TITLE

Secondary organic aerosol (SOA) formation by limonene ozonolysis: Parameterizing multi-generational chemistry in ozone- and residence time-limited indoor environments

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ABSTRACT

Terpene ozonolysis reactions can be a strong source of secondary organic aerosol (SOA) indoors. SOA formation can be parameterized and predicted using the aerosol mass fraction (AMF), also known as the SOA yield, which quantifies the mass ratio of generated SOA to oxidized terpene. Limonene is a monoterpene that is at sufficient concentrations such that it reacts meaningfully with ozone indoors. It has two unsaturated bonds, and the magnitude of the limonene ozonolysis AMF varies by a factor of ~4 depending on whether one or both of its unsaturated bonds are ozonated, which depends on whether ozone is in excess compared to limonene as well as the available time for reactions indoors. Hence, this study developed a framework to predict the limonene AMF as a function of the ozone $[O_3]$ and limonene $[lim]$ concentrations and the air exchange rate (AER, h^{-1}), which is the inverse of the residence time. Empirical AMF data were used to calculate a mixing coefficient, β , that would yield a 'resultant AMF' as the combination of the AMFs due to ozonolysis of one or both of limonene's unsaturated bonds, within the volatility basis set (VBS) organic aerosol framework. Then, β was regressed against predictors of $\log_{10}([O_3]/[lim])$ and AER ($R^2 = 0.74$). The β increased as the $\log_{10}([O_3]/[lim])$ increased and as the AER decreased, having the physical meaning of driving the resultant AMF to the upper AMF condition when both unsaturated bonds of limonene are ozonated. The $\log_{10}([O_3]/[lim])$ impacted β by an absolute factor of 3.6 more than the AER for this dataset. Modeling demonstrates that using the correct resultant AMF to simulate SOA formation owing to limonene ozonolysis is crucial for accurate indoor SOA prediction.

Keywords: Particle formation; SOA yield; aerosol mass fraction; indoor chemistry; terpenes; ozone

1. INTRODUCTION

Ambient air quality is impacted by oxidative reactions of the hydroxyl radical ($\cdot\text{OH}$), nitrate radical ($\text{NO}_3\cdot$), ozone (O_3) with reactive organic gases (ROG) in the atmosphere (Seinfeld and Pandis, 2012). The hydroxyl radical strongly and nitrate radical less strongly react with saturated and unsaturated ROGs, and ozone reacts with unsaturated ROGs, such as terpenes (Atkinson, 2000, 1990; Atkinson and Arey, 2003). Indoors, oxidative reactions are also key chemistry drivers, and the relative influence of different oxidative reactions may be characterized by comparing indoor lifetimes of different ROGs to residence times of air in buildings. Lifetime analyses indicate that ozone/ terpene reactions are among the most important reactions indoors (Waring and Wells, 2015; Weschler, 2000). The residence time of indoor air, τ_{res} (h), is governed by the building air exchange rate, λ or AER (h^{-1}), which is the frequency with which indoor air is replaced by outdoor air, so $\tau_{\text{res}} = \lambda^{-1}$. The AER can include unintentional infiltration and/ or intentional mechanical or natural ventilation. For instance, AERs range from 0.2 to 1.5 h^{-1} for infiltration in residences (Murray and Burmaster, 1995) and from 0.26 to 4.2 h^{-1} for mechanical ventilation in offices (Persily and Gorfain, 2008), between the 10th and 90th percentiles of measured distributions.

Ozone typically occurs at indoor/ outdoor (I/O) ratios of 0.2 to 0.7 owing to outdoor-to-indoor transport (Weschler, 2000), though indoor emissions from some appliances are sometimes active (Lee et al., 2001; Waring et al., 2008). Indoor terpenes have I/O ratios higher than unity (Rackes and Waring, 2015, 2013; Weisel et al., 2005), so indoor sources are chief concentration drivers. Wooden building materials emit terpenoids (Uhde and Salthammer, 2007), though stronger indoor emissions correspond to usage of consumer products such as general-purpose cleaners and air fresheners (Nazaroff and Weschler, 2004). About a decade ago, a set of articles (Coleman et al., 2008; Destailats et al., 2006; Singer et al., 2006a, 2006b) characterized cleaner and air freshener emissions and their secondary emission potentials. Singer et al. (2006a, 2006b) conducted ‘typical use experiments’ with products identified as customer preferred by surveys in a 50 m^3 room at $\text{AER} = 1 \text{ h}^{-1}$. Some terpenoids (e.g. limonene) reached 1-hr integrated concentrations of 100s of ppb. Also, in the Relationship of Indoor, Outdoor and Personal Air (RIOPA) study,

which measured a set of pollutants in 310 occupied homes, 48-hr time-averaged limonene indoor concentrations reached a 99th percentile of ~50 ppb (Weisel et al., 2005).

