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# Mass yields of secondary organic aerosols from the oxidation of $\alpha$ -pinene and real plant emissions

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Received: 19 October 2010 – Accepted: 19 October 2010 – Published: 24 November 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

## Abstract

Biogenic volatile organic compounds (VOCs) are a significant source of global secondary organic aerosol (SOA); however, quantifying their aerosol forming potential remains a challenge. This study presents smog chamber laboratory work, focusing on SOA formation via oxidation of the emissions of two dominant tree species from boreal forest area, Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies*), by hydroxyl radical (OH) and ozone (O<sub>3</sub>). Oxidation of  $\alpha$ -pinene was also studied as a reference system. Tetramethylethylene (TME) and 2-butanol were added to control OH and O<sub>3</sub> levels, thereby allowing SOA formation events to be categorised as resulting from either OH-dominated or O<sub>3</sub>-initiated chemistry. SOA mass yields from  $\alpha$ -pinene are consistent with previous studies while the yields from the real plant emissions are generally lower than that from  $\alpha$ -pinene, varying from 1.9% at an aerosol mass loading of 0.69  $\mu\text{g m}^{-3}$  to 13.6% at 32.8  $\mu\text{g m}^{-3}$ . Mass yields from oxidation of real plant emissions are subject to the interactive effects of the molecular structures of plant emissions and their reaction chemistry with OH and O<sub>3</sub>, which lead to variations in condensable product volatility. SOA formation can be reproduced with a two-product gas-phase partitioning absorption model in spite of differences in the source of oxidant species and product volatility in the real plant emission experiments. Condensable products from OH-dominated chemistry showed a higher volatility than those from O<sub>3</sub>-initiated systems during aerosol growth stage. Particulate phase products became less volatile via aging process which continued after input gas-phase oxidants had been completely consumed.

## 1 Introduction

The largest uncertainties in predicting anthropogenic influences on climate are associated with global aerosol burdens. One of the most significant global contributions of aerosol is secondary organic aerosol (SOA), which is formed when the atmospheric

ACPD

10, 28787–28820, 2010

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oxidation products of volatile organic compounds (VOCs) undergo gas to particle conversion. On a global scale, biogenic VOC (BVOC) emissions contribute an overwhelming fraction of 90% of the overall VOC emissions (Guenther et al., 1995), which underscores the importance of BVOC as a significant source of SOA.

The traditional model estimates of the global biogenic SOA flux range from 25 to 210 TgC/yr to the atmosphere (Hallquist et al., 2009). Field observations usually find higher SOA burdens than predicted by the current global aerosol models (e.g., Hallquist et al., 2009). It has been generally accepted that some unrecognized hydrocarbons are missing from these models. Recent studies have also focused on uncertainties in experimental variables for determining SOA mass. These include the initial hydrocarbon level (e.g., Shilling et al., 2008; Presto and Donahue, 2006), NO<sub>x</sub> level (e.g., Ng et al., 2007; Presto et al., 2005), oxidant species (e.g., Fry et al., 2009; Cai and Griffin, 2006; Griffin et al., 1999; Hoffmann et al., 1997), seed aerosol (e.g., Kroll et al., 2007; Pathak et al., 2007; Chan et al., 2007; Cocker et al., 2001), temperature (e.g., von Hessberg, et al., 2009; Saathoff et al., 2008; Pathak et al., 2007), relative humidity (RH) (e.g., von Hessberg, et al., 2009; Cocker et al., 2001; Seinfeld et al., 2001), UV intensity (e.g., Presto et al., 2005) and inorganic acid (e.g., Northcross and Jang, 2007; Kleindienst et al., 2006).

Most parameters used in modelling SOA mass loadings are based on observations from laboratory chambers. In these experiments, a single VOC compound is commonly used and individual mass yields are summed in order to model SOA from multiple species. The extension of single compound yields for the estimation of real SOA may miss the contribution of unknown BVOCs to SOA formation. This may be especially true for chemically complex aerosol formed from BVOC oxidation. In order to mimic more realistic atmospheric conditions, recent studies have been carried out to investigate SOA formation using direct biogenic emissions in the laboratory, varying from macroalgae (McFiggans et al., 2004), herbaceous plant white cabbage (Joutsensaari et al., 2005; Pinto et al., 2007) to the woody plant, oak and loblolly pine (Lang-Yona et al., 2010; VanReken et al., 2006) and silver birch, Scots pine and Norway spruce

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(Mentel et al., 2009; Hao et al., 2009; Kiendler-scharr et al., 2009a, b; Vaattovaara et al., 2009; Virtanen et al., 2010). Most of these studies focused on the phenomenon of new particle formation, rarely reporting SOA mass yields (Mentel et al., 2009; Lang-Yona et al., 2010).

