ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW

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Illuminating the dark side of indoor oxidants

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The chemistry of oxidants and their precursors (oxidants*) plays a central role in outdoor environments but its importance in indoor air remains poorly understood. Ozone (O_3) chemistry is important in some indoor environments and, until recently, ozone was thought to be the dominant oxidant indoors. There is now evidence that formation of the hydroxyl radical by photolysis of nitrous acid (HONO) and formaldehyde (HCHO) may be important indoors. In the past few years, high time-resolution measurements of oxidants* indoors have become more common and the importance of event-based release of oxidants* during activities such as cleaning has been proposed. Here we review the current understanding of oxidants* indoors, including drivers of the formation and loss of oxidants*, levels of oxidants* in indoor environments, and important directions for future research.

Environmental significance

A clear understanding of oxidants and their precursors in indoor environments is necessary to constrain much of the chemistry that can occur indoors. Most indoor oxidant studies have focused on ozone, since oxidation indoors was thought to be dominated by ozone reactions. Recent measurements have demonstrated that other oxidants could be of equal or greater importance under many conditions, and that episodic chemistry (*e.g.*, initiated by cooking or cleaning) could be critical to oxidation indoors. This review describes the considerations important for indoor oxidant formation and loss, as well as observations and models of oxidants indoors. Important areas of future research are also identified.

Introduction

Indoor oxidants and their precursors (the combination of which will be referred to as "oxidants*") are widely studied in atmospheric science, but are considerably less explored in indoor environments.[1] There are many important differences between indoor and outdoor environments including differences in sources of oxidants*, the intensity and wavelength of light available, increased surface area-to-volume ratios, and the increased likelihood of human exposure.[1] Photochemistry, initiated by sunlight at wavelengths shorter than ~320 nm, drives oxidation outdoors. These high energy photons are not generally available indoors, so the oxidizing capacity has been thought to be controlled by physical transport and non-photochemical reactions (also known as "dark chemistry"). This results in very different oxidizing atmospheres indoors and outdoors. While hydroxyl radicals (OH) are the most important oxidants outdoors, their concentrations are generally expected to be very low indoors, and ozone (O_3) is the only oxidant that has been widely investigated. Because of the prevalence of O_3 and nitrogen dioxide (NO_2) in several indoor environments, the

importance of the nitrate radical (NO_3) in indoor oxidation has also been suspected.[2] Recent studies suggest that photolysis of molecules that absorb light at wavelengths longer than 320 nm, such as nitrous acid (HONO) and formaldehyde (HCHO), may lead to higher indoor OH concentrations than previously expected.[3–6] It has also recently been shown that human activities including use of bleach can lead to the formation of numerous reactive chlorine species, many of which are photo-labile and could form Cl indoors.[7,8] While Cl is not often considered a major oxidant outdoors, recent work has shown that it can contribute significantly to oxidation chemistry under some conditions,[6,7] although its importance for the indoor oxidizing capacity is largely unexplored. The objectives of this review are to describe: (i) environmental factors important for oxidation chemistry indoors; (ii) the importance of different oxidant species and their precursors indoors; and (iii) future research directions to understand the extent and impacts on indoor oxidative chemistry.

Indoor environmental factors affecting oxidants

Sources of oxidants indoors

Chemicals present outdoors can impact oxidant* levels and chemistry indoors (*e.g.* ref. 9). The extent of this effect depends on pollutant levels outdoors, the air exchange rate, and penetration through the heating, ventilation, and air-conditioning

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*Environ. Sci.: Processes Impacts*, 2019, **21**, 1229–1239 | **1229**

(HVAC) system (mechanical ventilation) or building enclosure (leakage). Numerous additional sources of particles and gas-phase compounds—both direct and indirect—exist indoors. These have been reported comprehensively in several reviews (e.g. ref. 10) and will be discussed only briefly here in the context of oxidants*. The components and contents of indoor environments, including building materials[11–14] and electronics,[15] are a direct source of indoor oxidant* emissions. Human and microbial occupants of indoor environments can also act as a direct source of oxidants*, such as acetaldehyde and other carbonyls.[12,16,17] Human activities can be a major source of indoor oxidants*. For example, oxidants* have been detected in simulated and real indoor environments after cleaning or disinfection of surfaces[7,18,19] and water,[20] as well as after the use of air fresheners.[21] Cooking is an important source of indoor oxidants*,[12,22–24] as is burning of candles or incense,[12,25] cigarette smoking,[12,26] and vaping.[27] Several types of air purifiers can increase indoor O_3 levels, either deliberately (e.g., O_3 generators) or as a byproduct of their operation (e.g., ion generators, electrostatic precipitators, and some UV-lamp containing air

cleaners).[28–30] Specific devices may emit oxidants other than O_3.[31] Most emission sources are constrained only to select chemicals (e.g. reactive chlorine species) under specific conditions (e.g. bleach cleaning) and may depend substantially on the context and environment investigated. As a result, significant uncertainty in primary emissions indoors remains.

