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Weschler, Charles J
Nazaroff, William W

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Ozone loss: a surrogate for the indoor concentration of ozone-derived products

Charles J. Weschler* [a, b] and William W Nazaroff [c]

[a] Environmental and Occupational Health Sciences Institute, Rutgers University, Piscataway, NJ, 08854 USA. E-mail: weschlch@rwmjs.rutgers.edu
[b] International Centre for Indoor Environment and Energy, Technical University of Denmark, Lyngby, Denmark
[c] Department of Civil and Environmental Engineering, University of California, Berkeley, CA, 94720-1710 USA

Abstract

Ozone concentrations tend to be substantially lower indoors than outdoors, largely because of ozone reactions with indoor surfaces. When there are no indoor sources of ozone, a common condition, the net concentration of gaseous products derived from indoor ozone chemistry scales linearly with the difference between outdoor and indoor ozone concentrations, termed "ozone loss." As such, ozone loss is a metric that might be used by epidemiologists to disentangle the adverse health effects of ozone's oxidation products from those of exposure to ozone itself. The present paper examines the characteristics, potential utility, and limitations of the ozone loss concept. We show that for commonly occurring indoor conditions, the ozone loss concentration is directly proportional to the total rate constant for ozone removal on surfaces (k_{sum}), and inversely proportional to the net removal of ozone by air exchange (λ) plus surface reactions (k_{sum}). It follows that the ratio of indoor ozone to ozone loss is equal to the ratio of λ to k_{sum}. Ozone loss is a promising metric for probing potential adverse health effects resulting from exposures to products of indoor ozone chemistry. Notwithstanding its virtues, practitioners using it should be mindful of limitations discussed in this paper.

Keywords

air pollution, epidemiology, exposure, oxidation, reactive organic compounds, secondary organic aerosols, toxicity

Short Synopsis Statement

Ozone loss can be used to estimate the exposure of building occupants to volatile products generated when outdoor ozone reacts indoors.

Introduction

Numerous studies from around the world have linked increases in outdoor ozone concentrations with adverse health outcomes. A long-term increase of 10 ppb in outdoor ozone concentrations has been linked to a 12% increase in respiratory mortality, a 3% increase in circulatory mortality and a 2% increase in all-cause mortality.[1] Critical assessments estimate that outdoor ozone contributes to premature mortality at a rate of 150,000–555,000 deaths/year globally.[2,3] Epidemiologic studies that have examined associations between ozone and morbidity and mortality are largely based on outdoor ozone concentrations measured at central monitoring sites.[1,4]. However, a large proportion of ozone is inhaled indoors. As a result of its reactivity, in the absence of indoor sources, ozone concentrations are lower indoors than

outdoors. This decrease in ozone from outdoors to indoors is accompanied by an increase in the indoor air concentrations of the products of ozone-initiated indoor chemistry. Modeling suggests that more moles of ozone-derived products are inhaled by building occupants than the moles of ozone inhaled.[5-8] Does inhaling the oxidation products of ozone indoors contribute to the morbidity and mortality associated with outdoor ozone? The answer to this important question should influence mitigation strategies and public health recommendations. "Ozone loss" is a metric that is relatively easy to evaluate and whose use may facilitate answering this question.

When ozone in outdoor air is transported indoors, it encounters an increased abundance of reactive organic compounds, especially on indoor surfaces. The ensuing chemistry generates oxidized products. Among the products of ozone-initiated indoor chemistry is the hydroxyl radical. Whereas ozone reacts at a meaningful rate chiefly with organic compounds that contain a -C=C- double bond, the hydroxyl radical reacts with almost all organic compounds at relatively fast rates. Consequently, the hydroxyl radical generates products that would not be present if ozone were the only oxidant. Together ozone and hydroxyl radicals combine with organic molecules to generate a diverse array of oxidation products.[9] These include stable species, such as saturated and unsaturated aldehydes, ketones, dicarbonyls, and organic acids; hydrogen peroxide (H_2O_2), organic peroxides, epoxides, and peroxy acids; organic nitrates and peroxyacyl nitrate-type species; and secondary organic aerosol (SOA).[10-16] Some of the stable products contain multiple functional groups. Also formed are short-lived, highly reactive species such as stabilized Criegee intermediates, hydroperoxyl- and alkylperoxyl radicals, nitrate radicals and dinitrogen pentoxide. Some products, such as secondary ozonides, α-hydroxyhydroperoxides and α-acyloxyalkylhydroperoxides, are thermally stable but react rapidly with water, decomposing to release H_2O_2.[13]. Worth emphasizing is that human skin oil contributes reactive organic compounds to all occupied environments.[17] Products resulting specifically from ozone skin/oil chemistry have been summarized in two recent reviews.[17,18] Some of the compounds produced by indoor ozone chemistry have other indoor sources with potentially large emission rates; examples are formaldehyde, formic acid, acetone, and acetic acid. However, recent studies[19] suggest that many ozone-derived products would be absent from indoor environments without the influence of ozone and hydroxyl radicals.

Most of the products generated by ozone-initiated surface chemistry are either gaseous or remain on indoor surfaces. Although products generated by surface chemistry can partition to airborne particles,[20,21] this occurs for only a small fraction (see *Supporting Information*). In the present analysis we focus on the products either inhaled or (potentially) dermally absorbed from air, namely gas-phase products and SOA. Besides inhalation, condensed-phase products can be dermally absorbed via contact transfer and can also be ingested (via hand-to-mouth activity and dust ingestion). However, these alternative exposure pathways would typically result in a smaller intake of ozone-derived products than those resulting from inhalation.