Here we present the results from chamber studies of new particle formation using the direct BVOC emissions of living trees. Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies*) were selected as the dominant tree species in the European boreal forest area (Manninen, 1998; Christensen, 2000). Both O<sub>3</sub> and OH were used as oxidants in the controlled conditions of these experiments. Similar experiments were conducted with  $\alpha$ -pinene as a reference. Our motivation was to evaluate mass yields of SOA derived from oxidation of VOC mixtures emitted from real plants, rather than individual precursors used to be applied in most previous studies. This approach is expected to give more realistic, quantitative yields, which can then be incorporated in global aerosol models.

## 2 Methods

The plant experiments were performed in the Kuopio aerosol research chamber during 12–26 October 2007. The experimental systems have been described previously in Hao et al. (2009). A short description of the facility and the experimental procedure is presented here. The facility consists of a 6 m<sup>3</sup> rectangular Teflon<sup>TM</sup> FEP film chamber and a biogenic emission enclosure. Prior to each experiment, the chamber is continuously flushed overnight with laboratory compressed clean air and exposed to high level ozone concentration (~2 ppm) the following morning. After this cleaning procedure, air was bubbled through purified water and introduced into the chamber with clean dry air to adjust chamber relative humidity (RH). Then two trial plants were placed into the emission enclosure and VOCs were emitted under irradiation from six lamps (24 W, Lival Shuttle Plus, Lival Oy, Sipoo, Finland). Another clean air flow transported plant emissions from the plant enclosure into the chamber. SOA

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formation events were categorized according to whether the reaction is hydroxyl radical (OH) reaction-dominated or ozone (O<sub>3</sub>)-initiated chemistry. In the OH-dominated cases, tetramethylethylene (TME; 99+%, Aldrich) was added to increase the OH levels (Lambe et al., 2007). As described in Hao et al. (2009), O<sub>3</sub>-initiated chemistry includes three OH+O<sub>3</sub> simultaneously initiated experiments in which the contribution fraction from ozonolysis reactivity is more than 50%; and one ozonolysis experiment where 2-butanol was added as an OH scavenger. The 2-butanol concentration was ~600 times higher than that of the terpenes so that the reaction rate of OH with the scavenger exceeded that of OH with the parent hydrocarbons by a factor of 100 (Keywood, et al., 2004; Docherty et al., 2003). In both sets of experiments, ozone enriched air (50–800 ppb) was introduced into the chamber at a flow 40 L min<sup>-1</sup> following of VOC precursor additions. The ozone injection marked the start of each experiment. After the addition of BVOCs and oxidants, the inlet flow was turned off and the chamber was operated in batch-mode, i.e., the chamber was gradually emptied by sample flows to the instruments. In all cases, SOA was formed under dark conditions. The chamber temperature varied around 25±2 °C with chamber RH at 35±5% (Table 1). Nine SOA formation events were selected in the present study. We employed α-pinene as the model biogenic compound and emissions from two dominant tree species from the boreal forest, Scots pine and Norway spruce, as parent precursors, respectively, in the chamber. In five experiments, we included a second ozone addition in order to achieve a broader range of aerosol mass loadings.

Rapid changes of chemical composition and concentrations in both gas- and particulate phases in the chamber were well characterised. The time evolution of VOC precursors was measured with an on-line proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH) (Lindinger et al., 1998; de Gouw and Warneke, 2007), supplemented with results from off-line measurements by a gas chromatography-mass spectrometer (GC-MS, GC model 6890/MSD 5973, Hewlett-Packard) (Vuorinen et al., 2004). Particle size distributions and volume concentration were measured by a Fast Mobility Particle Sizer (FMPS) spectrometer (model 3091; TSI) and an Aerodyne

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Quadrupole-Aerosol Mass Spectrometer (Q-AMS) (Jayne et al., 2000; Canagaratna et al., 2007), respectively. The chemical composition of the formed particles was measured directly with Q-AMS and indirectly using a Volatility Tandem Differential Mobility Analyzer (V-TDMA) (Joutsensaari et al., 2001; Tiitta et al., 2010). The V-TDMA sequentially directs size selected aerosol (30 and 50 nm) through three volatilization tubes at a controlled temperature (50 °C, 150 °C and 280 °C). Volatile compounds evaporate from the particles in the heated tube and the resulting size distributions are measured using a differential mobility particle sizer. Aerosol volatility is presented, expressed as the volatility growth factor ( $V$ -GF), the ratio of particle size after evaporation to the original particle size. Other routine measurements included  $O_3$  (model 1008-RS; DA-SIBI Environmental Corporation, Glendale, CA),  $NO_x$  (model AC 30M; Environment S.A.),  $SO_2$  (model AF21M; Environment S.A.) and RH/Temperature transmitter (model Y50; Vaisala, Finland).