Secondary oxidant formation

In addition to direct emission and transport from outdoors, oxidants* can be formed chemically indoors. For example, a dominant OH source indoors may be reactions between O_3 and alkenes.[9] Photochemistry (especially of HONO) is thought to also be an important indoor OH source under some conditions.[32–35] Due to the high surface areas encountered indoors (discussed in more detail below), heterogeneous chemistry may be very important. Some reactions of known importance are the disproportionation of NO_2 on surfaces to form HONO[36] and reactions of O_3 with components of skin oil.[37] Heterogeneous reactions on indoor surfaces are even less well understood than
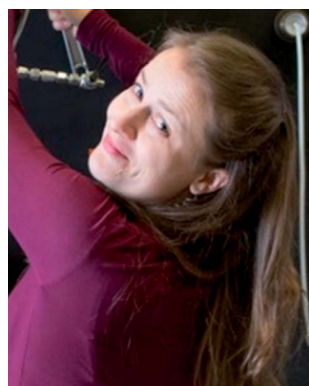
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gas-phase reactions, largely due to the large range of materials present indoors and the unknown, and likely variable, nature of surface soiling.

Light conditions indoors

Outdoors, oxidant chemistry is primarily initiated by photons in the 290 to 400 nm range. Indoors, solar radiation at wavelengths shorter than ~330 nm is completely attenuated by windows (Fig. 1).[4,22,33–35] This precludes many photochemical reactions that are important outdoors, including the formation of hydroxyl radicals (OH) by O_3 photolysis. Recent studies suggest that OH may be formed photochemically indoors from species such as HONO and HCHO that absorb at longer wavelengths,[4,7,22,34,38] but the overall importance of photochemistry in indoor chemistry remains unclear. Different factors govern photochemical reaction rates indoors and outdoors, and different reactions are likely to be important. While the sun is generally the only important light source outdoors, this is not the case indoors. As shown in Fig. 1, artificial lights including fluorescent and incandescent halogen lamps emit at wavelengths short enough to affect photolysis of several chemicals likely to be important oxidants* indoors. Spectral profiles, and therefore photolysis rates, vary depending on the light source and the presence and construction of light coverings. Outdoors, photon fluxes will be uniform within a given volume of air unless the light is attenuated or reflected (e.g. by clouds, trees, or the ground). Solar photon fluxes are also expected to be relatively constant in directly illuminated indoor regions. However, the volume of air illuminated may be small relative to the total volume, and the volume of illuminated air (as well as its location) may change more dramatically over the course of the day than that observed outdoors due to the placement of windows. Photon fluxes from most compact light bulbs

decrease as approximately r^{-2} with increasing distance from the source, which leads to large gradients in photon fluxes.[34] Other factors are likely to additionally impact the photon flux, including lamp manufacturer, style, wattage, number of bulbs in a fixture, and coverings such as lamp shades.[34] Due to the large anticipated spatial heterogeneity of photon fluxes indoors, mixing ratios of photochemically formed species may also display large spatial heterogeneity.

Photochemistry follows a clear diurnal pattern outdoors, with additional variability introduced by clouds or particulate matter, as well as by changes in the solar zenith angle (SZA) in different seasons. Temporal trends indoors are much more variable and depend on building construction and human activity. The construction of buildings influences the distribution of windows and artificial lights, which will determine the photon fluxes in the actinic region at different times of the day. Human activity – e.g. closing blinds and turning on lights in occupied rooms – will play a large role in determining the extent of photolysis occurring at any given time. Given the different emission spectra of artificial lights compared to that of sunlight in the ultraviolet region, different photochemical reactions may dominate when sunlight vs. artificial lights is the primary illumination source (e.g. during the day vs. during the evening). Indirect (i.e. diffuse and scattered) light contributes to photon fluxes outdoors, depending on factors such as cloud cover, SZA, and surface albedo. Reflected light may also impact photon fluxes indoors, though this has been examined in only one laboratory study, which observed that reflected light contributed less than 5% of total light in a laboratory illuminated by sunlight filtered through a window.[33] It is probable that, as is the case outdoors, the importance of indirect light indoors will depend on variables such as the SZA and the colour and material of surfaces.