Given their different chemical natures, a vast range of potential health effects may arise from the many oxidation products that are formed from ozone-initiated indoor chemistry. Some gaseous ozone-derived products are known or suspected to be toxic (e.g., formaldehyde, hydrogen peroxide, organic peroxides). However, we know little about the toxicity of the broad mix of ozone-derived products inhaled by occupants in different indoor environments. Ozone

oxidation products likely have different influence on morbidity and mortality risk than does ozone, both in kind and in intensity. For example, many gas-phase oxidation products penetrate more deeply into the respiratory tract than ozone,[22] and certain gas-phase products may be dermally absorbed,[23] which does not occur for ozone. Historically, the health effects of ozone were believed to be chiefly associated with lung function, respiratory symptoms, and airway inflammation.[24] Over the past decade, evidence has accrued to indicate that increases in outdoor ozone pollution are also associated with increased frequency of adverse cardiovascular events.[25,26] It has been hypothesized that ozone oxidation products may have a larger influence on cardiovascular health than does ozone itself.[27]

Experimental studies that have investigated the adverse health effects of ozone, using either animal or human subjects, have focused on delivering a known concentration of ozone for a known duration and at a fixed breathing rate.[24,28] These studies have been designed in such a way that inhalation of byproducts is either avoided or poorly mimics the inhalation of ozone-derived products that would occur in normally occupied indoor environments. Epidemiology offers a possible route for investigating the health impacts of ozone-derived products. However, to pursue this aim, it is necessary to distinguish between exposure to ozone and exposure to its oxidation products.

Indoor ozone concentrations can be estimated from outdoor ozone levels.[29] On the other hand, the variety of products that result from indoor ozone chemistry makes quantifying the speciated abundances of these products in any indoor environment a major undertaking.[30] This characteristic has been an obstacle to studies that attempt to account for adverse health effects of indoor exposure to oxidation products in addition to ozone itself. In a recently published exploratory study, the difference between outdoor and indoor ozone concentrations (termed "ozone loss") was used as a surrogate indicator for the aggregate concentrations of volatile ozone-derived products to which occupants were exposed.[27] The present paper examines the attributes, potential utility, and limitations of the "ozone loss" concept. We focus on "ozone loss" as a surrogate for gas-phase products generated by ozone-initiated indoor chemistry. We derive and discuss basic relationships between ozone loss and key parameters such as air-change rate, the rate constant for ozone removal by indoor surfaces, and the net yield of gas-phase products.

Quantitative relationships describing indoor ozone loss
Preamble. The equations that follow are derived assuming (as is commonly true) that there is no indoor source of ozone large enough to significantly affect its indoor concentration. Ozone loss ($[O_3]_{loss}$) is defined as the difference between the time-averaged outdoor and time-averaged indoor ozone concentrations. As illustrated in the *Supporting Information*, averaging times of one hour (or longer) are suitable. Ozone loss can be decomposed into several additive components: ozone loss on indoor surfaces, ozone reaction with organic compounds in air (e.g., terpenoids), ozone reaction with nitrogen oxides in air, and ozone loss by deliberate control measures.[29] Under typical conditions, the removal of ozone via indoor reactions is dominated by surface chemistry; gas-phase reactions are typically responsible for less than 10% of total removal.[17,29] Ozone loss to nitrogen oxides occurs primarily in residences with gas-fired appliances, is episodic, and, with the replacement of pilot lights by electronic ignition, is less impactful than it once was.[29] Ozone control measures to treat indoor air are uncommon:

filtration with activated carbon[31,32] or deliberate use of surfaces that have been modified to passively remove ozone.[33-35]

Ozone can be lost during transport across the building envelope.[36] This loss is commonly parameterized as a penetration factor, P, representing the flow-rate weighted fraction of ozone that remains unreacted in air during its passage from outdoors to indoors. Stephens et al.[36] reported a mean value (± standard deviation) of P = 0.79 ± 0.13 for eight homes when windows and doors were closed. Their method used a large fan to "elevate air exchange rates and steady-state indoor ozone concentrations to levels that can be accurately measured, so there is a potential for overpredicting ozone penetration factors." The expected value of P is close to unity if ventilation airflows are primarily through open windows or other unobstructed pathways. Lai et al.[37] concluded that "Neglecting the penetration factor would lead to a small overestimation (for infiltration), which is tolerable." New and retrofitted buildings may be equipped with mechanical ventilation systems, whose design and operation could influence P.[38] Even if P is substantially less than unity, a large fraction of volatile products generated as ozone traverses the building envelope would be carried into the indoor space with the ventilation air, and the presence of these products would be captured by the metric "ozone loss". For these reasons we have not explicitly included a penetration factor in the equations that follow.

To summarize, in most situations, ozone removal indoors is dominated by ozone loss on indoor surfaces. When this is the case, ozone loss attributable to surface reactions is approximately equal to the total ozone loss, which, in turn, can be evaluated as the difference between outdoor and indoor time-averaged concentrations.

Ozone loss on indoor surfaces can be decomposed into loss on inanimate interior surfaces (walls, floor, ceiling, furnishings) and loss on occupant surfaces. The former varies with the interior surface-to-volume ratio and the latter varies with occupant density.[17] This decomposition is quantitatively explored in Tables S1 and S2 of the *Supporting Information*. Estimates suggest that, for a typical U.S. residence, 5% of ozone loss occurs on human surfaces and 95% on inanimate surfaces. For a representative 270 m^3 office with 5 occupants, the loss apportionment is 17% to human surfaces and 83% to inanimate surfaces. For a densely occupied 270 m^3 classroom with 35 young adult students, the estimated apportionment of loss is 58% to human surfaces and 42% to inanimate surfaces.

Indoor ozone. Indoor and outdoor ozone concentrations ($[O_3]_{in}$ and $[O_3]_{out}$) are commonly compared using the ratio of the time-averaged indoor concentration to the time-averaged outdoor concentration. To a good approximation, in the absence of indoor sources, this ratio can be estimated as a simple function of the air change rate (λ) and the total rate constant for ozone removal on surfaces (k_{sum}):[5,29,39,40]

$$\frac{[O_3]_{in}}{[O_3]_{out}} \approx \frac{\lambda}{\lambda + k_{sum}} \qquad (1)$$

See the *Supporting Information* for the derivation of eq (1), obtained by integrating over time the differential material balance that describes the dependence of the indoor ozone concentration on the outdoor level and on key building factors. (In this paper, the symbols $[O_3]_{in}$

and $[O_3]_{out}$ represent time-average values, with averaging times on the order of 1 h or longer.) The total rate constant for surface removal, k_{sum}, accounts for ozone loss on all exposed indoor surfaces, including those associated with occupants.[17,41] Eq (1) has been demonstrated to agree reasonably with measured values in several studies.[5,40,42,43] It also has been used to estimate k_{sum} in situations where the indoor/outdoor ozone concentration ratio and the ventilation rate have been measured.[39] Reassuringly, k_{sum} values estimated in this fashion are also consistent with those measured directly.[39,44,45]