Measured aerosol volume concentrations were converted to mass loading for aerosol mass yield calculations by determining aerosol densities ( $\rho_{\text{eff}}$ ) from parallel measurements of size distributions with FMPS and Q-AMS. Density is determined from the ratio of vacuum aerodynamic diameter ( $D_{\text{va}}$ ) to mobility diameter ( $D_m$ ) multiplied by unit density ( $\rho_0$ , defined as  $1 \text{ g cm}^{-3}$ ) (DeCarlo et al., 2004; Bahreini et al., 2005).

$$\rho_{\text{eff}} = \rho_0 \frac{D_{\text{va}}}{D_m} \quad (1)$$

The measured densities in this study are  $1.34 \text{ g cm}^{-3}$  for Scots pine SOA (P1012, P1023, P1022, P1025; see Table 1),  $1.38 \text{ g cm}^{-3}$  for ozonolysis-dominated Scots pine SOA (P1026) and  $1.40 \text{ g cm}^{-3}$  for Norway spruce/ $\alpha$ -pinene SOAs (S1015, S1019, R1024), respectively.

## 2.1 Aerosol wall loss corrections

An important factor to consider in any chamber study is the effect of aerosol losses to the walls of the measured concentrations. To address wall loss deposition, a correction

method developed in previous studies (Presto and Donahue, 2006; Pathak et al., 2007) was employed. It is assumed that the wall loss rate is first order and the loss rate constant is independent of particle size. Therefore, the rate constant,  $k$ , of aerosol mass loss to the wall is given by a linear fitting of aerosol volume concentration against time:

$$\ln V(t) = -kt + C \quad (2)$$

where  $V(t)$  is the aerosol volume concentration measured at time  $t$ . Parameter  $C$  is a constant. A plot of  $\ln V(t)$  versus time, such as that shown in Fig. 1a, provides the aerosol mass loss rate constant  $k$  ( $\text{min}^{-1}$ ). The fits were excellent ( $R^2 > 0.95$ ) consistent with our assumptions. The parameter  $k$  varied from 0.0026 to 0.0084  $\text{min}^{-1}$  in these experiments (0.16  $\text{h}^{-1}$  – 0.5  $\text{h}^{-1}$ ). It is presumed to reflect air circulation in the chamber and variations of chamber volume due to the experimental operations as a sequence of introducing clear air into the chamber and continuously sampling with the instruments FMPS, PTR-MS and GC-MS, etc.

The produced SOA volume concentration is, therefore, given by

$$V'(t) = V(t) + k \int_0^t V(t) dt \quad (3)$$

where  $V'(t)$  is the aerosol volume concentration after wall loss correction and  $V(t)$  is the aerosol concentration before correction.

## 2.2 Dilution effects on aerosol mass concentrations

In this study, the addition of ozone into the chamber was operated at a fixed flow rate 40  $\text{L min}^{-1}$  for a fixed time as shown in Table 1. The changes of aerosol mass concentration caused by the dilution from the ozone addition must also be taken into account. The effect of dilution on the aerosol mass can be estimated by the following equation

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$$M'_{o,t} = M_{o,t} + \int_0^t (F \cdot M_{o,t}) dt \quad (4)$$

where  $M'_{o,t}$  is aerosol mass concentration after taking into account the dilution effect at time  $t$ ,  $M_{o,t}$  is aerosol mass loading before the dilution effect correction at time  $t$ .  $F$  is the dilution effect factor on the aerosol mass concentration, which is estimated from model simulation according to the inlet flow  $40 \text{ L min}^{-1}$  and out flow  $15 \text{ L min}^{-1}$  and simulated chamber volume during the operation of smog chamber. It is approximated to be  $6.7 \times 10^{-5} \text{ s}^{-1}$  during ozone addition into the chamber in this study. As an example, the corrected aerosol mass loading after the dilution effect is shown in Fig. 1b.

## 2.3 Modelling

Kinetic degradation mechanisms of  $\alpha$ -pinene and real plant emissions by the  $\text{O}_3$  and OH in the chamber were simulated by a kinetic chemical box model. Detailed model description and simulation parameters are provided in Hao et al. (2009). Briefly, the evolution of  $\text{O}_3$  concentration in the chamber can be expressed as

$$\begin{aligned} \frac{d[\text{O}_3]}{dt} = & \frac{d[\text{O}_3]_{\text{inlet}}}{dt} - \gamma k_{\text{O}_3}^{\text{TME}} [\text{TME}] [\text{O}_3] - \gamma'_{\text{isoprene}} k_{\text{O}_3}^{\text{isoprene}} [\text{isoprene}] [\text{O}_3] \\ & - \sum_i \gamma'_i k_{\text{O}_3}^{\text{MT}_i} [\text{MT}]_i [\text{O}_3], \end{aligned} \quad (5)$$

where MT represents monoterpenes,  $\gamma$  and  $\gamma'$  are the correction factors to take into account the secondary loss of ozone with products and  $k$  represents rate constants.