Surface area

Indoors, the available surface area is much greater than that outdoors for a given volume of air, and heterogeneous reactions may affect indoor oxidants*. Indoor surfaces are known to be an important sink for O_3. The reactive uptake of O_3 by indoor surfaces including glass, green building materials, drywall, HVAC ducts, office materials and contents, carpets, and skin oil and skin oil proxies has been investigated by several research groups,[37,43–60] but uptake kinetics of many of the diverse surfaces found in indoor environments are not known. The reactive uptake of HOCl by skin oil proxies was recently studied,[61] but little literature about the reactive uptake of oxidants other than O_3 by indoor surfaces is available. Relationships between indoor surface properties and uptake coefficients of O_3 or other oxidants* have not been established.[62,63] It is possible that there is little variance in the uptake efficiency of oxidants* by different indoor surfaces due to films that coat indoor surfaces.[64,65] These surface coatings are dependent on indoor concentrations of film components and surface properties and have been studied for only a narrow subset of compounds and surfaces, e.g., organic films formed by the deposition of semivolatile organic compounds (SVOCs) on impermeable glass surfaces.[65] The effect of the indoor surface coatings relative to the underlying surfaces
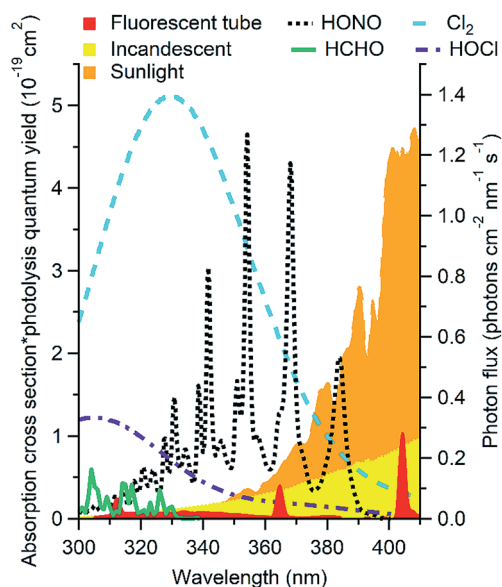

Fig. 1 Photon flux of common indoor light sources (right axis) shown with the product of absorption cross section and photolysis quantum yield of likely indoor oxidants* (left axis). Data from ref. 34, 39–42.

on gas phase oxidant* levels can be critically important. Further, most investigations of surface chemistry have focused on visible surfaces. However, most indoor surfaces are hidden, including the vast surface areas of indoor textiles and other porous materials,[56,58] and unseen surfaces in building interstitial spaces (e.g., wall cavities), buffer zones (e.g., dropped ceiling spaces, attics and crawlspaces), and HVAC systems. The role of oxidant* interaction with hidden spaces has been explored for narrow sets of materials (e.g., ref. 53), often only for O_3 and with little acknowledgement of soiling.

Physical processes

Exchange with outdoor air is an important driver of indoor oxidant* concentrations. In general, more rapid exchange with outdoor air will lead to diminished indoor concentrations of indoor emitted oxidants* and increased concentrations of oxidants* that originate outdoors. The nature of the air flow is potentially important: in some buildings air leaks through the enclosure (leakage or infiltration) where oxidants* may react or be deposited. The penetration factors for contaminants through building enclosures have generally only been studied for O_3 and for particles (e.g., ref. 66 and 67), but are potentially important for other oxidants. Air exchange is also provided by HVAC systems (mechanical ventilation) which can serve as sources and sinks for oxidants* (e.g., ref. 68 and 69). HVAC systems often recirculate some portion of the air in a building which can lead to loss within the system and serve to increase mixing and interzonal transport of oxidants throughout the building. Air exchange and HVAC system operation are also important factors in local indoor air velocities and mixing, which can promote oxidant interaction with surfaces.

Which oxidants* are important indoors?

