were the strongest ozone sinks among building materials tested, roughly 10 times more reactive than carpet. Concrete and gravel were at least as reactive as carpet. None of these are anticipated to produce volatile products, but this inference has not been experimentally verified. Glass, which is a prominent surface material in buildings, is a modest to poor sink for ozone, comparable to aged paint [6], and is also unlikely to be an important source of reactive byproducts.

Some materials emit organic compounds that can react with ozone in air, forming a suite of chemical byproducts. Wood products [12] and natural paints release terpenes, some of which react rapidly on time scales comparable to or faster than air exchange [13]. Irritating carbonyl compounds, organic acids, radicals and secondary particulate matter can be generated. Given the uncertain health consequences of terpene-ozone products, the deliberate use of such gas-phase reactions to reduce indoor ozone concentrations is not advisable. Longer drying times before installation might be used to reduce terpene emissions from wood.

4 Building ventilation systems

A well-maintained ventilation system is key to providing sufficient fresh air to building occupants. Yet, heating, ventilating, and air conditioning (HVAC) systems can negatively affect perceptions of indoor air quality [14], and loaded HVAC filters have been linked to sick building syndrome symptoms and decreases in work performance among building occupants [15]. Such impacts may be due, in part, to the influence of HVAC systems on indoor chemistry.

There is increasing evidence that important ozone-induced reactive chemistry can occur on the particles captured on HVAC filters. The total surface area of these particles can exceed 500 m² for a 0.6 m × 0.6 m filter [16], which is on the same order as the combined surface areas of return and supply duct walls in typical mid-sized office buildings [17]. Hyttinen et al. [18] reported field measurement of the ozone removal efficiency (η) equal to 4-26% for filters that had been in service for 6-12 months. They observed significant increases in η with increases in temperature and
relative humidity. Hyttinen et al. [19] found that initial values of η were proportional to dust loading on pre-filters and that both the dust loadings and ozone removal efficiencies were lower for fine filters employed downstream of pre-filters. Removal efficiency decreases in a matter of hours, with continued ozone exposure [20–22], but filters can experience partial to complete regeneration after days of isolation [21, 22]. Zhao et al. [22] observed an approximate convergence (reported as steady-state) to a mean value of η = 41% at an upstream ozone concentration of 80 ppb. One filter removed from a restaurant was visibly coated with oil and maintained η = 100% for the entire test period. Bekò et al. observed greater than 100% regeneration (η greater than initial η) following the isolation and heating of filters to 100 °C for 48 hours.

Given these results, can we conclude that soiled filters and other HVAC components are preferred because they help protect building occupants from ozone exposure? Particles that deposit on the surfaces of these components contain reactive compounds that release potentially irritating or harmful oxidized products. While Morrison et al. [23] observed only small amounts of ozone removal on several HVAC components, they concluded that such reactions could increase indoor concentrations by up to 20% of the odor thresholds for some aldehydes. Emissions of C4 to C10 aldehydes were greater for used than for new HVAC duct liners, suggesting the importance of particle deposition in HVAC ducts. Hyttinen et al. [20] observed the release of formaldehyde (HCHO) from HVAC filters exposed to ozone. Formaldehyde emissions were greatest during the first 70 minutes of each experiment and decreased rapidly thereafter. Molar yields (moles HCHO released per mole of ozone removed) were 0.08, 0.11, and 0.071 for unused fine filters, used fine filters, and “sooty” filters, respectively. However, by 150 to 360 minutes molar yields had decreased to 0.026, 0.028, and 0, respectively. Ozone removals for unused and used fine-particle filters were similar. Finally, making the conservative assumptions of a sustained HCHO molar yield of 0.1, η = 41% [22], outdoor ozone concentration of 100 ppb, and all building air exchange due to HVAC make-up air, the incremental increase in the building formaldehyde mixing ratio would be approximately 4 ppb.

HVAC surfaces may also promote ozone reactions with more volatile organic compounds. Fick et al. [24] observed a significant effect of duct surface area on the reaction of three monoterpenes in an experimental ventilation reach exposed to 25 to 75 ppb of ozone. Fick et al. [24] speculated that ozone reacts with galvanized metal HVAC ducts, leading to the formation of islands of ZnO that facilitate the catalytic dissociation of ozone, formation of monatomic oxygen and hydroxyl radicals, and a general increase in the reactivity of HVAC surfaces.