Rearranging eq (1) provides an estimate of the indoor ozone concentration in terms of the outdoor ozone concentration multiplied by an "ozone infiltration factor" ($\lambda/(\lambda + k_{sum})$):

$$[O_3]_{in} \approx [O_3]_{out} \times \left(\frac{\lambda}{\lambda + k_{sum}} \right) \qquad (2)$$

Net concentration of gas-phase products derived from surface reactions. Surface reactions generate three types of products in terms of volatility: nonvolatile products that stay on the surface, semivolatile products that partition between surfaces and the gas-phase, and volatile products that are present chiefly in the gas-phase.[46] As shown in the *Supporting Information*, on a time-averaged basis, the net concentration of gas-phase oxidation products, $\sum[\textit{Oxidation products}]_{gas}$, can be estimated from eq (3):

$$\sum[Oxidation\ products]_{gas} \approx [O_3]_{in} \times \left(\frac{Yield_{gas} \times k_{sum}}{\lambda} \right) \qquad (3)$$

Here $Yield_{gas}$ is the net moles of gaseous product produced per mole of ozone consumed in surface reactions, sometimes referred to as the "formation factor".[6] $Yield_{gas}$ is not a fundamental chemical parameter; environmental conditions can affect its value. Even when relatively constant values for $Yield_{gas}$ would apply, the component yields for species that contribute to the net yield can vary. Measured net yields for gas-phase products are detailed in Table 1 and discussed later in this paper. We also explore later the contribution of various species to the total $Yield_{gas}$.

Using eq (2), one can substitute for $[O_3]_{in}$ in eq (3) to obtain eq (4), which expresses the net concentration of ozone-derived products in the gas-phase as a function of the outdoor ozone concentration:

$$\sum[Oxidation\ products]_{gas} \approx [O_3]_{out} \times \left(\frac{Yield_{gas} \times k_{sum}}{\lambda + k_{sum}} \right) \qquad (4)$$

Ozone loss. As defined in this paper, "ozone loss" ($[O_3]_{loss}$) is the difference between time-averaged outdoor and indoor ozone concentrations:

$$[O_3]_{loss} = [O_3]_{out} - [O_3]_{in} \qquad (5)$$

Substituting the identity from eq (2) in eq (5) and rearranging, one obtains:

$$[O_3]_{loss} \approx [O_3]_{out} \times \left(\frac{k_{sum}}{\lambda + k_{sum}} \right) \qquad (6)$$

Expressed instead in terms of *indoor* ozone concentration, one can write:

$$[O_3]_{loss} \approx [O_3]_{in} \times \left(\frac{k_{sum}}{\lambda} \right) \qquad (7)$$

Taken together, eqs (4) and (6) show that, as expected, $\sum[Oxidation\ products]_{gas}$ is related to $[O_3]_{loss}$ through $Yield_{gas}$:

$$\sum[Oxidation\ products]_{gas} \approx Yield_{gas} \times [O_3]_{loss} \qquad (8)$$

Implicit in eqs (3), (4), and (8) is that the concentrations of products resulting from reactions of ozone with indoor surfaces scale in a linear fashion with indoor ozone concentrations. (See *Supporting Information* for a more detailed examination of this proportionality.) The validity of this assumption is supported by two recent studies. Liu et al.[30] found that in measurements made with a PTR-MS in a normally occupied residence over an eight-week period, the concentrations of several ozone-derived products scaled in a roughly linear fashion with the indoor ozone concentration. (See Figure 3 of the cited paper.) In a chamber study of products resulting from ozone reactions with human surfaces, Qu et al.[47] observed that for most volatile products resulting from indoor ozone reactions, there was a linear relationship between emission rates and the ozone concentration. Byproduct concentrations would be proportional to byproduct emission rates if byproduct loss from indoor air occurs only by ventilation and there are no other meaningful emission sources, including outdoor air. For the products noted in the Qu et al.[47] study, these conditions were met.

