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## Degradation of indoor limonene by outdoor ozone: A cascade of secondary organic aerosols<sup>☆</sup>



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## ABSTRACT

In indoor air, terpene–ozone reactions can form secondary organic aerosols (SOA) in a transient process. ‘Real world’ measurements conducted in a furnished room without air conditioning were modelled involving the indoor background of airborne particulate matter, outdoor ozone infiltrated by natural ventilation, repeated transient limonene evaporations, and different subsequent ventilation regimes. For the given setup, we disentangled the development of nucleated, coagulated, and condensed SOA fractions in the indoor air and calculated the time dependence of the aerosol mass fraction (AMF) by means of a process model. The AMF varied significantly between 0.3 and 5.0 and was influenced by the ozone limonene ratio and the background particles which existed prior to SOA formation. Both influencing factors determine whether nucleation or adsorption processes are preferred; condensation is strongly intensified by particulate background. The results provide evidence that SOA levels in natural indoor environments can surpass those known from chamber measurements. An indicator for the SOA forming potential of limonene was found to be limonene ketone. Multiplying its concentration (in  $\mu\text{g}/\text{m}^3$ ) by 450 ( $\pm 100$ ) provides an estimate of the concentration of the reacted limonene. This can be used to detect a high particle formation potential due to limonene pollution, e.g. in epidemiological studies considering adverse health effects of indoor air pollutants.

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## 1. Introduction

Airborne particles are of greatest concern worldwide because of their potential adverse health impacts (Brook et al., 2010; Rohr, 2013). This refers not only to the outdoor pollution but much more to the quality of indoor air to which people are exposed for the longest time. Besides infiltration (Han et al., 2015; Wang et al.,

2016) and indoor emission (Wei et al., 2014) of particles, the formation of secondary particles in indoor air from organic compounds and infiltrated ozone is an issue of current interest. In indoor air, a variety of volatile organic compounds is prevalent (Edwards et al., 2006; Eklund et al., 2008; Missia et al., 2010; Yrieix et al., 2010), depending on the sources, which arise with temporary activities (such as renovation (Jia et al., 2012; Reitzig et al., 1998)), with permanent emissions (wooden furniture), or in result of repeated habitual release (air freshener, cleaning agents). Therefore, concentrations can strongly depend on household (Sarigiannis et al., 2011) and season (Schlink et al., 2004). Especially terpenes are ubiquitous in indoor air (Wainman et al., 2000), often because limonene and  $\alpha$ -pinene are used as solvents and scented agents (Nazaroff and Weschler, 2004). At ventilation, photo-chemically formed ozone can enter the room from outdoors and can reach up to 70% of outdoor concentrations (Weschler, 2000). Terpene–ozone reactions generate numerous gaseous products as well as

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secondary organic aerosols (SOA).

This process has been intensively researched in box and chamber experiments (Langer et al., 2008; Presto et al., 2005; Sarwar and Corsi, 2007; Schripp et al., 2012; Song et al., 2011; Toftum et al., 2008). SOA created by degradation of reactive organic compounds can dominate the overall organic aerosol budget (Robinson et al., 2007). The gas-phase degradation is initiated by reaction with hydroxyl radicals (OH), ozone, nitrate (NO<sub>3</sub>) radicals or via photolysis and leads to organic products containing one or more polar oxygenated functional groups, which tend to make the products less volatile (Hallquist et al., 2009; Waring and Wells, 2015). Here, ozonolysis and oxidation by OH are the two major pathways that were recently compared for limonene (Zhao et al., 2015). The authors concluded that the ozonolysis produced a higher aerosol yield than the respective OH oxidation. For some other possible SOA forming reactions, such as between methanol and OH, the exact mechanism still remains elusive (Elm et al., 2013).

The mixture of semi-volatile oxidized reactive organic gases (OROG) resulting from the degradation of reactive organic compounds (ROG, which is limonene in our study), can generate SOA by partitioning to available aerosols or self-nucleation (Youssefi and Waring, 2014). The yield of SOA formation is measured as the aerosol mass fraction ( $AMF = c_{SOA}/c_{\Delta ROG}$ ), that is the mass concentration ratio of generated organic aerosol particles ( $c_{SOA}$ , in  $\mu\text{g}/\text{m}^3$ ) and the ROG mass reacted ( $c_{\Delta ROG}$ , in  $\mu\text{g}/\text{m}^3$ ) (Odum et al., 1996). In SOA reaction models, the AMF is typically in the range of 0.05–0.80 for limonene ozonolysis (Fadeyi et al., 2009; Grosjean et al., 1993; Hoffmann et al., 1997; Youssefi and Waring, 2012) in a static system at steady state. However, recent findings (Youssefi and Waring, 2014) suggest a dynamic framework for the indoor SOA formation with air exchange. Efforts to identify factors influencing the AMF were focused on the type of the oxidized compound and the organic aerosol mass concentration (Odum et al., 1996), temperature (Saathoff et al., 2009), and air humidity (Chang and Pankow, 2006). As SOA formation is subject to ongoing chemical degradation (multi-generation oxidation/aging depending on the air composition including nitrogen oxides and UV radiation (Kroll et al., 2006)) and to the achievement of an equilibrium between gas and particle-phase, the AMF is expected to change in time (Hallquist et al., 2009). While some previous studies assumed a constant AMF, here we assessed the time dependence of the SOA yield.