The time-dependent OH concentration can be approximated by

$$\begin{aligned} \frac{d[\text{OH}]}{dt} = & \omega_i k_{\text{O}_3}^{\text{TME}} [\text{TME}] [\text{O}_3] + \omega'_{\text{isoprene}} k_{\text{O}_3}^{\text{isoprene}} [\text{isoprene}] [\text{O}_3] + \sum_i \omega'_i k_{\text{O}_3}^{\text{MT}_i} [\text{MT}]_i [\text{O}_3] \\ & - \gamma'' k_{\text{OH}}^{\text{TME}} [\text{TME}] [\text{OH}] - \gamma'''_{\text{isoprene}} k_{\text{OH}}^{\text{isoprene}} [\text{isoprene}] [\text{OH}] - \sum_i \gamma'''_i k_{\text{OH}}^{\text{MT}_i} [\text{MT}]_i [\text{OH}], \end{aligned} \quad (6)$$

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where  $\omega_i$  and  $\omega_i'$  denote the yields of hydroxyl radicals from the  $O_3$  reactions with VOCs,  $\gamma$  and  $\gamma'$  are the correction factors to take into account the secondary loss of OH by reaction with products.

The degradation of VOCs is modelled as follows:

$$\frac{d[VOC]_i}{dt} = -k_{O_3}^{VOC_i} [VOC]_i [O_3] - k_{OH}^{VOC_i} [VOC]_i [OH]. \quad (7)$$

As a result, we can calculate  $O_3$  and OH oxidation rates with VOCs as follows:

$$r_{O_3} = \sum_i k_{O_3}^{MT_i} [MT]_i [O_3] + k_{O_3}^{isoprene} [isoprene] [O_3], \quad (8)$$

$$r_{OH} = \sum_i k_{OH}^{MT_i} [MT]_i [OH] + k_{OH}^{isoprene} [isoprene] [OH]. \quad (9)$$

According to the above simulations, OH and  $O_3$  initiated reactivity fractions (Fra.) can be determined:

$$Fra_{(OH)} = \frac{\int_0^t r_{i,OH(t)} dt}{\int_0^t r_{i,OH(t)} dt + \int_0^t r_{i,O_3(t)} dt} \quad (10a)$$

$$Fra_{(O_3)} = \frac{\int_0^t r_{i,O_3(t)} dt}{\int_0^t r_{i,OH(t)} dt + \int_0^t r_{i,O_3(t)} dt}, \quad (10b)$$

where  $r_{i,OH(t)}$  and  $r_{i,O_3(t)}$  are the reaction rates of  $VOC_i$  with OH and  $O_3$  at time  $t$  (min), respectively.

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### 3 Results and discussions

#### 3.1 SOA mass yield

The SOA mass yield ( $Y$ ) is determined by calculating the ratio of aerosol mass concentration  $M_o$  (in  $\mu\text{g m}^{-3}$ ) to the amount of the total precursor VOCs reacted ( $\Delta\text{HC}$ , in  $\mu\text{g m}^{-3}$ ) at the end of each experiment

$$Y = M_o / \Delta\text{HC} \quad (11)$$

The yields can also be further described by a semi-empirical model based on absorptive gas-particle partitioning of semi-volatile products (Odum et al., 1996; Pankow, 1994a, b). Usually one or two products can generally reproduce the chamber data:

$$Y = M_o \left( \frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o} \right) \quad (12)$$

where  $\alpha_i$  is the mass-based gas-phase stoichiometric fraction for semi-volatile species  $i$  and  $K_{om,i}$  is the gas-phase partitioning coefficient for species  $i$ .

#### 3.2 SOA yields from $\alpha$ -pinene

Aerosol yields can be determined by the progressive changes in VOC concentration and in aerosol mass concentration during a single experiment for the compound with one C=C bond (Ng et al., 2006). Figure 2 shows SOA mass yields as a function of absorptive organic mass concentration from  $\alpha$ -pinene oxidation (R1024, ref. Table 1). The effect of dilution on  $\alpha$ -pinene concentration is shown in Fig. 1a (where ozone addition into the chamber occurred at a flow of  $40 \text{ L min}^{-1}$  for 50 min). This dilution effect has been taken into account in the mass yield calculations. Comparisons of our SOA mass yields are made to literature reports for dark ozonolysis of  $\alpha$ -pinene (Fig. 2b). The temperature (298 K) in this study is 3 K higher than Presto et al. (2005) and Presto and Donahue (2006) and 5 K lower than Griffin et al. (1999) and Cocker et al. (2001).