Dependence of $[O_3]_{in}$ and $[O_3]_{loss}$ on air-change rate and k_{sum}. Eq (2) states that the indoor ozone concentration scales with outdoor ozone concentration attenuated by the ratio $\lambda/(\lambda + k_{sum})$. As implied by this simple expression, at a constant value of k_{sum}, the indoor ozone concentration increases with increasing air-change rate, whereas at a constant value of λ, the indoor ozone concentration decreases with increases in the total rate constant for ozone removal on surfaces. Conversely, eq (6) states that ozone loss scales with outdoor ozone concentration attenuated by the ratio $k_{sum}/(\lambda + k_{sum})$. At a constant value of k_{sum}, ozone loss decreases with increasing air-change rates, while at a constant value of λ, ozone loss increases with increases in the total rate constant for ozone removal on surfaces. The complementary influence of the ratio λ / k_{sum} on the indoor ozone concentration and ozone loss, each normalized by the outdoor ozone concentration, is illustrated in Figure 1. The sum of the indoor ozone concentration and the ozone loss concentration equal the outdoor ozone concentration. Consider, for example, common values of $[O_3]_{out}$ = 30 ppb and k_{sum} = 3.0 h^{-1}. If λ = 0.5 h^{-1}, then $[O_3]_{in}$ = 4.3 ppb and $[O_3]_{loss}$ = 25.7 ppb, whereas if λ = 2.0 h^{-1}, then $[O_3]_{in}$ = 12 ppb and $[O_3]_{loss}$ = 18 ppb. In both cases, $[O_3]_{in}$ and $[O_3]_{loss}$ sum to 30 ppb. This feature reflects the definition of ozone loss presented in eq (5).
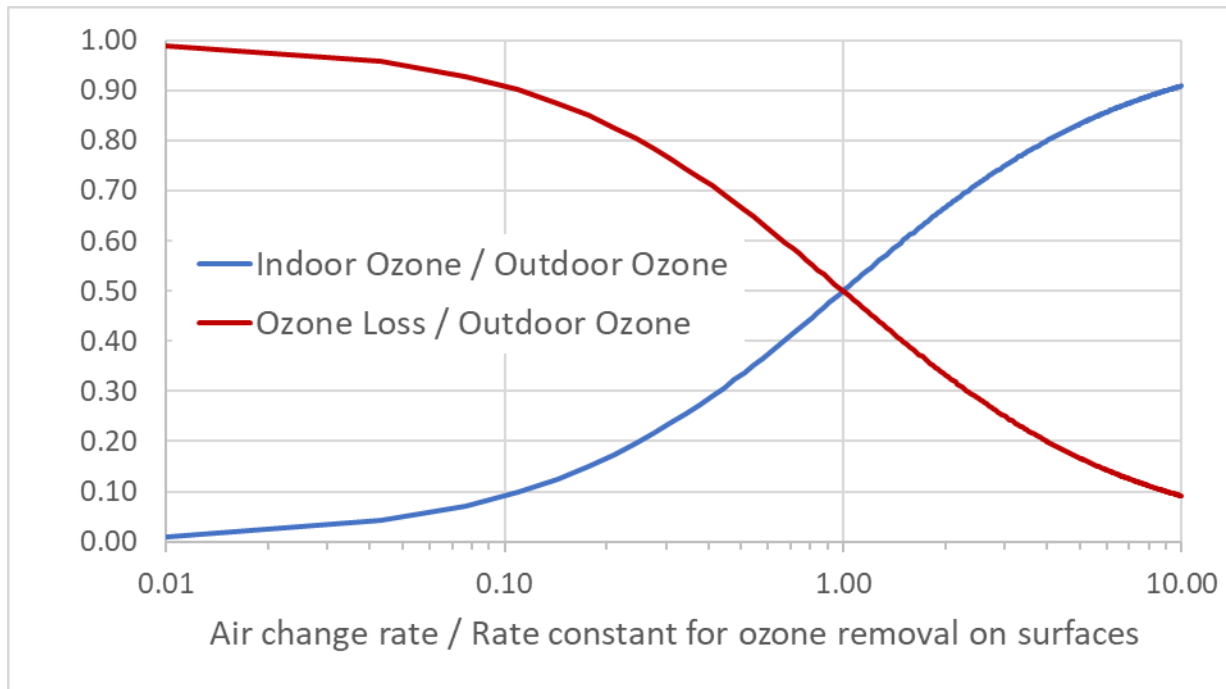
Figure 1. Dependence of the concentrations of indoor ozone or ozone loss (in each case normalized by the outdoor ozone concentration) on the ratio of air change to surface removal rates. The *y*-axis represents the normalized time-averaged concentration of indoor ozone (blue line: indoor ozone / outdoor ozone) and of ozone loss (red line: ozone loss / outdoor ozone). The *x* axis represents the ratio: air-change rate, λ, divided by rate constant for ozone removal on surfaces, k_{sum}.

The ratio of the time-averaged concentration of indoor ozone to time-averaged ozone loss is given by eq (9):

$$\frac{[O_3]_{in}}{[O_3]_{loss}} \approx \frac{\lambda}{k_{sum}} \qquad (9)$$

In this simple expression, one sees that the ratio of indoor ozone concentration to ozone loss varies as the ratio of the air-change rate to the total rate constant for ozone removal on indoor surfaces. Figure 2 illustrates the relationship between concentrations of indoor ozone and ozone loss for different indoor environments. The stacked bars in each of the three clusters represent the concentrations of indoor ozone and ozone loss for a typical residence, office, and classroom in a condition where the average outdoor ozone concentration is 30 ppb, typical of daily-average ozone concentrations during warmer months. The first cluster shows values for air-change rates frequently encountered in these building groups: 0.5 h^{-1} for a 485 m^3 residence with two occupants;[48] 0.6 h^{-1} for a 270 m^3 office with 5 workers and 3.0 h^{-1} for a 270 m^3 classroom with 35 young adult students (Table 6.1 in reference 49). In the second cluster, air-change rates are a factor of two lower than in the first cluster, and in the third cluster, air-change rates are a factor of two higher. Note that the total rate constant for ozone removal on surfaces varies with occupant density, reflecting ozone reactions with human surfaces.[17] For the stipulated residence, office, and classroom, the respective values of k_{sum} are 3.1 h^{-1}, 3.4 h^{-1}, and 6.4 h^{-1}. (See Table 6 in reference 17.) Ozone loss dominates for all conditions displayed in Figure