Limonene is doubly unsaturated and therefore has a much higher potential for SOA formation compared to  $\alpha$ -pinene (Leungsakul et al., 2005). Limonene is often used as a model compound to study terpene ozonolysis in reaction chambers (Langer et al., 2008). Here we studied the reaction  $limonene + O_3 \rightarrow OROG \rightarrow SOA$  in a real indoor environment. As the calculation of AMF demands for the amount of reacted limonene that cannot be measured directly, we apply a framework developed by Youssefi and Waring (2012). These authors consider the concentration of a hypothetical product dROG,  $c_{dROG}$  (in  $\mu\text{g}/\text{m}^3$ ), which is a lumped compound representing limonene oxidation products, and which develops in time  $t$  (in h) according to (eq. (1)), including the effects of the source (chemical reaction between ozone of concentration  $c_{O_3}(t)$  (in  $ppb$ ) and limonene of concentration  $c_{lim}(t)$  (in  $\mu\text{g}/\text{m}^3$ )) and losses due to air exchange rate ( $\lambda$  in  $[h^{-1}]$ ) and surface deposition rate ( $\beta_{SOA}$  in  $[h^{-1}]$ ):

$$\frac{dc_{dROG}(t)}{dt} = \kappa c_{O_3}(t)c_{lim}(t)\Gamma - \left( \lambda + \beta_{SOA} + \frac{1}{AMF(t)} \frac{dAMF(t)}{dt} \right) c_{dROG}(t) \quad (1)$$

where  $\kappa = 0.018 \text{ ppb}^{-1} \text{ h}^{-1}$  is the reaction rate constant for ozone reactions with limonene at 25 °C (Waring et al., 2011) and  $\Gamma$  a

transformation factor to change units between [ $ppb$ ] and [ $\mu\text{g}/\text{m}^3$ ]. Note, that due to the non-vanishing air exchange rate in a transient system,  $c_{dROG} < c_{\Delta ROG}$  (Youssefi and Waring, 2014), and  $c_{dROG}(t)$  is relevant for the yield of SOA formation. Eq. (1) involves the time-dependent  $AMF(t)$ , which we aim to determine ultimately in our study. As an approximate solution, Youssefi and Waring (2014) suggested an iterative procedure that was applied here (details in Supplementary Information (SI)).

Particle yields, observed in chamber experiments, are not unconditionally applicable to real indoor environments (Youssefi and Waring, 2012). The ozone concentrations considered in many previous studies were at the top end of indoor ozone concentrations for mid-European cities and the chamber conditions are transferable to air conditioned environments, but not to the more common situation of manual ventilation associated with moderate indoor ozone levels of about 10–40  $\mu\text{g}/\text{m}^3$  (Fan et al., 2003; Waring et al., 2011; Weschler and Shields, 1999; Zhang et al., 2006). Our previous analysis (Rösch et al., 2015) of SOA formation in a genuine indoor environment suggested that the number concentration of newly formed particles significantly exceeds the number concentration resulting from ventilation and that the particulate background might impact the SOA formation. We are unaware of any studies that explicitly addressed the temporal development of the AMF, considered the impact of background particle concentrations occurring in furnished indoor spaces with natural ventilation, and decomposed the SOA forming processes.

To explore the effects of airborne particles in the initial phase of SOA formation and to estimate  $AMF(t)$ , we modelled our measurements (Rösch et al., 2015) of the temporal development of ozone, limonene, limona ketone (which is a stable product of the ozonolysis of limonene's exogenous double bond (Leungsakul et al., 2005)), and particle number concentrations in real indoor environments. The protocol comprised two consecutive series of ventilation, limonene evaporation, and ageing phases, and we disentangled the processes of SOA formation. Numerically solving eq. (1), we estimated the time dependent concentration of dROG, calculated  $AMF(t)$  and drew conclusions for the cascade of SOA formation indoors. Furthermore, we accounted for background particle concentrations and suggested an indicator substance for limonene ozonolysis.

## 2. Experimental methods

### 2.1. Location

The study site (Rösch et al., 2015) was a room (walls and ceiling painted, PVC flooring, no lighting, no ventilation and air conditioning system) of about 24  $\text{m}^3$  (3.5  $\text{m} \times 2.0 \text{ m} \times 3.4 \text{ m}$ ) volume in the basement of a five-story building. Opposite the door (protected by an antechamber) were two adjacent laminated glass windows (1.5  $\text{m}$  height; 0.8  $\text{m}$  width; not influenced by direct sunlight). Analyzers for organic compounds, temperature, and relative humidity were on a cupboard inside the room (Fig. 1).

Pre-experimental test samples indicated low levels of organic compounds except for 1-butanol (Merck, 99.8 %) used in the particle counter (see Table S1 in SI). To have realistic indoor characteristics, the room was not cleaned from background particles. Indoor air temperatures before ventilation were between 19 and 20 °C with a relative humidity of 45 %; they were similar for all experiments (OPUS 10 instrument of Lufft company, Germany, accuracy  $\pm 0.1 \text{ K}$  and  $\pm 0.1 \%$ ). The air exchange rate (AER) of this room was 0.07  $\text{h}^{-1}$  for closed windows and 1.0  $\text{h}^{-1}$  when windows were partially opened for ventilation (trace gas method using CO<sub>2</sub>, Q-Track 5757, TSI Instruments, accuracy  $\pm 3 \%$ ). Analyzers for particle number and ozone concentrations were arranged outside the room

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