The majority of indoor oxidant* studies have been performed in non-residential buildings such as offices and classrooms.

Relatively high air exchange rates (often of the order of 5 h^{-1}) in these environments lead to significant influence of outdoor air on the indoor air composition. Ozone is generally the dominant oxidant* measured in these locations.[9] Conversely, we know surprisingly little about the indoor oxidizing capacity in occupied residences. A low AER (often < 0.5 h^{-1}) reduces the influence of outdoor air, and indoor oxidant* sources such as gas appliances can elevate nitrogen oxide levels significantly compared to those detected outdoors and in commercial buildings.[5,22] Table 1 lists the sources and mixing ratios of some oxidants* that may be important in residential buildings. The mixing ratios are those reported in North American residences to give an idea of the range of possible oxidant* levels. Indoor mixing ratios of some oxidants* may be different in other regions (e.g. indoor HCHO mixing ratios in excess of 100 ppbv have recently been reported[14] in Chinese residences). The mixing ratios of all oxidants* listed are subject to high uncertainty due to factors including a lack of measurements (especially highly time-resolved measurements) and a poor understanding of indoor sources and sinks. Reported or predicted ambient mixing ratios for most of the oxidants* in Table 1 span two or more orders of magnitude; this prevents accurate prediction of the oxidizing capacity in general for residences.
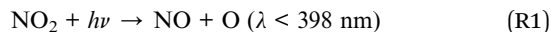
Nitrogen oxides

Nitrogen oxides ($NO_x = NO + NO_2$) are not oxidants themselves, but play a critical role in oxidant cycling, as both oxidant sources and sinks. These compounds are emitted from combustion processes, resulting in levels of up to 10s of parts-per-billion-by-volume (ppbv) in polluted and <1 ppbv in remote outdoor environments. Indoor combustion sources (e.g. gas appliances)[22,24] and transport from outdoors[3,5,80] can contribute to NO_x levels indoors. The photolysis of NO_2 could contribute to the formation of O_3:

Table 1 Measured average levels of indoor oxidants* in North American residences, major known production sources, and sources of uncertainty. Measurements are reported in parts-per-billion-by-volume (ppbv), defined as 10^{-9} mol mol^{-1}. At 25 °C and 1 bar, 1 ppbv is equivalent to approximately 2.5×10^{10} molecules per cm^3

Oxidant	Mixing ratios (ppbv)	References	Major indoor sources	Sources of uncertainty
Nitrogen dioxide (NO_2)	1–394	Ref. 22 and references therein	Emission from gas appliances and transport from outdoors	Few highly time-resolved measurements; measurements subject to HONO interference
Nitric oxide (NO)	0.8–400	Ref. 22 and references therein	Emission from gas appliances and transport from outdoors	Few measurements
Nitrous acid (HONO)	<1–35.9	Ref. 22 and 70 and references therein	Emission from gas appliances and surface reactions of NO_2	Few measurements
Ozone (O_3)	<1–73	22,71–78	Transport from outdoors	Commonly used levels measured in non-residential environments
Formaldehyde (HCHO)	10–70	Ref. 12 and references therein	Building and furnishing materials and residential combustion	Few highly time-resolved measurements
Nitrate radical (NO_3)	$<4 \times 10^{-3}$	79	$NO_2 + O_3$	Only one measurement

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$$NO_2 + h\nu \rightarrow NO + O \ (\lambda < 398 \ nm) \qquad (R1)$$

$$O + O_2 \rightarrow O_3 \qquad (R2)$$

To our knowledge, the importance of this chemistry has never been demonstrated indoors, although Kowal *et al.* predicted that ozone levels in indoor locations illuminated by sunlight could be 5 times greater than those in shaded regions due to NO_2 photolysis.[34] In the presence of NO, this O_3 can react to re-form NO_2:
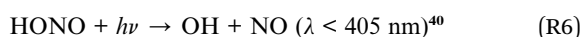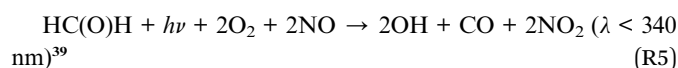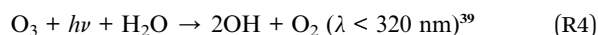
$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (R3)$$
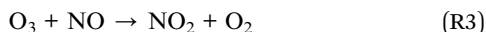
The reduction of O_3 levels during use of a gas stove has been attributed to titration by NO (R3).[29]