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No adjustments for temperature effects on the mass yields were made, which might cause over- or under-estimation on the mass yields (Pathak et al., 2007). The findings resented in this study were reproduced by a two-product absorptive partitioning model with parameters of values 0.3326, 0.0760, 0.0129 and 2.6826 for  $\alpha_1$ ,  $K_{om,1}$ ,  $\alpha_2$ , and  $K_{om,2}$ , respectively. These results compare well to literature values, though lower than those at low organic mass loading from Shilling (2008), which is attributed to changes of product species from the unique mix of both parent hydrocarbon species and oxidants used in these two studies (possibly peroxy radicals or hydroperoxide species; Shilling et al., 2008).

### 3.3 Chemical composition of living plant emissions

BVOC precursors in this study came from the emissions of 1-year-old Scots pine and Norway spruce seedlings. Cultivation and pretreatments of these seedlings have been described in Hao (2009). In order to enhance total BVOCs emissions and simulate herbivore attack on tree bark, 3 cm long and 2 mm deep cuts were made on the base of the main stem by a knife. Abiotic or biotic damage on the plant can change the BVOC emission profiles (e.g., Blande et al., 2009). However the BVOC emission spectrum in this study (major compounds in the emission profile) is comparable to ambient observations. Molar chemical composition of emissions from these two types of forest trees are shown in Fig. 3. Emitted monoterpenes from Scots pine mainly included  $\alpha$ -pinene and  $\Delta^3$ -carene, matching the field observations in the boreal Scots pine dominated forest (e.g., Räisänen et al., 2009; Manninen et al., 1998). No fractional contribution of  $\Delta^3$ -carene in P1025 and P1026 were observed which depends on the  $\Delta^3$ -carene genotype Scots pine (Manninen et al., 1998). The most abundant contributions from Norway spruce emission are  $\alpha$ -pinene and  $\beta$ -pinene, making up 64.8%, 60.2% and 57.3% of total emitted monoterpenes for S1019, S1017 and S1015, respectively. These results are comparable to 70% of flux contribution of  $\alpha$ -pinene and  $\beta$ -pinene to total emissions during measurements made in a spruce dominated forest (Christensen et al., 2000). Other major contributions to emissions from these two types of trees came

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from myrcene,  $\beta$ -phellandrene and limonene. In all experiments, sesquiterpenes in the emitted compounds were lower than 0.05ppb as determined with PTR-MS. The molecular structures of these compounds can have an impact on the final formed SOA mass yields and will be discussed in the next section.

### 3.4 SOA yields from pine and spruce emissions

Once ozone is introduced into the chamber, the parent hydrocarbon precursors from tree seedlings decay and new particle formation begins within 20–40 min. Observations from these experiments are analysed using the same processing procedures as the  $\alpha$ -pinene experiment and are tabulated in Table 2. The SOA mass yields from these real plant emissions varied from 1.9% at  $M_o = 0.69 \mu\text{g m}^{-3}$  to 13.6% at  $M_o = 32.8 \mu\text{g m}^{-3}$ . The mass yield curve ( $Y$  vs.  $M_o$ ) can be reproduced by a two-product gas-particle partitioning model with parameters of 0.1462, 0.3850, 0.0531 and 0.0160 for  $\alpha_1$ ,  $K_{om,1}$ ,  $\alpha_2$  and  $K_{om,2}$ , respectively at the 95.4% confidence level through datasets scattered in Fig. 4. Previous studies have shown the presence of a  $=\text{CH}_2$  bond, the position of  $\text{C}=\text{C}$  bonds in the molecular ring structure and the numbers of  $\text{C}=\text{C}$  bonds in these types of compounds can affect the volatility of condensable products and the final yields (Kroll et al., 2008; Ng et al., 2006, 2007; Bonn and Moortgat, 2002; Griffin et al., 1999). The interactive effects of these complex mixtures of different compounds and chemical mechanisms during the reactions with OH and  $\text{O}_3$  are likely reasons for this scatter.