2. Indoor ozone concentration is closest to ozone loss in the instance of the classroom in the third cluster, reflecting an air-change rate (6 h^{-1}) similar to k_{sum} (6.4 h^{-1}). For the typical air-change rates and k_{sum} values in the first cluster of bars, the ratio $[O_3]_{loss}$ /$[O_3]_{indoor}$ is about six for the home and office, and about two for the classroom.
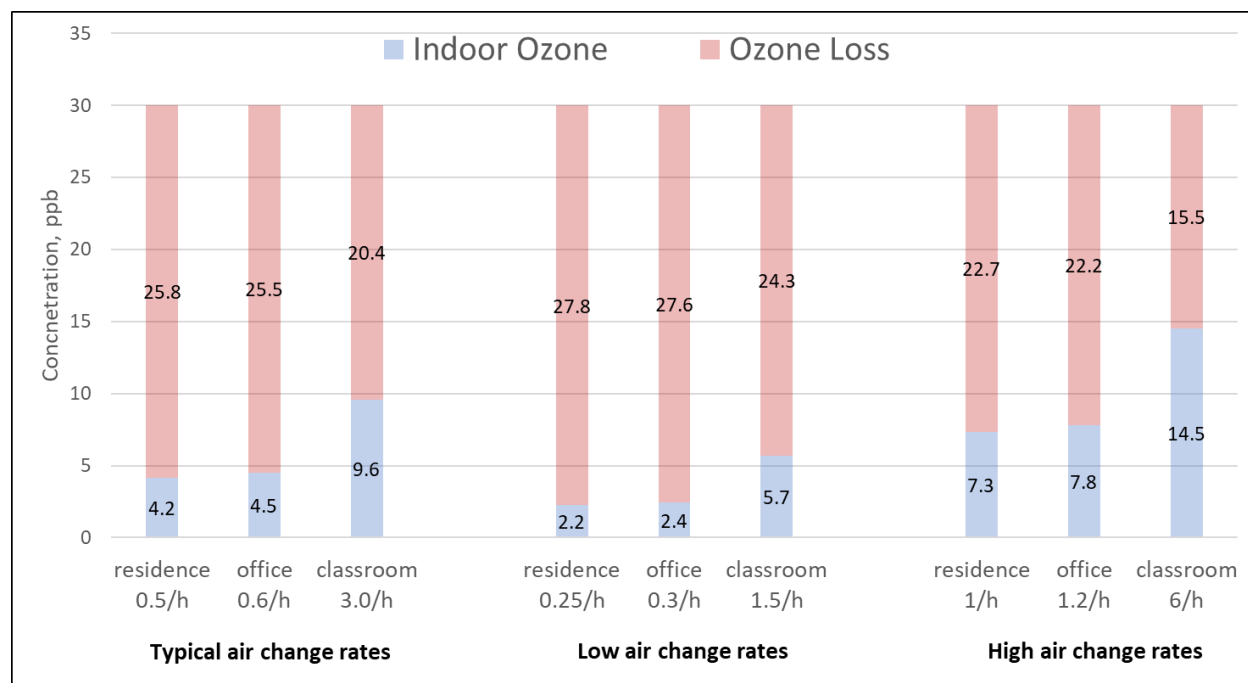
Figure 2. Assuming an outdoor ozone concentration of 30 ppb, concentrations of indoor ozone and ozone loss for a residence, office, and classroom at typical air-change rates (1st cluster), at air-change rates a factor of two lower (2nd cluster), and air-change rates a factor of two higher (3rd cluster). Residence: 2 occupants, 485 m^3; office: 5 occupants, 270 m^3; classroom: 35 occupants, 270 m^3. Loss rates are k_{sum} = 3.1 h^{-1} (residence), 3.4 h^{-1} (office), 6.4 h^{-1} (classroom).

The reader is reminded that the net concentration of gas-phase products derived from indoor ozone, $\sum[Oxidation\ products]_{gas}$, is the product of $Yield_{gas}$ and ozone loss (eq (8)). As detailed below, based on suggestive albeit limited evidence, the value of $Yield_{gas}$ is likely to be in the range 0.8–1.2. If generally true, then $\sum[Oxidation\ products]_{gas}$ would be comparable to $[O_3]_{loss}$. Hence, in typical indoor environments, aggregate evidence suggests that the net concentration of ozone-derived products in the gas-phase would tend to be substantially larger than the concentration of ozone itself.

It is apparent from Figure 2 that for the same outdoor ozone concentration, different indoor environments can have different concentrations of indoor ozone and ozone loss. It is also true that indoor environments can possess the same indoor ozone concentration but quite different values for ozone loss. Indoor ozone concentrations, alone, are an incomplete description of inhalation exposures, as are outdoor ozone concentrations alone.

As illustrated in both Figures 1 and 2, the outdoor ozone concentration is equal to the sum of the indoor ozone and ozone loss concentrations. This characteristic might prompt a critic to say:

"why does one need to consider 'ozone loss' concentrations, since the sum of indoor ozone and ozone loss matches the ozone concentrations being measured outdoors." Such a statement overlooks the possibility that the health effects of ozone-derived products may differ from those of ozone itself. Although the sum of the indoor ozone and ozone loss concentrations equals the outdoor ozone concentration, the ratio of the concentrations of indoor ozone to ozone-derived products varies with building design and operational conditions. Since people mainly breathe indoor air, conditions inside buildings are germane to understanding mechanistic aspects of the health consequences associated with elevated outdoor ozone concentrations. Furthermore, the common advice to shelter indoors when outdoor ozone levels are high may need to be reconsidered if, in fact, the byproducts of ozone-initiated chemistry indoors pose consequential health risks.

Measured values for *Yield*$_{gas}$

Most of the reactive organic compounds that consume indoor ozone contain carbon-carbon double bonds (-C=C-), and it is at this location in the molecule that ozone reacts. In wipe samples of windows and painted vertical surfaces in university buildings, Deming and Ziemann[50] measured -C=C- bonds at levels typically of 1–2 μmoles m^{-2} and inferred that the lifetime of these -C=C- bonds was about an hour. At an indoor ozone concentration of 5 ppb and assuming an ozone deposition velocity of 1 m h^{-1}, the flux of ozone to inanimate indoor surfaces would be 0.2 μmoles m^{-2} h^{-1}. These values suggest that double bonds are replenished on indoor surfaces at rates comparable to the molar flux of ozone to these surfaces. Actual rates of -C=C- replenishment and consumption are expected to vary with factors such as indoor occupancy and ozone concentration.

When ozone reacts with a carbon-carbon double bond, a primary ozonide is formed, which subsequently cleaves to form either an aldehyde or ketone (product 1) plus a Criegee intermediate. The highly excited Criegee intermediate is either collisionally stabilized or decomposes via various pathways, generating another oxidized product (product 2).[51] Hence, two moles of oxidized products are normally generated for each mole of ozone reacting with -C=C- bonds. Among the products formed via decomposition of Criegee intermediates is the hydroxyl radical. The yield of hydroxyl radicals from ozone/alkene reactions depends on the alkyl groups attached to the carbon atoms that form the original -C=C- bond.[52,53] The OH yield varies: 0.13 for ethene, ~0.25 for isoprene, and ~0.9 for a variety of terpenes including limonene, α-pinene, and 3-carene.[52,53] Zannoni et al.[54] found that an OH concentration of $(7.1 \pm 2) \times 10^5$ molecules cm^{-3} resulted when volunteers were exposed to 35 ppb ozone in a ventilated chamber. "Key to the generation of OH around humans is the presence of reactive alkenes generated from the reaction of O_3 with various components of skin oil (e.g., squalene), particularly 6-MHO but also geranyl acetone, OH-6-MHO, 4-MON, and 4-MOD."