Ozone

Photochemistry outdoors generates O_3, a major component of photochemical smog. Levels of 10s to 100s of ppbv of O_3 are common in polluted outdoor environments. The dominant source of indoor O_3 is outdoor air, with O_3 levels in many indoor environments closely tracking outdoor levels.[9] Direct O_3 emissions from human activities, including use of office equipment (*e.g.*, photocopiers[81]) and devices marketed as air purifiers (*e.g.*, ref. 28 and 30), can occur. Several studies suggest that O_3 is an important oxidant in many indoor environments, and the dominant OH source is expected to be dark reactions between O_3 and unsaturated organics.[9] Indoor-to-outdoor ratios (I/O) of O_3 in the absence of major sources or sinks are commonly between 0.2 and 0.7 and change as a function of the air exchange rate (AER).[82] Thus, in residences that use natural ventilation or have a high AER, O_3 levels are likely to be higher. Similarly, under conditions of direct emission (*e.g.* office equipment or O_3-emitting air cleaners), O_3 could be an important oxidant. Some (albeit relatively rare) HVAC systems may also contain activated carbon air filters that can effectively remove O_3 from indoor environments.[83,84] Furthermore, residences are more likely to contain cooking appliances that can act as a source of NO. As described above, high NO levels titrate O_3 from indoor environments through reaction (R3).[29]

Hydroxyl radicals

The hydroxyl radical (OH) is the dominant oxidant in the daytime outdoor atmosphere. Dominant fates of OH include abstraction of a hydrogen from or addition to organic molecules, as well as reaction with NO_2. Production of OH outdoors from various sources has been the subject of many studies. The vast majority have been conducted at low latitudes or in mid-high latitude summer, where photolysis of O_3, carbonyls (*e.g.* HCHO), and HONO are the dominant sources (*e.g.* ref. 85–87):

$$O_3 + h\nu + H_2O \rightarrow 2OH + O_2 \ (\lambda < 320 \ nm)^{[39]} \qquad (R4)$$

$$HC(O)H + h\nu + 2O_2 + 2NO \rightarrow 2OH + CO + 2NO_2 \ (\lambda < 340 \ nm)^{[39]} \qquad (R5)$$

$$HONO + h\nu \rightarrow OH + NO \ (\lambda < 405 \ nm)^{[40]} \qquad (R6)$$

A few studies have examined the impact of OH sources under low-light outdoor conditions that may be more like conditions indoors. For example, during spring in Los Angeles, photolysis of HONO dominates OH production from dawn to mid-morning.[87] Similarly, studies examining OH formation during high-latitude winter showed that OH production was dominated by HONO or carbonyl photolysis.[88,89] Formation of OH is also possible in the absence of light through oxidation reactions of O_3 with unsaturated organics, which are a major source of OH outdoors at night:[87]

$$O_3 + alkene \rightarrow R' + OH + RO_2 \qquad (R7)$$
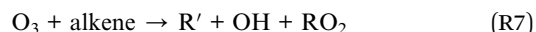
Under the low light conditions indoors, reaction of O_3 with organics has been historically considered the dominant oxidation process (*e.g.*, ref. 90). Studies proposing this have primarily focused on high-O_3 indoor environments. As described above, in many indoor environments (and especially in residences) O_3 levels are low. Under these conditions, production of OH from other sources can compete with or dominate OH production from the reaction of O_3 with unsaturated organics.[5]

Formaldehyde (HCHO) is known to be present in many indoor environments. The levels, sources, and impacts of indoor HCHO have been extensively reviewed by Salthammer *et al.*[12] Indoor HCHO mixing ratios are in the range of tens to hundreds of ppbv and indoor sources include building materials (*e.g.* pressed-wood products), combustion (*e.g.* cooking and cigarette burning), human metabolism and heterogeneous or gas-phase oxidation of organics.[12] It is possible that HCHO could be photolyzed indoors and generate OH radicals (R5). This has not yet been investigated experimentally, but calculations based on measured photon fluxes and estimated indoor HCHO and NO mixing ratios suggest that photolysis of HCHO initiated by fluorescent tubes could be an important indoor OH source under some conditions.[34] Analogously, other volatile carbonyl compounds could be photolyzed and lead to OH formation, including acetaldehyde, acetone, and glyoxal.[34] These compounds are emitted from similar sources as HCHO.[25-27,91]