The oxidation of ROGs initiates reactions that generate myriad semivolatile organic compounds (SVOC) that can partition or nucleate to the condensed phase to form secondary organic aerosol (SOA), which may comprise a large fraction of the global aerosol budget (Kanakidou et al., 2005; Robinson et al., 2007). Over time in the atmosphere, ‘fresh’ SOA that is composed of early generation products ‘ages’ due to later generation reactions (e.g. oxidation, oligomerization) that make it more hydrophilic while also lowering the overall aerosol volatility, such that it may be less volatile than much of that from primary organic aerosol (POA) emissions (Donahue et al., 2009; Jimenez et al., 2009). The focus of this article is indoor SOA formation due to terpenoid ozonolysis. Waring (2014) modeled SOA formation over the RI-OPA dataset and concluded that SOA comprised a large amount of indoor organic aerosols and PM_{2.5} (total mass with aerodynamic diameter $\leq 2.5 \mu\text{m}$) for a subset of the results (e.g., > 47% of indoor organic aerosol and > 30% of total PM_{2.5} for 10% of the modeled cases).

Not all of the products generated by ROG oxidation have low enough volatility to partition to generate SOA (Kroll and Seinfeld, 2008). SOA formation strength is most often parameterized with what is known as the aerosol mass fraction (AMF), also called the SOA yield. The AMF is the mass ratio of the SOA formed to reactive organic gas (ROG) consumed (Odum et al., 1996). Because SOA formation is predominately an absorptive phenomenon, AMFs for ROGs span a range of values and increase with organic aerosol (OA) concentrations over 2 to 3 orders of magnitude, depending on the particular ROG oxidized (Griffin et al., 1999; Hoffmann et al., 1997). To recreate this behavior, AMF frameworks lump the numerous products generated by ROG reactions into *n*-bins of like products, where each lumped product bin has an effective saturation concentration and formation strength associated with it (Donahue et al., 2006; Kanakidou et al., 2005; Odum et al., 1996; Presto and Donahue, 2006).

Figure 1 displays the structures for some monoterpenes (C₁₀H₁₆, 136.24 g/mol) and a few monoterpene alcohols (C₁₀H₁₈O, 154.25 g/mol) likely to be meaningfully present indoors, based on measurements of consumer product emissions (Singer et al., 2006a, 2006b). Moreover, the monoterpenes α -pinene, β -

pinene, and limonene are routinely measured indoors (Brown et al., 1994; Hodgson and Levin, 2003; Weisel et al., 2005). Table 1 lists ranges of some measured AMFs for ozonolysis of α -pinene, β -pinene, limonene, α -terpineol, and linalool; other than for these ROGs, ozonolysis-dominated AMFs have been measured in limited numbers for the terpenoids in Figure 1 (e.g. one measured AMF for α -terpinene and terpinolene, from Ng et al., 2006), though fuller sets of photochemical AMF chamber experiments exist for them (Griffin et al., 1999; Hoffmann et al., 1997).

Figure 1. Chemical structures for common indoor terpenoids, as well as a surrogate for limonene used in experiments probing the SOA formation owing to endo bond ozonolysis only.

While indoor residence times are short enough that indoor SOA is unlikely to age appreciably as compared to ambient SOA, multigenerational chemistry can still impact SOA formation strength indoors. One reason for this is because alkene ozonolysis reactions produce hydroxyl and other radicals (Atkinson and Arey, 2003; Kroll and Seinfeld, 2008). A second reason is because many of the terpenoids in Figure 1 are doubly unsaturated and may react with ozone at multiple locations. This article focuses on parameterizing the impact of limonene's multigenerational ozone reactions on SOA formation within the context of indoor environments. Limonene has one methyl-substituted endocyclic double bond in a six-member ring and an exocyclic terminal unsaturation. The endo bond may react 10–50× faster than the exo bond (Zhang et al., 2006), so ozone reactions with the endo bond yield most first generation SOA forming products. Following this reaction, the SOA formation strength can increase further for the same reacted

limonene mass as the second double bond in first generation products are further ozonated (Ng et al., 2006), likely with ozone in the aerosol phase (Maksymiuk et al., 2009; Zhang et al., 2006).

Table 1. Ranges of formed secondary organic aerosol (SOA) concentrations, aerosol mass fractions (AMF), and chamber conditions for ozonolysis of important indoor reactive organic gas (ROG) terpenoids.