In this study, SOA yields from real plant emissions are generally lower than that from  $\alpha$ -pinene, as shown in Fig. 4. One possible reason for this is that lower volatility condensable products were formed in the  $\alpha$ -pinene experiment compared to the real plant cases; this will be discussed in the next section. Field observations from a typical boreal monoterpene-emission dominated forest site in Hyytiälä, Finland, show the organic mass loading ranges from around  $0.5 \mu\text{g m}^{-3}$  to about  $6 \mu\text{g m}^{-3}$  (Raatikainen et al., 2010; Tunved et al., 2006a). These particulate organics are in a form of oxygenated organic aerosol (OOA) (Allan et al., 2006; Raatikainen et al., 2010) and can be approximated to be organic absorption materials ( $\sum M_o$ ). Thus, corresponding SOA

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mass yields from these observations are estimated to range from 3% to 11%, in good agreement with the suggested values 5–10% derived for the boreal forest (Tunved et al., 2006a, b). Ambient biogenic SOA mass loadings (assumed to be organic absorption materials) on a global scale vary from 0.1 to 20  $\mu\text{g m}^{-3}$  (Shilling et al., 2009), spanning the measured mass yields of 0.5% to 14% based on the interpolation in our study (Fig. 4). Assuming an average mass concentrations for global biogenic SOA of  $M_o = 5 \pm 3 \mu\text{g m}^{-3}$  (Slowik et al., 2010; Raatikainen et al., 2010; Tunved et al., 2006a), this corresponds to an average mass yield  $10 \pm 2\%$  on a global scale.

Few mass yields have been reported from chamber studies of real plant BVOC oxidation. Mentel et al. (2009) reported incremental mass yields of SOA from OH/O<sub>3</sub> initiated pine/spruce emissions. They used a flow reaction chamber with VOC residence time of about 65 min and ozone level  $\leq 80$  ppb. For better comparison with our study, we used mass yields only from monoterpene precursors in their studies, observed to be  $5.2 \pm 0.5\%$ ,  $5.3 \pm 0.6\%$  and  $3.5 \pm 0.6\%$  for  $\alpha$ -pinene, pine and spruce SOAs, respectively. Mass yields in their study were independent on the mass concentrations of absorption materials (see Fig. 10, Mentel et al., 2009), in contrast to our study. Mass yields in this study were interpolated to be 9%, 5% and 8% for  $\alpha$ -pinene, pine and spruce SOAs, respectively, based on the maximum organic absorption concentrations in their study (Fig. 10). The reason for this difference in mass yields is still unknown, which might be due to aerosol formation mechanisms (aerosols are more aged in this study in a batch-mode operated chamber in contrast to a flow chamber in their study).

### 3.5 OH- and O<sub>3</sub>-initiated chemistry

OH initiates oxidation of VOCs either by abstraction of a hydrogen atom or addition to a C=C bond. The subsequent reactions are dominated by the organic peroxy radical (RO<sub>2</sub>) and alkoxy radical (RO) chemistry. Oxidation of VOCs by ozone proceeds by the formation of ozonide and decomposition of this compound to generate various products via Criegee intermediate (CI). The fundamentally different mechanisms of O<sub>3</sub> versus OH initiated oxidation play a crucial role in determining the product volatility

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and are, thus, controlling factors in SOA mass yield. Further oxidation of semi-volatile products in the gas and particle phase (Kroll et al., 2007; Chan et al., 2007) and secondary generation products (Ng et al., 2006) caused by OH and O<sub>3</sub> could also alter final SOA production. Moreover, organic products in the condensed phase may also undergo chemical reactions, affecting their physicochemical properties (Joutsensaari et al., 2004) and volatility (Paulsen et al., 2006; Dommen et al., 2006; Baltensperger et al., 2005; Kalberer et al., 2004). The volatility of 30 nm and 50 nm diameter SOA at a temperature of 150 °C, formed in the OH-dominated and O<sub>3</sub>-initiated chemical systems, is displayed in Fig. 5. The volatility growth factors in the OH-dominated experiments are consistently 20–50% smaller than those in the O<sub>3</sub>-initiated systems with the exception of P1012, indicating a higher volatility of condensable products for OH-dominated chemistry in these experiments. The difference in volatility of these two types of systems might be due to the RO<sub>2</sub> and RO chemistry, where the dissociation reaction of condensable products might dominate in the OH-dominated chemistry leading to the higher volatility products. The volatility of these particles can be further investigated with Q-AMS measurements of aerosol composition. It has been reported that aerosol volatility is positively correlated to the oxidation state of the particulate matter (Ng et al., 2010; Jimenez et al., 2009). The fraction of fragment mass 44 to total measured organics (f<sub>44</sub>) in our OH-dominated chemistry, a marker of aerosol oxidation degree (e.g., Ng et al., 2010; Jimenez et al., 2009), contributes to around 3–4% of total organic mass loading. This is systematically lower than the 5–6% observed in the O<sub>3</sub>-initiated systems except for P1012, indicating less oxidized and, thus, higher volatility, SOA in our OH-dominated systems. Note that though the diameter cutoff of the Q-AMS is around 30 nm (Zhang et al., 2004), the fraction of mass 44 presented here is from the entire bulk aerosol but still should be the representative of 50 nm particle size, since an internal mixture can be assumed for the SOA. The low volatility in P1012 appears related to the higher fractional contribution of ozonolysis reactivity than the other three OH-dominated systems (see Table 2).