High levels of HONO have been measured in a few indoor environments, including residences, laboratories, and offices.[22,70,92] The few studies performed in residences report indoor HONO levels 5–10 times higher than those outdoors. As discussed above, HONO photolysis could be an important OH source indoors under some conditions. Sunlight filtered through windows will generally be the most important light source, but Kowal *et al.* have predicted that artificial light sources including halogen, incandescent, and fluorescent bulbs could also initiate photochemistry, especially in close proximity to the source.[34] Recent studies have reported HONO levels that vary from <1 ppbv to over 30 ppbv in residences across North America.[22,70] More studies are required to better understand indoor HONO levels, especially time-resolved levels. Accurately measuring HONO is challenging, but recent advances in instrumentation present an opportunity for more widespread measurements indoors.
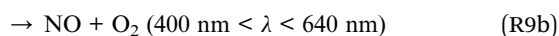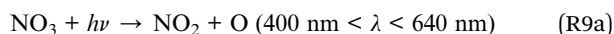
Several modelling studies have targeted OH concentrations indoors. Predicted concentrations typically range from 1 to 5 $\times$ 10^5 molecules per cm^3.[3,5,90] The first measurement of OH indoors was made by Weschler and Shields using an indirect technique to obtain a time-integrated concentration. They observed OH concentrations of $\sim 7 \times 10^5$ molecules per cm^3 in a commercial building that had elevated O_3 and alkenes as well as a moderate AER.[93] Under most conditions, predicted levels of OH indoors are below the detection limit of the instrument used to quantify OH at high time resolution in the outdoor environment (fluorescence assay by gas expansion, limit of detection 6.5×10^5 molecules per cm^3).[31] Two high time resolution OH measurements have been made in cases where OH concentrations exceed this value. In the first case, concentrations up to 1.8×10^6 molecules per cm^3 were observed in the presence of high HONO levels in a classroom in France in the summer.[32] This concentration is comparable to typical outdoor concentrations of OH.[24] The *in situ* technique has also been applied to an office in the presence of a commercially available air purifier.[31] Under background conditions, OH concentrations were close to or below the limit of detection of the instrument. During air purifier operation, OH concentrations increased to 2 $\times 10^7$ molecules per cm^3.

Nitrate radicals

Nitrate radicals (NO_3) can abstract a hydrogen from or add to organics. These radicals are formed in environments with high O_3 and NO_2:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R8}$$
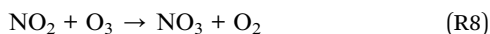
Outdoors, accumulation of NO_3 can only occur at night because it is rapidly photolyzed:[39]

$$NO_3 + h\nu \rightarrow NO_2 + O \ (400 \ nm < \lambda < 640 \ nm) \tag{R9a}$$

$$\rightarrow NO + O_2 \ (400 \ nm < \lambda < 640 \ nm) \tag{R9b}$$

The formation of NO_3 cannot occur in areas with appreciable NO (*e.g.* above soil surfaces[94]), which prevents the accumulation of NO_3 radicals in two ways: by (i) titrating O_3 (R3) and preventing NO_3 radical formation through (R8) and (ii) depleting any NO_3 radicals formed by conversion to NO_2:

$$NO_3 + NO \rightarrow 2NO_2 \tag{R10}$$
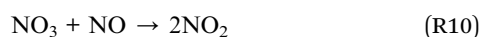
The importance of NO_3 radicals in indoor oxidation has long been suspected.[2] In the past few years, models have predicted very low NO_3 levels indoors. Using a box model, Carslaw observed NO_3 levels <0.03 parts-per-trillion-by-volume (pptv).[3] Similarly, Waring and Wells used a time-averaged model to show that NO_3 radicals could be present at mixing ratios of ~ 0.001 to 0.01 pptv in residences.[5] Zhou *et al.* recently predicted steady-state NO_3 concentrations in a residence based on measured O_3, NO_2, and NO mixing ratios.[22] Low O_3 and high NO levels led to the conclusion that NO_3 levels would be negligible in residences under most conditions. A subsequent study made the first direct measurements of NO_3 radicals in a residence.[79] As predicted, NO_3 radical mixing ratios were below the detection limit (1.5 pptv) under most conditions. In scenarios where O_3 levels were artificially increased using a commercial O_3 air purifier, NO was completely titrated through reaction (R3) and average NO_3 mixing ratios of 3–4 pptv were observed. These studies suggest that NO_3 can be an important indoor oxidant if O_3 levels are high and NO levels are low. The high O_3 and low NO conditions required for NO_3 levels to be significant are uncommon in residences, but may exist at times, for example under natural ventilation (with significant influence from high O_3 and low NO outdoor air), or during the use of ozone air purifiers.
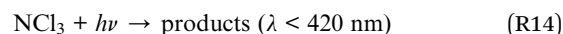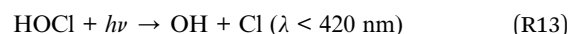
Chlorine atoms