Terpenoid ¹	AMF ²	SOA ($\mu\text{g}/\text{m}^3$)	ROG ³ (ppb)	ozone ³ (ppb)	ozone/ ROG	OH scavenger	Temp. (K)	RH (%)	Ref. ⁴
limonene	0.26-1.09	1.7-718.4	1.1-108.7	800-3950	14-909	2-butanol	296-300	2-10%	a
	0.63-0.94	400-3390	180-650	120-810	0.38-1.2	None	288-302	13-100%	b
	0.025-0.79	5.4-330	20-663	41-300	0.068-15	None	295-301	<10%	c
	0.33-0.67	35-88	10-81	9-120	0.13-12	None	295-297	7%	d
linalool	0.003-0.019	0.3-3.75	6.2-72	4-116	0.056-19	None	295-296	7%	e
α -pinene	0.02-0.4	0.15-404	0.3-212	24-3100	1-300	None, 1- or 2-butanol, cyclohexane	293-322	<2-65%	f-q
β -pinene	0-0.052	0-22.5	11.9-80.1	48-320	4	2-butanol	292-308	5%	i
α -terpineol	0.056-0.24	2.21-301	6.39-226	25000	110-3900	None	297-298	<3.5%	r

1. Rate constants with ozone ($\text{ppb}^{-1} \text{h}^{-1}$) are: limonene 0.019; α -pinene 0.0076; β -pinene 0.0013 (Atkinson, 1990); linalool 0.040 (Atkinson et al., 1995); α -terpineol 0.027 (Wells, 2005).
2. AMFs from Hoffmann et al. (1997) generally had higher AMFs than other studies for the same terpenoids: linalool had an ozonolysis AMF of 0.078, α -pinene of 0.671, and β -pinene of 0.321.
3. ROG and ozone concentrations were initial concentrations for batch or flow through experiments when available; otherwise they were reported change in ROG or ozone. All concentrations from (d), (e), and (f) and some from (o) were steady state concentrations.
4. References for ozonolysis AMFs and experimental conditions: (a) (Zhang et al., 2006); (b) (Leungsakul et al., 2005); (c) (Youssefi and Waring, 2014); (d) (Chen and Hopke, 2010); (e) (Chen and Hopke, 2009a); (f) (Chen and Hopke, 2009b); (g) (Cocker III et al., 2001); (h) (Gao et al., 2004); (i) (Griffin et al., 1999); (j) (Pathak et al., 2007a); (k) (Pathak et al., 2007b); (l) (Presto et al., 2005); (m) (Presto and Donahue, 2006); (n) (Song et al., 2007); (o) (Shilling et al., 2008); (p) (Shilling et al., 2009); (q) (Youssefi and Waring, 2015); (r) (Yang and Waring, 2016).

For limonene, a picture has emerged regarding its SOA formation owing to first- and second-generation ozonolysis chemistry. Zhang et al. (2006) measured AMFs from limonene ozonolysis at strong ozone excess conditions so that both bonds were fully oxidized. Conversely, Donahue et al. (2007) estimated limonene AMFs at ozone limited conditions so that the endo bond only would be oxidized, using a surrogate compound having a single endo unsaturated bond, limonene ketone ($\text{C}_9\text{H}_{14}\text{O}$, 138.21 g/mol), as also shown in Figure 1. Over an OA concentration range of 0.1 to 1,000 $\mu\text{g}/\text{m}^3$, AMFs for endo only oxidation range from 0.0092 to 0.31 and are a mean (standard deviation) factor of 0.25 (0.0082) lower than those for endo and exo ozonolysis, which range from 0.034 to 1.2. To explore conditions when ozone is neither in excess or limited, Leungsakul et al. (2005), Chen and Hopke (2010), and Youssefi and Waring

(2014) measured AMFs for limonene ozonolysis over conditions when ozone and limonene were similar in magnitude, and those AMFs existed between the endo only and endo + exo boundaries.

Besides ozone/ limonene ratios, conditions differed among these experiments according to their residence times. Zhang et al. (2006), Leungsakul et al. (2005), and Donahue et al. (2007) conducted batch experiments without air exchange, while Chen and Hopke (2010) conducted steady state flow through experiments at $AER = 0.67 \text{ h}^{-1}$, and Youssefi and Waring (2014) conducted transient flow through experiments at $AERs = 0.28 \text{ to } 0.97 \text{ h}^{-1}$. Since they varied residence times, Youssefi and Waring (2014) observed that the AMF decreased linearly with the logarithm of the ratio of the heterogeneous ozone oxidation rate and chamber residence times. The work herein improves upon that earlier work by parameterizing limonene formation within the volatility basis set (VBS) framework (Donahue et al., 2006; Presto and Donahue, 2006), while also incorporating more limonene AMF data into the parameterization itself. Using this study, one can predict indoor SOA formation due to limonene ozonolysis at various ozone, limonene, and AER conditions within a broader VBS organic aerosol modeling effort.