The operation and maintenance of HVAC systems also affects chemistry in the occupied space of buildings. For example, the relative humidity inside buildings is significantly affected by the presence and operation of an HVAC system. Relative humidity influences the extent of molecular water films on indoor surfaces, which in turn can affect the rate of ozone removal at those surfaces [25]. Furthermore, increased air flow through building zones should increase mass-transfer processes that facilitate ozone transport to surfaces, and changes in building interior temperature will affect chemical reaction kinetics within the occupied space.

Taken collectively, the published literature indicates that some ozone is removed by reactions in HVAC systems, that such removal is primarily due to reactions on HVAC filters, and that some oxidized products are released to the occupied space following ozone reactions in the HVAC system. The extent of ozone removal, and thus by-product generation, is likely affected by the nature of HVAC system operation, e.g., continuous operation versus cycling, switching off of HVAC system at nighttime or on weekends, and the frequency of filter replacement. However, the importance of ozone chemistry in HVAC systems remains unresolved. It is not clear whether ozone reactions in HVAC systems are as important as the effects of HVAC systems on chemistry in the occupied space of buildings. Additional research is needed to better understand the effects of temperature, relative humidity, filter face velocity, rates of continuous particle deposition, types of particles, and HVAC maintenance and operation, on both ozone removal and by-product releases in buildings. This is especially important given trends toward the use of in-situ ozone generators and zonal or whole-building fragrance releases that lead to an additional reactive load on HVAC systems.

Preventing ozone from interacting with HVAC surfaces appears to be a key strategy for controlling the adverse effects of indoor ozone chemistry. Mechanically-ventilated HVAC systems are ideally suited to “first pass” control of ozone, and thus for potential reductions in the extent of indoor chemistry in both HVAC systems and a building's occupied space. While the extent of benefit gained from the former remains unclear, the latter should be of significant benefit to the quality of indoor air.

5 Occupant activities

Building occupants can contribute significantly to the indoor levels of reactive chemicals by activities such as cooking, smoking, and using fragrance products. Certain maintenance activities may also contribute, such as cleaning, floor waxing, and polishing metal surfaces. These activities may
increase indoor levels of certain reactive chemicals, such as nitrogen dioxide from unvented combustion [26] and terpenes from cleaning products and air fresheners [27]. Even actions like burning a scented candle introduces a wide variety of compounds into the indoor environment [28], some of which may be reactive.

In some cases, occupant activities are a source of primary pollutants that are themselves harmful. In other situations, the chemicals released are not necessarily harmful themselves. However, volatile and semivolatile organic chemicals (VOCs and SVOCs) emitted during various activities can react with ozone and other reactive atmospheric constituents to yield gaseous pollutants and airborne particulate matter.

Cleaning and fragrance addition
Scents can influence the sense of well being and “bad” or offensive smells can have negative impacts on personality and/or work performance. An increasing number of consumer products promise “better” smelling indoor air by the introduction of fragrances into the indoor environment via heated oils, solids that release chemicals via sublimation, scented cleaners, and candles. The terpenes or terpenoids used for this purpose are cyclic alkenes (i.e., they contain at least one carbon-carbon double bond) that may also contain an alcohol group. Sources of these compounds are present in essential oils from flowers (lavender), pine trees, orange peel and other vegetation sources. Limonene, α-pinene, α-terpineol, geraniol, are just a few of the many compounds that are introduced into the indoor environment in this manner [27, 29]. Semivolatile organic compounds (SVOCs) can sorb to surfaces (countertops, tables, or floors) by direct application or after being initially released into the gas-phase. Ozone can react with terpenes in the gas-phase as well as on surfaces, yielding stable gas-phase products that could be more irritating than their precursors, such as formaldehyde, acetaldehyde, glyoxal, methyl glyoxal, glycolaldehyde, OH radical and aerosols [30-32]. Sustained ozone consumption in a simulated indoor environment was measured for a period of 10-12 hours following a short-term cleaning event with a terpene-based product, suggesting that reactive chemistry can persist for extended periods after the initial terpenoid release [33].