Chlorine atoms (Cl) are 1–2 orders of magnitude more reactive than OH and can abstract a hydrogen atom from or add to organics. The occurrence of Cl outdoors is driven by the formation and/or emission of photolabile chlorine atom precursors such as nitryl chloride ($ClNO_2$) and molecular chlorine (Cl_2). These compounds can be photolyzed under illumination by visible light to produce Cl:[39,95]

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \ (\lambda < 475 \ nm) \tag{R11}$$

$$Cl_2 + h\nu \rightarrow 2Cl \ (\lambda < 493 \ nm) \tag{R12}$$
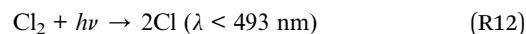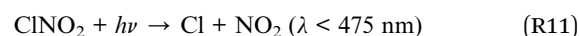
Like HONO described above, Cl_2 and $ClNO_2$ are photolabile under low-light outdoor conditions and have been shown to contribute up to half of the primary radicals in an urban area during the morning[87] and to be a significant contributor to total radicals in continental mid-latitude winter.[88]

Only very recently has production of Cl atoms been considered in indoor environments. After application of bleach to a laboratory floor, up to 481 ppbv of Cl_2 was observed, along with $ClNO_2$ and other photolabile chlorinated species (*e.g.* hypochlorous acid (HOCl) and nitrogen trichloride (NCl_3)).[7,39,96,97]

$$HOCl + h\nu \rightarrow OH + Cl \ (\lambda < 420 \ nm) \tag{R13}$$

$$NCl_3 + h\nu \rightarrow products \ (\lambda < 420 \ nm) \tag{R14}$$

A model incorporating the reactive chlorine species released from mopping with bleach predicted the formation of Cl through photolysis by window-attenuated sunlight. Modelled Cl concentrations were up to $\sim 2 \times 10^5$ molecules per cm^3 and were of a similar magnitude to those of predicted OH.[7] Typical lights used indoors could also photolyze these reactive chlorine species to form Cl.[8,35] These levels cannot be verified through measurement since there is currently no analytical technique capable of measuring atmospheric Cl. Typical levels of chlorinated species are not well-understood indoors and appear to be limited to specific activities or environments, such as bleach use[7] and chlorinated swimming pools,[20] respectively. The photolability of Cl_2, $ClNO_2$, HOCl, and NCl_3 under visible wavelengths suggests that Cl atoms could play an important role in indoor oxidation.

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An additional oxidation pathway can be derived from the reaction of chlorinated compounds with unsaturated organics. Schwartz-Narbonne et al.[61] recently demonstrated the heterogeneous oxidation of skin-oil proxies by HOCl, where reactions could occur fast enough to effectively compete with loss via transport of HOCl. This is consistent with the unidentified loss process of HOCl observed by Wong et al. following bleaching.[7]

Potential effects of changing policy and human behaviour on indoor oxidant levels