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Lower volatility of condensable products in the O<sub>3</sub>-initiated systems appears at first counterintuitive to previous results (Hao et al., 2009) reporting that OH oxidation products are more effective in causing nucleation; whereas the ozonolysis products are more effective in driving particle growth. In principle, the nucleation rate depends on the ratio of the density of the nucleating vapour to its saturation vapour density (i.e., saturation ratio), whereas the particle growth rate depends on the difference of the vapour density and saturation density. Thus, a compound with low volatility can have a supersaturation high enough for nucleation but still a relatively low vapour density so that the growth rate remains slow. On the other hand, a compound which has a higher volatility and becomes supersaturated may cause a rapid growth although the saturation ratio is not high enough for nucleation.

However, a simple calculation example shows that the Hao et al. (2009) results are not necessarily in contradiction with the volatilities detected with the V-TDMA. Consider experiments E1b (OH chemistry) and E3 (O<sub>3</sub> chemistry) in Hao et al. (2009). From the growth rates it can be roughly estimated that the concentration differences between vapour densities and saturation densities are 0.03 ppb in experiment E1b and 0.11 ppb in E3. Assuming that the saturation vapour density of the OH products is two times that of the ozonolysis products and that the saturation ratio in experiment E1b was 5, it can be calculated that the saturation ratio in E3 was 30. This is completely possible, especially as the temperature in the experiments was similar and, thus, the reduced temperature (temperature divided by critical temperature) was lower in E3. It is well known that the onset saturation ratio for nucleation usually increases exponentially with decreasing reduced temperature (see, for example, McGraw, 1981).

Note, however, that we cannot exclude the possibilities explaining the nucleation in E1b such as a minor reaction channel forming very low volatility species that dominates nucleation, or the formation of sulfuric acid in OH reaction with contaminant background SO<sub>2</sub>. In any case, more thorough examination of the different pathways for nucleation requires future experiments.

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For the O<sub>3</sub>-initiated systems, volatility growth factors in R1024 show the highest value as displayed in Fig. 5a, suggesting that the volatility of condensable products is not only oxidant-dependent, but also depends on the molecular structure of the parent hydrocarbons. The compound  $\alpha$ -pinene has one double bond internal to the ring structure, which is more likely to form condensable products when compared to compounds with external double bonds during ozonolysis reaction (Griffin et al., 1999). Whereas the high fractional contribution of compounds with external double bonds to emissions such as  $\beta$ -pinene and  $\beta$ -phellandrene can be, in part, responsible for the higher volatility of condensable products in the other three O<sub>3</sub>-initiated experiments. In contrast, for OH-dominated chemistry, compounds with =CH<sub>2</sub> bond and internal double bond to ring structure, such as  $\beta$ -pinene and  $\Delta^3$ -carene, lose fewer carbon atoms under oxidant attack, which generally leads to lower volatility condensable products (Griffin et al., 1999).

In this study, volatility growth factors generally increased as a function of reaction time in this study as shown in Fig. 5a; the trend is especially noticeable for the OH-dominated experiments. With a closer look at the mechanism, Fig. 6 shows the time evolution of volatility of the 50 nm sized particle at 150 °C in P1023 as one representative of OH-dominated chemistry. It is interesting to observe that aerosol volatility is still decreasing (that is, volatility growth factor trends closer to 1) during the time period marked by pink bar. During this period, both O<sub>3</sub> and OH were completely consumed and no new particle formation was observed (geometric mean diameter remains constant and aerosol volume concentration goes down due to the aerosol deposition to the chamber wall). This is a strong indication that an aging process is occurring in the particle phase, resulting in a lower volatility of aerosols. Note that Virtanen et al. (2010) found that particles formed in the plant chamber are in a glassy state, and we cannot rule out the possibility that the particles are initially in a liquid state, but become more glass-like and less volatile with the aging. Formation of low-volatility components of SOA formed from photooxidation of  $\alpha$ -pinene (Paulsen et al., 2006; Baltensperger et al., 2005), aromatic compounds (Kalberer et al., 2004; Baltensperger et al., 2005), and

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isoprene (Dommen et al., 2006) have also been observed even after the completion of gas-phase chemistry. Those components are usually as a result of the formation of high molecular weight compounds from oligomerization or polymerization processes. This mechanism should also be applicable to our systems. The decrease of aerosol volatility will favour the final SOA condensation but the magnitude of this effect on final SOA yield remains uncertain and needs to be addressed in future studies.