Ozone and secondhand tobacco smoke
In addition to the direct deleterious effect of exposure to secondhand tobacco smoke (SHS), indoor chemical processes involving SHS components and ozone can increase occupant exposure to irritant air contaminants. The deliberate generation of O2 by “air purifiers” is promoted by some to reduce the concentration of indoor pollutants in general, and for SHS odor abatement in particular, despite some evidence suggesting that this is an unhealthful practice. Ozone reactions with volatile constituents of SHS (such as isoprene, 2,5-dimethylfuran, pyrrole, styrene, 2-furancarboxaldehyde and d-limonene) are depleted by ozone yielding higher concentrations of several aldehydes that include acetaldehyde, formaldehyde, hexanal, benzaldehyde, nonanal and decanal [34]. Ventilation is the most common removal mechanism for volatile SHS constituents and for aerosol particles emitted during smoking. However, a significant amount of semi-volatile chemicals sorb to indoor surfaces and remain in contact with indoor air during extended residence times. Indoor surfaces of buildings and residences where smoking is habitual can become heavily contaminated with SHS. Complex physicochemical transformations of SHS components that occur after smoking takes place — referred to as aging — affect both short-term and long-term occupant exposure patterns. Aging of residual components of tobacco smoke deposited on indoor surfaces can generate secondary pollutants over periods ranging from a few hours to several months. Hence, heterogeneous indoor chemistry can be an important factor influencing exposure to SHS constituents. For example, large amounts of nicotine are present in SHS. This alkaloid has a long residence time in homes and buildings owing to its strong sorption to indoor surfaces [35]. It reacts with ozone to generate volatile aldehydes (formaldehyde, nicotinealdehyde), together with other volatile and semivolatile species (N-methylformamide and cotinine, respectively) that can be emitted into the gas phase [36]. Hence, ozone-surface reactions of nicotine and other sorbed tobacco compounds can potentially be a long-term source of irritant airborne chemicals.

Ozone and cooking residues
Surfaces are usually impacted by residues from cooking and activities related to cooking and food handling. Oil residues, for example, contain unsaturated fatty acids that can react with ozone. Similarly, the formulation of soaps and detergents includes fatty acids and esters that are also reactive with ozone. Nonanal and hexanal emissions were observed in a controlled experiment where ozone was put in contact with cooking oil, bath soap and a liquid detergent applied to a laminated countertop [37]. Exposure of real indoor surfaces to ozone in a field study also exhibited very high nonanal emissions from a kitchen counter. In some cases, other indoor surfaces exhibited high emissions owing to the reaction of ozone with surface constituents, such as the case of carpet [4].
6 Control opportunities

Several approaches are available for controlling ozone-induced indoor reactive chemistry. One strategy is to limit the introduction of ozone into indoor air. Activated carbon filters are a proven technology for effectively reducing ozone in ventilation supply air [38]. Source-oriented controls on photocopyers and air filters that generate ozone are also appropriate. Guideline values for indoor ozone to limit secondary pollutant formation have not been established. It is conceivable that appropriate limits to control indoor reactive chemistry will be lower than those aimed at protecting human health from the direct adverse effects of ozone exposure.

A second strategic approach is to select indoor materials with attention to their effect on ozone-initiated chemistry. The best materials in this regard might be those that scavenge ozone effectively, but do not produce harmful or irritating volatile byproducts as a result. Second best might be materials that are either relatively inert with respect to ozone-initiated chemistry or that react with ozone but have relatively low yields of harmful byproducts. The information needed to support this strategic approach is not yet available. Efforts have been established in several countries to improve the healthfulness of indoor environments through emissions testing and labeling programs [39]. These efforts focus entirely on characterizing primary pollutant emissions. Analogous effort to characterize secondary emissions from materials owing to reactive chemistry appears warranted.

Building occupants can impact exposure in the indoor environment by their choices of consumer products and activities. For manufacturers, it may be possible to reformulate consumer products to minimize formation of irritant reaction products or even redesign indoor surfaces to more effectively remove reactive chemicals or irritants from the indoor environment.

The health risks associated with indoor environments may be influenced by reactive chemistry. Because of this, health-protective public policies that are aimed at source characterization and control must incorporate appropriate information about the formation of secondary pollutants and their relationship to source emissions. Research tools and techniques for studying the formation of secondary pollutants are available. To date, these have been applied, but only on a limited basis, to understand the nature, scale, and significance of secondary pollutant formation owing to reactive chemistry in indoor air. Devising practical methods of incorporating this emerging information into practice remains a challenge.

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References


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