The indoor oxidizing capacity may change substantially in the future, due to new policies or regulations, changing construction practices, or human behaviour. This has been observed in the past through substantially decreased indoor O_3 levels in the United States in response to the passing of the Clean Air Act in 1997. Average O_3 levels in houses prior and subsequent to 1997 were of the order of 5–73 ppbv (ref. 71, 76 and 78) and <2 ppbv,[73,77] respectively. This Act targeted outdoor air quality but had clear effects on indoor oxidant levels. Another example is the current movement by several local and national governments to improve outdoor air quality by restricting wood burning indoors. An example of policy directed toward indoor air quality that could change indoor oxidant* levels is the recent move by some jurisdictions (including Canada and the United States) to regulate HCHO emissions from composite wood products used in building materials. While indoor HCHO levels in North America and western Europe are generally fairly low (~20 ppbv),[12] they can be higher in some cases, such as in newly constructed homes.[13] Levels of the order of 80 ppbv and as high as 590 ppbv were measured in emergency trailers supplied by the government of the United States as temporary housing for those displaced by Hurricane Katrina in 2006.[98] In addition to reducing people's direct exposure to HCHO, regulating emissions from building materials could reduce photochemical radical formation, since HCHO photolysis has been predicted to be an important OH source under some lighting conditions.[34] These effects would be even greater in other areas of the world, such as China, where indoor HCHO levels exceeding 1000 ppbv have been measured in newly constructed buildings.[14] Although most indoor O_3 comes from outdoors, some jurisdictions have promulgated regulations to limit the O_3 emissions from air cleaners. A final example of a policy change that could affect indoor oxidant levels is the recent move in several countries to phase out the use of incandescent lightbulbs. The overall (room-averaged) effect of these lights on photochemical OH production is minimal, but significant amounts of OH can be produced locally. Local OH levels could change substantially depending on what type of replacement is used in place of the incandescent bulb. LEDs do not generally emit at wavelengths shorter than 400 nm,[34] so their use will result in decreased local OH levels. Conversely, fluorescent lights can rapidly photolyze HONO and HCHO.[34] Therefore, if CFLs are the primary replacement for incandescent bulbs, we might expect local OH levels near lights to increase.

Changes in building design and construction will also likely alter the indoor oxidizing capacity. For example, "green" or energy-efficient buildings often reduce the amount of outdoor air brought into the building. However, energy savings can come with air quality tradeoffs. For example, HCHO levels in energy-efficient homes in Colorado were recently reported to be higher than those in conventional homes.[99] The increased use of "green" building materials and cleaning products can introduce additional oxidative capacity and such secondary emissions are rarely considered in product evaluation and labeling.

Changing human behaviour patterns may also greatly affect indoor oxidant levels. For example, if people change their stove-type (e.g. from electric to gas or from gas to induction), oxidant levels during cooking events will also change. Changes in window-opening patterns (e.g. decreased use of natural ventilation as wealth and access to air conditioning increases as well as increased frequency of severe urban air pollution events) will have large effects on both the identity and concentration of oxidants indoors.

Future directions

Many of the uncertainties surrounding indoor oxidant* levels can be addressed through additional measurements. Of special importance is obtaining artifact-free measurements under a range of conditions (including, but not limited to, geographic location, building type, AER, exposure to sunlight). Measuring several species simultaneously with high time resolution will elucidate rapid and complex interactions between oxidants* and help quantify their sources and sinks (and thereby explain their concentrations under different conditions).

Another area where further study is necessary is the effect of surfaces on indoor gas-phase oxidant levels. Indoor surface interactions and their contribution to the indoor oxidizing capacity remain poorly understood. Given the diversity of indoor surfaces and soiling amounts/compositions, it is also critically important to characterize realistic surfaces from the perspective of elucidating oxidant* interactions. Part of this effort should include surfaces that represent a large surface area in indoor spaces, but are hidden from view, not often/ever cleaned, and may have different soiling patterns compared to visible room surfaces. These include HVAC ducts and components and surfaces in buffer spaces (e.g., attics, crawlspaces, and attached garages), surfaces in interstitial spaces (e.g., wall cavities and dropped ceilings) and in porous materials. The conditions in these hidden spaces may also differ greatly from those in occupied areas. For example, attics and crawl spaces may experience extreme temperature conditions. Similar extreme temperature conditions may exist within HVAC systems, with the additional possibility of high relative humidity and the presence of disinfecting light sources. A final surface type that warrants further study is catalytic surfaces, such as self-cleaning surfaces and surface coatings.

Given the uncertainties around indoor oxidants* and their interactions with building materials, contents, and systems, it is imperative that the research community focuses efforts on well-characterized and high time-resolution measurements of different oxidant* mixtures. Emphasis should be placed on oxidants in addition to O_3 and its reaction products as well as

on phenomena surrounding extreme oxidant chemistry (*e.g.*, during cleaning activities or the impact of strong UV light sources) and in building locations that are likely to be important for oxidants* but have not been widely studied (*e.g.*, HVAC systems).

Conflicts of interest

There are no conflicts to declare.

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