The products of ozone-initiated chemistry, including those generated by hydroxyl radicals, can be in either the gas phase or the condensed phase. Table 1 summarizes the net yield of gas-phase products, *Yield*$_{gas}$, obtained using PTR-MS measurements, which have been reported for ozone reactions with surfaces in simulated or actual indoor environments, as well as with T-shirts, squalene particles, and bare skin. These yields should be viewed as lower limits, since there are stable gas-phase products (e.g., hydrogen peroxide, formaldehyde, formic acid and, in one study, acetone) not included in these PTR-MS measurements. Some of the yields in Table 1

are empirical (i.e., net moles of gaseous product per mole of ozone consumed) and include products formed via secondary reactions in the gas phase. Such yields are anticipated to vary with experimental conditions.[55] The yields reported by Qu et al.[47] are true surface yields (i.e., net moles of gaseous product emitted per mole of ozone consumed in a surface reaction) and are less sensitive to experimental parameters. The yields from Weschler et al.[8], Arata et al.[56], and Morrison et al.[57] are close to surface yields, since the high air-change rates used in these studies allowed little time for gas-phase chemistry. However, even true surface yields are likely to exhibit variability that depends on the chemical composition of the surface, especially among unsaturated organic compounds.

Table 1. Values of $Yield_{gas}$ [a], derived from PTR-MS measurements, for ozone-initiated reactions with T-shirts, squalene particles, skin, or all surfaces in simulated or actual indoor environments.

Surfaces	Conditions	$Yield_{gas}$	Reference
Simulated aircraft cabin, 17 soiled T-shirts	λ = 3 h^{-1}; 7% RH	~0.8	58
Simulated aircraft cabin, 16 occupants, Groups A & B	λ = 8.8 h^{-1}; 10% RH λ = 4.4 h^{-1}, 20% RH	~0.8 @10% RH ~1.0 @20% RH	8 (Fig. 1)
Simulated office, 2 occupants	λ = 1.0 h^{-1}, 20-25% RH	Lower bound: 0.55 [b]	55
Squalene aerosol	High λ; variable RH	0.66 @30% RH 1.3 @ 70% RH	56
Flow reactor affixed to skin surface; 20 volunteers	High λ	Lower bound: 0.33-0.93 [c]	57
Occupied home during summer	Variable λ, sum of identified products	Lower bound: 0.20-0.25 [d]	30
Four occupants in 22.5 m^3 stainless-steel chamber	λ = 3.2 h^{-1}; variable RH	0.64 @28% RH 0.98 @70% RH	19 (Table S5)
Occupant in 1.5 m^3 stainless-steel chamber; 36 experiments	λ = 2.1 h^{-1}; ~50% RH	0.75	47

[a] $Yield_{gas}$ represents the net moles of gaseous product generated, as measured by PTR-MS, per mole of ozone consumed in surface reactions. The latter is assumed to be the difference between measured "outdoor" and indoor concentrations of ozone. In the chamber studies the "outdoor" ozone concentration is the concentration of ozone in the inlet air. [b] Sum of acetone, 6-MHO, geranyl acetone, decanal, 4-OPA, 1,4-butanedial, 4-MON and 4-MOD. [c] Does not include acetone. [d] Sum of measured 6-MHO, 4-OPA, C8-C12 aldehydes and inferred acetone and geranyl acetone.

In addition to the PTR-MS studies listed in Table 1, yields have also been measured using sorbent sampling with Tenax TA and DNPH cartridges followed by GC-MS analyses. Rai et al.[59] reported yields for total volatile organic compounds resulting from ozone reacting with T-shirts in chamber experiments. These yields ranged from 0.2 for a laundered T-shirt to 0.6 for a T-shirt that had been worn six hours and should be considered lower bounds since many volatile organic oxidation products are not measured with sorbent sampling. Rai et al.[59] observed that, for worn T-shirts, yields increased from ~0.25 at 10-20% RH to ~0.55 at 25-50% RH. An increase of $Yield_{gas}$ with relative humidity has been observed in other studies listed in Table 1. In the

simulated aircraft study with 16 "passengers,"[8] the yield increased from a mean of 0.8 at 10% RH to a mean of 1.0 at 20% RH. Using a flow-tube reactor, Arata et al.[56] found that the yield of gas-phase products resulting from ozone reactions with squalene particles increased from 0.66 at 30% RH to 1.3 at 70% RH. In measurements of ozone reactions in a chamber containing four volunteers, Wang et al.[19] measured larger yields of gas-phase products at higher relative humidities (0.64 at 28% RH; 0.98 at 70% RH). Heine et al.[10] have shown that as the water vapor concentration increases, Criegee intermediates, resulting from ozone reactions with -C=C-bonds, are more likely to form α-hydroxyhydroperoxides as opposed to secondary ozonides. α-Hydroxyhydroperoxides subsequently decay to carbonyls and hydrogen peroxide. Since the resulting carbonyls are more volatile than the complementary secondary ozonides, the yield of gas-phase products increases at higher relative humidity.

Contribution of various species to *Yield*gas
Most of the *Yield*gas values in Table 1 are dominated by products of ozone/skin oil chemistry: 16 "passengers" in a 28 m^3 simulated aircraft cabin,[8] two occupants in a sparsely furnished 28 m^3 simulated office,[55] four volunteers in a 22 m^3 chamber,[19] a single occupant in a very small (1.5 m^3) chamber.[47] The major products contributing to *Yield*gas in these studies were acetone, 6-MHO, 4-OPA, decanal, nonanal, nonenal, and acetic acid. These products are similar to those resulting from reactions of ozone with i) T-shirts soiled by skin oil,[58] ii) squalene aerosol,[56] and iii) skin surfaces of volunteers.[57] Only one of the entries in Table 1 made measurements in an indoor environment with a low occupant density: two inhabitants of a 350-m^3 home.[30] In that home, the concentration of nonanal resulting from ozone chemistry was larger than would be expected from skin oil constituents alone, and presumably reflected precursors in addition to skin oil.