2. METHODOLOGY

2.1. Parameterizing SOA formation with the AMF

This work aims to improve SOA prediction indoors due to limonene ozonolysis and relies on the established method of using the aerosol mass fraction (AMF), a.k.a. the SOA yield, to parameterize the SOA formation strength due to ROG oxidation. The AMF is defined as in Equation 1:

$$AMF = \frac{\Delta C_{SOA}}{\Delta ROG} \quad (1)$$

where ΔC_{SOA} ($\mu\text{g}/\text{m}^3$) is the formed SOA mass concentration; and ΔROG ($\mu\text{g}/\text{m}^3$) is the reacted ROG mass concentration. Since ROG oxidation initiates chemistry that produces a suite of products, some of which form SOA, the ROG oxidation may be generally cast as in Equation 2:

where α_i is the mass-based yield of product species or group of species i ; and c_i^* ($\mu\text{g}/\text{m}^3$) is the effective gas phase saturation concentration of species or group i . Following the partitioning theory of Pankow (1994), the magnitude of the AMF may be expressed as a function of the total organic aerosol (OA) concentration, as in Equation 3 (Odum et al., 1996; Presto and Donahue, 2006):

$$\text{AMF} = \sum_i \alpha_i \xi_i = \sum_i \alpha_i \left(1 + \frac{c_i^*}{C_{\text{OA}}} \right)^{-1} \quad (3)$$

where ξ_i is the condensed phase mass fraction of species or group i ; and C_{OA} ($\mu\text{g}/\text{m}^3$) is the total organic aerosol mass concentration, including any background indoor organic aerosol, $C_{\text{OA,bg}}$ ($\mu\text{g}/\text{m}^3$), plus formed SOA. Thus, in chambers where background OA is negligible, $C_{\text{OA}} = C_{\text{SOA}}$, and when the AMF is used to model real indoor environments, $C_{\text{OA}} = C_{\text{OA,bg}} + C_{\text{SOA}}$.

As Equation 3 demonstrates, for any i the $\xi_i = (1 + c_i^*/C_{\text{OA}})^{-1}$. As discussed by Donahue et al. (2009), when the total OA concentration equals the saturation concentration of i and $c_i^* = C_{\text{OA}}$, that product will exist in equilibrium at 50% in the condensed phase and 50% in the gas phase (i.e., $\xi_i = 0.5$). It also shows that for a product i with $c_i^* = 0.1 \cdot C_{\text{OA}}$ then that product will be 90% in the condensed phase ($\xi_i = 0.9$), but for $c_i^* = 10 \cdot C_{\text{OA}}$ then only 10% of it will exist as condensed ($\xi_i = 0.1$). This behavior demonstrates why the AMF is larger and SOA formation is stronger at higher C_{OA} , because at higher values of C_{OA} the ROG oxidation products with higher volatilities (c_i^*) meaningfully partition to the condensed phase.

Until the last decade, the most popular AMF framework that used Equation 3 has been the ‘two-product model’ as first proffered by Odum et al. (1996). Early seminal AMF articles (Griffin et al., 1999; Hoffmann et al., 1997) used this framework. For AMFs over a range of ΔC_{SOA} corresponding to a range of ΔROG , the two-product model fits the observed data using four free parameters $\{\alpha_1, c_1^*, \alpha_2, c_2^*\}$, where the first product is a hypothetical lumped concentration of lower volatility products $\{\alpha_1, c_1^*\}$ and the second product is similar but for higher volatility products $\{\alpha_2, c_2^*\}$. These fits are unconstrained, highly covariant, and dependent on the range of SOA generated in the chamber experiments (Donahue et al., 2009; Kroll and Seinfeld, 2008; Presto and Donahue, 2006).

The ‘volatility basis set (VBS)’ similarly assigns reaction products into a small set of bins of lumped products (Donahue et al., 2006). However, it capitalizes on the behavioral interplay embedded in the relationship of $\zeta_i = (1 + c_i^*/C_{\text{OA}})^{-1}$ and constrains c_i^* at $\log_{10}$ spaced intervals and fits only α_i , which indicates the strength of mass formation of each binned group of compounds, using empirical data. Therefore, for a VBS fit to SOA concentration data ranging from 10 to 100 $\mu\text{g}/\text{m}^3$, one might constrain the c_i^* at {1, 10, 100, 1000 $\mu\text{g}/\text{m}^3$ } and then fit four parameters of $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4\}$, respectively. Though the VBS and the two-product model both have four free parameters, the VBS fit is better behaved since the volatilities of the fitted products have been fixed at decadal spacing and therefore the fitting parameters α_i are less covariant (Donahue et al., 2009). The VBS is also superior to one- or two-product models because it is part of a larger framework that describes OA behavior generally (Donahue et al., 2006).