Besides skin oils, other sources contribute to the soiling of indoor surfaces with ozone reactive organics. These include cooking oils containing unsaturated fatty acids, wooden building materials and furnishings that emit terpenes, household cleaning agents and "air fresheners" scented with terpenes and terpene alcohols, and spices containing sesquiterpenes. Ozone reactive compounds can also be intrinsic to a surface as is the case for latex paint with unreacted vinyl monomers or unsaturated bonds in various elastomers. Only limited information is available regarding the abundance and speciation of ozone-reactive organics on inanimate indoor surfaces. Wang and Morrison[60,61] exposed indoor surfaces to ozone in four homes during summer 2005, summer 2006, and winter 2007 and measured the yields of targeted aldehydes. The surfaces investigated included living room and bedroom carpets, bare kitchen floors, and kitchen countertops. Total aldehyde yields were typically in the range from 0.1 to 0.5, with a few outliers of ~0.9, and were close to total aldehyde yields measured for carpet.[62] These targeted aldehyde yields represent only a fraction of the net volatile oxidation products generated by ozone reactions with inanimate indoor surfaces and consequently are lower bounds for *Yield*gas in these homes. Based on wipes of vertical inanimate surfaces in seven buildings on a university campus, Deming and Ziemann[50] estimated that alkenes comprised roughly 20% of the organic compounds present in organic films on the surfaces. However, that study did not measure gaseous products resulting from ozone reacting with these surfaces.

When introducing Table 1, we mentioned that hydrogen peroxide, formaldehyde, and formic acid are not included in the tabulated yields, yet each of these are generated by ozone reactions on indoor surfaces. Measurements by Zhou and Abbatt[13] can be used to estimate the contribution that hydrogen peroxide might add to the tabulated yields. Using cavity ring down spectroscopy, they measured a molar H_2O_2 yield of 35% for ozone reacting with squalene, 7.4% for ozone/triolein, and 8.5% for ozone/cooking oil. It is more challenging to estimate the contribution that formaldehyde and formic acid might add to the values of $Yield_{gas}$ in Table 1. Any compound with a terminal -C=C- can react with ozone to generate formaldehyde. However, it isn't known what fraction of the alkenes present on indoor surfaces contain terminal double bonds. Adding an intermediate contribution of 0.3 moles of H_2O_2, formaldehyde, and formic acid per mole of reacted ozone to the various yields listed in Table 1, one would estimate that 0.8 to 1.2 moles of gas-phase products are produced for each mole of ozone that reacts on indoor surfaces. This estimated range is based on relatively sparse evidence and warrants refinement through additional measurements.

Secondary organic aerosols (SOA) derived from gas-phase ozone chemistry
As noted in the *Introduction*, the focus of the present paper is "ozone loss" as a surrogate for the gas-phase products generated by ozone-initiated surface chemistry. While only a small fraction of outdoor ozone that is transported indoors is typically lost in gas-phase reactions, such gas-phase reactions are a source of SOA,[12,63-70] and inhaling SOA presents known health concerns.[71] The relationship between ozone loss and attributable SOA increase can be expressed by an equation analogous to eq (8):

$$[SOA] \approx Yield_{SOA} \times [O_3]_{loss} \qquad (10)$$

where $Yield_{SOA}$ is the mass concentration of SOA produced per molar unit of ozone consumed in all indoor reactions (e.g., $(\mu g/m^3)$/ppb). Here, [SOA] represents the time-averaged increase in indoor SOA concentration attributable to ozone-initiated indoor chemistry. We have chosen to define $Yield_{SOA}$ in terms of the mass concentrations of the resulting SOA, since mass concentrations are commonly used when characterizing the morbidity or premature mortality risk associated with airborne particles, as well as in standards and guidelines that address acceptable levels of such particles.

Based on a detailed simulation study of gas-phase ozone chemistry for US residences, Waring[72] reported a central tendency of approximately 1.0 $\mu g/m^3$ of SOA formed for a 15-ppb ozone loss, which translates to a $Yield_{SOA}$ of 0.07 $(\mu g/m^3)$/ppb. (See *Supporting Information*.) A large fraction of the indoor SOA derived from gas-phase ozone chemistry is the result of ozone reacting with limonene,[72] the most abundant terpene observed indoors. Grosjean et al.[73] reported 0.2 $\mu g/m^3$ of SOA generated per $\mu g/m^3$ of limonene that reacts with ozone. If we use limonene as representative of indoor gas-phase alkenes that react with ozone to generate SOA, the Grosjean yield of 0.2 $\mu g/m^3$ of SOA per $\mu g/m^3$ of SOA precursor is equivalent to 0.03 $\mu g/m^3$ of SOA formed per ppb of ozone loss (see the Supporting Information), or roughly half the yield inferred from Waring.[72]

The hydroxyl radicals produced by gas-phase ozone/alkene reactions can abstract hydrogen atoms from indoor organics, leading to the formation of alkylperoxyl radicals. When nitric oxide

(NO) concentrations are low, there is time for the alkylperoxyl radicals to undergo an H-shift, leading to autoxidation chain reactions.[12,68,74-76] Indoor NO concentrations tend to be low when ozone concentrations are elevated.[77] Hence, in the absence of gas-fired appliances, indoor conditions would be favorable for autoxidation reactions. Such chain reactions can result in substantial amounts of highly oxidized molecules (HOMs) per mole of OH consumed, and HOMs efficiently form SOA.[67] Ozone-initiated autoxidation of limonene has been observed in a museum with an SOA mass yield of ~0.5 per mass of limonene consumed, equivalent to $Yield_{SOA}$ (autoxidation) = 0.07 ($\mu g/m^3$)/ppb.[78]

We expect that the linkage between ozone loss and the concentration of SOA derived from gas-phase indoor ozone chemistry is variable and weak. The spread in these crude estimates of $Yield_{SOA}$ (0.03–0.07 ($\mu g/m^3$)/ppb) reflects, in part, the sensitivity of $Yield_{SOA}$ to the pre-existing concentration of airborne particles, the fraction of airborne particles that are organic matter, and the chemical properties of that organic matter. Taken together, the estimates of $Yield_{SOA}$ indicate that only a small fraction of indoor ozone loss would result in the generation of SOA. Nonetheless, given the relatively high potency of particulate matter as an air pollution risk factor, further studies to better elucidate the relationship between ozone loss and indoor SOA formation are warranted.