AMF fits may be used in mass balances to predict indoor SOA concentrations. The most common method to predict SOA formation is with a mass balance that computes the indoor SOA formation rate as the product of the AMF and the rate of terpenoid ozonolysis (Waring and Siegel, 2010; Youssefi and Waring, 2012). For a well mixed box, the simplest mass balance accounts for the source of indoor-formed SOA and losses of air exchange and deposition, as in Equation 4:

$$\frac{dC_{\text{SOA}}}{dt} = \text{AMF} \cdot k C_{\text{O}_3} C_{\text{terp}} \Gamma_{\text{terp}} - (\lambda + \beta_{\text{SOA}}) C_{\text{SOA}} \quad (4)$$

where t (h) is time; k ($\text{ppb}^{-1} \text{h}^{-1}$) is the gas phase reaction rate constant between ozone and a terpenoid; C_{O_3} (ppb) and C_{terp} (ppb) are the ozone and terpenoid concentrations, respectively; Γ_{terp} is a factor to transform the terpenoid from concentration units of ppb to $\mu\text{g}/\text{m}^3$ (e.g. 5.57 $\mu\text{g}/\text{m}^3/\text{ppb}$ at 25 °C for monoterpenes); λ (h^{-1}) is the AER; and β_{SOA} (h^{-1}) is the SOA deposition rate. The formulation of the AMF in Equation 3 is then substituted into Equation 4 for solution. If desired, Equation 4 can be expanded to include other processes, such as loss by mechanical aerosol filtration, which is represented as the product of the mechanical recirculation rate, λ_r (h^{-1}), and filtration efficiency, η .

2.2. Parameterizing limonene formation

This work offers a methodology to predict SOA formation owing to first and second generation reactions of ozone with limonene, within the VBS framework. Five sets of experiments were used, including four sets of limonene ozonolysis experiments (Chen and Hopke, 2010; Leungsakul et al., 2005; Youssefi and Waring, 2014; Zhang et al., 2006) and one set of limona ketone ozonolysis experiments (Donahue et al., 2007). Figure 2a plots AMF data points from the four limonene experiments. Figure 2a further shows the overall VBS fit (dashed line) for the Zhang et al. (2006) experiments, which were at high ozone excess conditions with ozone to limonene ratios of $[O_3]/[lim] = 14$ to 909 (Table 1). Accordingly, the endo and exo bonds in these experiments were both ozonated, so this AMF fit represents the AMF upper bound owing to limonene ozonolysis SOA formation. Also plotted is the VBS fit (solid line) from Donahue et al. (2007), which quantified formation by ozonolysis of limona ketone and was used as a surrogate. SOA generated from this ozonolysis of this surrogate approximates formation as if only the limonene endo bond were ozonated, so it serves as a good AMF lower bound for limonene ozonolysis SOA formation. For $c_i^* = \{1, 10, 100, 1000 \mu\text{g}/\text{m}^3\}$, the Zhang et al. (2006) $\alpha_i = \{0.34, 0.28, 0.32, 0.59\}$ and the Donahue et al. (2007) $\alpha_i = \{0.096, 0.039, 0.096, 0.18\}$. Note that the Zhang et al. (2006) α_i were refit for this work to account for use of fewer bins ($n = 4$ versus 6).

The other three sets of limonene experiments were at ratios of $[O_3]/[lim] = 0.068$ to 15, so neither reactant was much in excess. Accordingly, all but two of those AMFs fall between the defined upper and lower limonene ozonolysis AMF boundaries. To parameterize SOA formation strength at any AMF between the two boundaries, this work follows a procedure from Presto and Donahue (2006) and Donahue et al. (2007) and uses a ‘mixing’ coefficient, β , to determine the makeup of a ‘resultant AMF’ situated between the lower and upper bound AMFs, such that:

$$\alpha_i(\beta) = \beta\alpha_i^{\text{enex}} + (1 - \beta)\alpha_i^{\text{en}} \quad (5)$$

where $\alpha_i(\beta)$ represents the weighted average of the mass-based yield parameters for the AMF upper bound with limonene endo + exo bond ozonolysis (α_i^{enex}) and for the limonene endo bond ozonolysis only (α_i^{en}) for

each product i , where the fraction of each contributing to the resultant AMF is set by β for each binned group of compounds equally. Therefore, when $\beta = 0$ the resultant AMF equals the lower bound AMF and when $\beta = 1$ the resultant AMF equals the upper bound AMF. For demonstration, Figure 2a plots the form of the resultant AMF for values of β ranging from -0.2 to 1.2 .

For the empirical AMFs on Figure 1 (Chen and Hopke, 2010; Leungsakul et al., 2005; Youssefi and Waring, 2014; Zhang et al., 2006), the β for each data point was determined by minimizing the sum of the squared difference between the resultant AMF and the measured AMF. After that, β was analyzed for trends corresponding to ozone and limonene concentrations, as well as the AERs.

This analysis ignores the impact of hydroxyl radicals (OH), which are generated when ozone reacts terpenes and other alkenes (Atkinson and Arey, 2003), including the ozone reactions with limonene itself. At ozone and limonene concentrations typical of indoors, Youssefi and Waring (2014) predicted that an average of $\sim 75\%$ and 25% of limonene would react with ozone and OH, respectively, that was generated by limonene ozonolysis. However, since OH reactions with limonene yield products similar to ozonolysis in terms of volatility (Larsen et al., 2001), the AMFs should be little affected. Potential impacts of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) on limonene AMFs are also ignored, though NO_x has been shown to have a small impact on limonene ozonolysis AMFs (Zhang et al., 2006). Relatedly, the potential impact of any NO_2 reactions with ozone or stabilized Criegee intermediates (SCI) to yield NO_3 (Shallcross et al., 2014) is also neglected, which is reasonable since the ozone/ limonene reactions typically have higher rates than NO_2 / ozone and NO_2 / SCI reactions (Waring and Wells, 2015). The source of OH production by nitrous acid (HONO) photolysis is also neglected in this work (Gómez Alvarez et al., 2013).

3. RESULTS AND DISCUSSION

3.1. Impact of concentrations and AER on mixing coefficient

Over the four considered sets of limonene ozonolysis experiments, the fitted mixing coefficient ranged from $\beta = -0.253$ to 1.31 . One β value was below and four β values were above this range over all 38 fitted data points. As is apparent, there was no boundary restriction on the fit parameter enforcing that

$0 \leq \beta \leq 1$. These $\beta < 0$ and $\beta > 1$ are due to the combined impact of AMF measurement uncertainty for (usually on the order of 10% of measured AMF), and because individual AMFs were used to generate the best-fit of Zhang et al. (2006), so some necessarily fall above the limit. To explore the dependence of β on the reactant and residence time conditions, Figure 2b plots β as a function of $\log_{10}([O_3]/[lim])$, along with the 95% confidence interval, with data points additionally color coded by AER ranges. Experiments from Zhang et al. (2006) and Leungsakul et al. (2005) were conducted in a batch chamber and were assigned an AER = 0.01 h^{-1} , as if 1% of the chamber volume of air were lost per hour due to leakage. As Figure 2b shows, the β had a strong dependence on $\log_{10}([O_3]/[lim])$ and a weak dependence on the AER.

Figure 2a. Aerosol mass fractions (AMF) from four limonene experimental sets (reference list in legend) at different ozone and limonene ratios ($[O_3]/[lim]$) and air exchange rates (AER); the dark ozonolysis VBS fit (dashed line) from Zhang et al. (2006), which represents the AMF upper bound owing to limonene ozonolysis SOA formation; the VBS fit to the limonene ketone ozonolysis VBS fit (solid line) from Donahue et al. (2007), which represents the lower bound owing to limonene ozonolysis SOA formation; and the 'resultant AMF' for different mixing coefficients, β , of $-0.2 \leq \beta \leq 1.2$. **2b.** Fitted mixing coefficients, β , as a function of $\log_{10}([O_3]/[lim])$, along with a 95% confidence interval, and data points color coded by AER ranges.

A series of multiple linear regressions was used to investigate the influence of different predictor variables on the outcome of the β coefficient, considering linear, quadratic, and interaction variables among the parameters of $[O_3]$, $[lim]$, $\log_{10}[O_3]$, $\log_{10}[lim]$, and AER. Of all the considered regression combinations, the best performing one was the simple:

$$\beta = 0.254 \cdot \log_{10} \left(\frac{[\text{O}_3]}{[\text{lim}]} \right) - 0.217 \cdot \text{AER} + 0.501 \quad (R^2 = 0.74) \quad (6)$$

This regression may be used in models to predict the resultant AMF for limonene ozonolysis over a range of reactant concentrations and AERs, so long as the predictors are within the bounds used to develop the fit. The relevant ozone and limonene concentration boundaries are given in Table 1, and the AERs ranged from 0.01 to 0.97 h⁻¹. Please note that if the regression is performed without using the Zhang et al. (2006) AMF data points, which were used to form the basis of the upper limit AMF curve, the fit is similar ($\beta = 0.309 \cdot \log_{10}([\text{O}_3]/[\text{lim}]) - 0.255 \cdot \text{AER} + 0.528$) but the coefficient of determination is lower ($R^2 = 0.53$). Other research using a mixing coefficient has defined it based on actual reactant ratios, such as NO_x/VOC (Presto and Donahue, 2006), but this work did not do so because of the multidimensional nature of the influencing parameters (i.e., reactant ratios and AER).