Limitations and Outlook

Variability of $Yield_{gas}$. As defined, $Yield_{gas}$ is the lumped yield of gas-phase products resulting from reactions between ozone and different indoor surfaces. The individual reactions that contribute to the sum of gas-phase products have yields that differ from one another, and these yields may vary somewhat with environmental conditions. A lumped yield is most useful if the relative contribution of yields from the various reactions is similar among the indoor environments that are being examined in a study. This condition is most likely to be met for a set of indoor environments that share a purpose (e.g., residences or schools or small offices) and are located within a relatively confined geographic area. To the extent that a subset of indoor environments has similar occupant densities and surfaces that are soiled with similar chemicals, we anticipate that the value of $Yield_{gas}$ for these environments will be similar. Available evidence indicates that human skin oil is responsible for roughly 15% to 55% of ozone removal in occupied indoor environments,[17] conferring a degree of commonality among the ozone-reactive compounds in these environments. Unsaturated organic compounds in cleaning products and cooking oils are anticipated to be similar among residences and schools in each location. We currently have scant information on how similar other sources of ozone reactive species might be among indoor environments. Regardless, the multitude of -C=C- bond sources indoors is anticipated to drive the value of $Yield_{gas}$ towards a common central tendency. Even if the value of $Yield_{gas}$ varies to some extent among indoor environments included in a study, ozone loss still offers promise as a metric to distinguish indoor ozone from its products in indoor environments. However, ozone loss should not be used to compare the net concentration of inhalable oxidation products among a set of buildings that are substantially different from one another and likely to have widely different values for $Yield_{gas}$.

Other considerations. We noted that the values for $Yield_{gas}$ listed in Table 1 are derived primarily from studies in which the dominant source of ozone reactive compounds is skin oil. It is not known how the value of $Yield_{gas}$ for other major sources of ozone reactive compounds

compares to that for skin oil. If almost all products formed when ozone reacts with a -C=C- bond were in the gas phase, the value of $Yield_{gas}$ would be close of two. The range for $Yield_{gas}$ estimated above (0.8 to 1.2) indicates that roughly half the products of ozone-initiated indoor chemistry with skin oil constituents are in the gas phase. Evidence suggests that most organic compounds that accumulate on indoor surfaces via partitioning have log K_{oa} values in the range of 10 to 12 and molecular weights consistent with log K_{oa} values in this range, where K_{oa} is the octanol-air partitioning coefficient.[79,80] The products that form from the decay of primary ozonides derived from such compounds may have a similar proportion of gas-phase and condensed phase products if the distribution of double bond locations resembles that in skin oil constituents. Additionally, although the unsaturated lipids that constitute skin oil are distinctive,[81] their range of volatilities resembles the mix of unsaturated lipids found in cooking oils and certain other sources known to soil indoor surfaces. That said, contact transfer can also deposit organic compounds on indoor surfaces resulting in surface grime with a potentially broad range of chemical properties.

When indoor environments are sufficiently alike, indoor ozone and ozone loss will be highly correlated. This characteristic would constrain efforts to disentangle the health effects of indoor ozone from those of ozone-derived products. Ozone loss is a useful metric when its concentration is not significantly correlated with indoor ozone concentrations. This outcome occurs when a set of indoor environments has a mix of values for air-change rates (λ) and rate constants for ozone removal on surfaces (k_{sum}).

As noted in the *Preamble*, $[O_3]_{loss}$ is not a useful metric when ozone is removed from indoor air, either centrally or locally by filters containing activated carbon or transition metal catalysts. It is also not appropriate for indoor environments that contain surfaces that have been deliberately modified to passively remove ozone.[33-35] Ozone loss as an indicator of ozone byproduct abundance is also not easily utilized when indoor environments have important ozone emission sources.

The limitations that currently apply to the use of $[O_3]_{loss}$ as a surrogate for products of ozone-initiated indoor chemistry can be reduced by several experimental approaches. These include: i) additional comprehensive measurements, similar to those made by Liu et al.[30] of the net products resulting from ozone-initiated chemistry under a variety of environmental conditions in occupied residences, offices, and schools; ii) passing ozone through flow reactors affixed to a variety of surfaces in different indoor environments[60,61] and quantifying products with a sensitive real-time instrument such as a PTR-MS; and iii) soiling substrates in actual indoor environments[82] and subsequently measuring the suite of reaction products formed when soiled substrates are exposed to ozone in controlled chamber experiments.

While certain products of ozone-initiated chemistry are known to be toxic at elevated concentrations, toxicities of most ozone-derived products remain to be evaluated. Selected products may penetrate deeper into the lung or enter the bloodstream from inhalation or dermal absorption,[22,83-85] resulting in health effects that differ from those of ozone. Ozone loss provides an approach that may help to identify biomarkers and related health outcomes most influenced by ozone oxidation products. As noted in the *Introduction*, ozone loss has already been used in an exploratory study that utilized data from prior investigations.[27] That study

found that ozone loss, more so than ozone, "was associated with biomarker concentration changes suggestive of adverse cardiorespiratory health effects." Ideally, when using ozone loss for a set of indoor environments, values will be based on outdoor and indoor ozone concentrations measured simultaneously at each study location. However, even when this is not possible, indoor ozone concentrations can be estimated from outdoor ozone concentrations using eq (2) coupled with information on variations in air-change rates and occupant densities in the set of indoor environments under study. While any use should be attentive to the limitations discussed above, ozone loss offers promise as a metric to investigate the health effects of ozone oxidation products separate from those of ozone.

Acknowledgements

Supporting Information

Time-averaged indoor-outdoor ozone relationship; relationship between ozone loss and concentration of gaseous byproducts; partitioning of the products of ozone surface chemistry to airborne particles; calculations related to $Yield_{SOA}$; illustrative calculations of the proportion of indoor ozone lost to skin oil on occupant and nonoccupant surfaces and associated indoor/outdoor (I/O) ratios in different indoor environments (Table S1); illustrative calculations of the percentage of indoor ozone lost to human surfaces and inanimate surfaces in indoor environments with different occupant densities (Table S2). The Supporting Information is available free of charge at https://pubs.acs.org/doi/...

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