For the regression in Equation 6, standardized regression coefficients (SRC) were used to contextualize the relative influence of each predictor on the outcome. The SRC is the actual regression coefficient normalized by the ratio of the standard deviations of the dependent to independent variables. SRCs range from -1 to +1 and indicate the importance of model predictors on the outcome. That is, a high |SRC| indicates a large influence, while a |SRC| near zero indicates no influence; an input with a -SRC changes the outcome negatively and a +SRC changes the outcome positively (Saltelli et al., 2006). SRCs for predictors of $\log_{10}([\text{O}_3]/[\text{lim}])$ and AER were 0.755 and -0.207, respectively. Hence, the $\log_{10}([\text{O}_3]/[\text{lim}])$ influenced β positively, by an absolute factor of 3.6 more than the AER, which influenced β negatively. Thus, the relative concentrations of the reactants have more potential to influence the resultant AMF for limonene ozonolysis than reaction constraints due to lower residence times indoors, though both predictors influence the rate at which the exo unsaturated bond may be ozonated (Youssefi and Waring, 2014).

3.2. Demonstration of resultant AMFs and indoor SOA formation

With a framework to predict how the parameters of $\log_{10}([\text{O}_3]/[\text{lim}])$ and AER influence the mixing coefficient, β , the next question is how this relationship manifests itself for indoor SOA formation due to

limonene ozonolysis at typical conditions. To explore this, a series of steady state simulations was performed at AER of $\lambda = 0.2, 0.5$, and 1.0 h^{-1} , a deposition rate of $\beta_{\text{SOA}} = 0.1 \text{ h}^{-1}$, and a background OA concentration of $C_{\text{OA,bg}} = 5 \text{ }\mu\text{g/m}^3$ (Waring, 2014), with indoor ozone $[\text{O}_3]$ fixed at 10 ppb and limonene $[\text{lim}]$ ranging from 0.1 to 100 ppb. The SOA concentrations were modeled with Equation 4 with a Runge Kutta order 4 numerical method, with Equation 3 substituted as the resultant AMF owing to the β from the fit in Equation 6, bounded at $0 \leq \beta \leq 1$. Therefore, this modeling assumes that the fit from Zhang et al. (2006) is the actual upper AMF limit, since AMF uncertainty would produce β values above 1 on the order of those observed and since the β from Zhang et al. (2006) were not a strong function of $\log_{10}([\text{O}_3]/[\text{lim}])$ on their own ($R^2 = 0.10$). Also, the AMFs and SOA concentrations that would be generated by lower bound ($\beta = 0$) and upper bound ($\beta = 1$) of the resultant AMF were computed for comparison. This modeling disregards SOA formed by ozone reactions with surface sorbed terpenoids (Wang and Waring, 2014; Waring and Siegel, 2013). Figure 3a-c illustrates the resultant, lower, and upper limit AMFs for these cases, while Figure 3d-f illustrates the predicted SOA concentrations.

For the ozone at $[\text{O}_3] = 10 \text{ ppb}$ and $[\text{lim}] = 0.1 \text{ to } 100 \text{ ppb}$, the $\log_{10}([\text{O}_3]/[\text{lim}])$ varied in the simulations from 2 to -1 from the low to high limonene concentrations, respectively. For the three AER cases, the resultant AMF was near or equal to the upper bound AMF when $[\text{lim}] \ll 1 \text{ ppb}$. Then, as the limonene concentration increased and $\log_{10}([\text{O}_3]/[\text{lim}])$ decreased, the resultant AMF decreased and tended toward the lower bound AMF limit. Furthermore, increasing the AER tended to decrease the resultant AMF. Indeed, when the AER was at its highest at 1 h^{-1} , the resultant AMF actually equaled the lower bound AMF as the limonene concentration approached 100 ppb. Regarding the SOA formation itself, the predicted SOA concentrations exhibited a large range of $C_{\text{SOA}} = 0.00360 \text{ to } 107 \text{ }\mu\text{g/m}^3$. Also, just as the resultant AMF transformed from being near the upper to lower bound as the limonene concentration increased for a fixed $[\text{O}_3] = 10 \text{ ppb}$, the SOA formed by the resultant AMF shifted from that predicted with the upper bound AMF to being more near that predicted by using the lower bound AMF.

Figure 3a-c. Predicted aerosol mass fractions (AMF) for steady ozone concentration of 10 ppb and range of steady indoor limonene concentrations, at three typical AERs, including the 'resultant AMF' as well as the upper and lower bound AMFs from Zhang et al. (2006) and Donahue et al. (2007), respectively (see text for details). **3d-f.** Corresponding steady state $\log_{10}$ SOA concentrations for those conditions.

This exhibited behavior of the resultant AMF tending toward the lower bound AMF as the limonene concentration increases has strong implications for exposure to SOA owing to limonene ozonolysis indoors. Accurately parameterizing formation due to limonene ozonolysis is important, since it is a component of many consumer products, can reach concentrations of >100 ppb, and has a reasonably fast reaction rate with ozone. Figure 3d-f demonstrate the large error possible for predicting SOA from limonene ozonolysis with incorrect AMFs. For example, at AER of 0.5 h⁻¹, for [lim] = 10 ppb with lower, resultant, and upper bound AMFs of 0.11, 0.25, and 0.52, the indoor SOA is predicted at 1.8, 4.3, and 8.8 $\mu g/m^3$, respectively. Moreover, for [lim] = 100 ppb, the lower, resultant, and upper bound AMFs are 0.15, 0.24, and 0.87, and predicted SOA is 25, 39, and 145 $\mu g/m^3$, respectively. Hence, in this simple example alone, SOA could be under-predicted at a percent difference (% diff. = abs[resultant AMF – boundary AMF]/

resultant AMF) of 58% and 37% at the lower bound AMF for $[\text{lim}] = 10$ and 100 ppb, respectively, and over-predicted by 106% and 268% at the upper bound AMF.

Finally, though not included herein, other physicochemical indoor processes can easily be modeled with this limonene AMF framework if desired—categorized into those that affect reactant concentrations, OA concentrations, or building air flow rates. Ozone is reduced by reactions with occupant skin (Fadeyi et al., 2013) and other surface or gas phase reactions, which influences both the amount of ozone available and the $\log_{10}([\text{O}_3]/[\text{lim}])$, so that the reaction rate ($kC_{\text{O}_3}C_{\text{terp}}$) and AMF are both reduced. Limonene can be reduced by sorption to surfaces (Singer et al., 2004), which would similarly reduce $kC_{\text{O}_3}C_{\text{terp}}$ but would tend to increase the AMF since $\log_{10}([\text{O}_3]/[\text{lim}])$ increases. Indoor OA due to other sources increase the AMF for the same $kC_{\text{O}_3}C_{\text{terp}}$, since condensable products will partition into any OA (see Equation 3), so building aspects and controls that reduce indoor OA, such as loss to the envelope from infiltration air (El Orch et al., 2014) or loss to PM filters in ventilation or recirculation air streams (Waring and Siegel, 2008), reduce the AMF for the same $kC_{\text{O}_3}C_{\text{terp}}$. Increases in recirculation air flow rates increase the efficacy of PM filters, and can also potentially reduce ozone by increasing air velocity above building surfaces, decreasing the thickness of the hydrodynamic boundary layer, and thus increasing the rate of ozone surface reactions (Cano-Ruiz et al., 1993).

3.3. Implications for real indoor SOA formation

To be meaningful from an exposure standpoint, terpene ozonolysis must generate SOA at such a rate that the SOA concentration at least on the order of $1 \mu\text{g}/\text{m}^3$, since competing sources such as outdoor-to-indoor transport (Johnson et al., 2016), smoking (Wallace, 1996; Waring and Siegel, 2006), or cooking (Wallace, 2006) often generate indoor particles greater than this threshold. To reach this SOA formation strength, limonene must be elevated to 1–10 ppb or over, which is typical with product usage (Singer et al., 2006a) and often reached from a time-averaged perspective in U.S. residences (Weisel et al., 2005). At $[\text{lim}] > 10$ ppb, however, the resultant AMFs will generally be nearer the lower bound AMF than the upper bound AMF for most AER conditions. Therefore, predicting formation with AMFs near the upper

bound AMF has the potential to greatly over-predict SOA for conditions likely to have meaningful ozone/limonene reactions. Moreover, in the example immediately above, the possibility of over-prediction for limonene increased as a % diff. from 106 to 268% as limonene increased from 10 to 100 ppb, demonstrating how this over prediction error can become quite large as limonene concentrations increase. Thus, using the correct resultant AMF for limonene ozonolysis is highly important.

Other doubly unsaturated terpenoids besides limonene (Figure 1) exhibit SOA formation behavior that depends on the prevalence of later generation ozonolysis reactions. Their SOA formation behaviors at higher ozone to terpene ratios depend on the location of unsaturated bonds in the carbon structure. That is, the cleaving that accompanies ozone reactions with unsaturated bonds within a ring result in ring opening but no loss of carbon and addition of three oxygen atoms, with associated lower product volatility and higher SOA formation potential. Conversely, ozone reactions with unsaturated bonds in straight chains cleave the molecule, generating products with higher volatility and lower SOA formation potential (Kroll and Seinfeld, 2008). Likely important indoor terpenoids with unsaturated bonds in rings include α - and β -terpinene and terpinolene, while some terpenoids with non-ring unsaturated bonds include linalool and γ -terpinene. Most of these terpenoids have not had their AMFs quantified, except for a few data points (Ng et al., 2006). However, SOA formation due to linalool ozonolysis has been explored (Chen and Hopke, 2009a), and its AMFs are small (Table 1), consistent with its two linear unsaturated bonds. Exploring the impacts of multigenerational chemistry on AMFs for likely important terpenoids with unsaturated bonds in ringed structures that have not yet been studied, e.g. α - and β -terpinene and terpinolene, is therefore a priority to develop a more complete understanding of SOA formation indoors.

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