## 4 Summary and conclusions

We have reported laboratory studies of newly formed aerosols resulting from the oxidation of direct emissions of two dominant tree species from boreal forest area; Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies*). New particle formation events from OH-dominated and O<sub>3</sub>-initiated chemistry were studied by adding TME and 2-butanol to adjust the OH and O<sub>3</sub> levels. Similar experiments were also conducted for  $\alpha$ -pinene as a reference compound. The evolution of gaseous species was measured by PTR-MS and GC-MS instrumentations. Aerosol mass loading was calculated from the FMPS measurements by applying the determined aerosol density after taking into account the aerosol deposition on the chamber wall and the dilution effect on the aerosol volume concentration.

The formation of SOA from  $\alpha$ -pinene oxidation can be reproduced with a two-product gas-particle partitioning absorption model. Determined mass yields in this study are in a good agreement with a number of previous studies. For the SOA formation from real plant emissions, aerosol mass yields varied from 1.9% at  $M_o$  0.69  $\mu\text{g m}^{-3}$  to 13.6% at  $M_o$  32.8  $\mu\text{g m}^{-3}$ . The volatility of condensable products from OH-dominated experiments is consistently higher than those from O<sub>3</sub>-initiated chemistry during the aerosol growth stage, whereas the condensable products in the  $\alpha$ -pinene experiments show the lowest volatility as a result of the effects of molecular structure of precursor compound on the product volatility. Products in the particle phase from OH-dominated chemistry undergo an aging process that continues after gas-phase oxidants have been consumed, further decreasing volatility, which can affect the final SOA formation.

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SOA production from real plant emissions depends on both chemical composition of plant emissions and oxidant species, but still can be reproduced with a two-product gas-phase partitioning model with parameters of 0.1462, 0.3850, 0.0531 and 0.0160 for  $\alpha_1$ ,  $K_{om,1}$ ,  $\alpha_2$ , and  $K_{om,2}$ , respectively. As a potential atmospheric application of this study, SOA mass yields (3–11%) obtained from these experiments are in the range reported for Hyytiälä, Finland, which is a typical European Boreal monoterpene-emission dominated forest region. On a global scale, the SOA mass yield of  $10 \pm 2\%$ , based on this study, can be recommended.

The studies carried out here are designed to closely match atmospheric conditions, so that the results are applicable to real atmospheric aerosol modelling. More studies are planned to continue to investigate the roles that OH and O<sub>3</sub> play in aerosol formation from real plant emissions.

**Acknowledgements.** The authors thank H. Korhonen for the helpful discussions on this work. The financial support by the Academy of Finland Centre of Excellence programme (project no 1118615), Academy of Finland (decision no. 110763, 131019, 218115, 111543, 123466) and the Saastamoinen Foundation and the Office of Science (BER), US Department of Energy, grant DE-FG-02-05ER63997 is gratefully acknowledged. The National Center for Atmospheric Research is sponsored by the US National Science Foundation.

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**Table 1.** Initial conditions of chamber operation (*P*, *S* and *R* codes are for Scots pine, Norway spruce and  $\alpha$ -pinene, respectively).

Exp. No.	Parent Precursor	TME (ppb)	First O <sub>3</sub> addition				Second O <sub>3</sub> addition				
			Inlet <sup>a</sup>	Duration <sup>b</sup>	[O <sub>3</sub> ] <sup>c</sup>	[OH] <sup>d</sup>	Inlet <sup>a</sup>	Start(min)	Duration <sup>b</sup>	[O <sub>3</sub> ] <sup>c</sup>	[OH] <sup>d</sup>
R1024	$\alpha$ -pinene	—	200	40	30.5	1.03	—	—	—	—	—
P1012	Pine	118	200	25	4.15	1.07	200	55	25	15.1	1.85
P1023	Pine	342	200	75	5.17	1.79	—	—	—	—	—
P1025	Pine	984	200	75	~ 0	< 0.19	800	80	30	17.8	3.32
P1022	Pine	—	200	13	20.7	0.33	—	—	—	—	—
P1026	Pine	2-butanol, 54 ppm	60	30	6.17	0.0036	200	85	30	37.4	0.012
S1015	Spruce	—	50	20	5.5	0.08	50	70	20	9.5	0.10
S1017	Spruce	—	50	25	5.6	0.10	200	119	60	76.0	0.56
S1019	Spruce	1285	200	80	0.2	< 0.2	800	80	40	19.3	3.77

<sup>a</sup> Ozone concentration at inlet of chamber (ppb);

<sup>b</sup> Duration of ozone addition into the chamber (min);

<sup>c</sup> Measured maximum O<sub>3</sub> concentration inside the chamber (ppb);

<sup>d</sup> Modelled maximum OH concentration inside the chamber (molecules cm<sup>-3</sup>,  $\times 10^6$ ).

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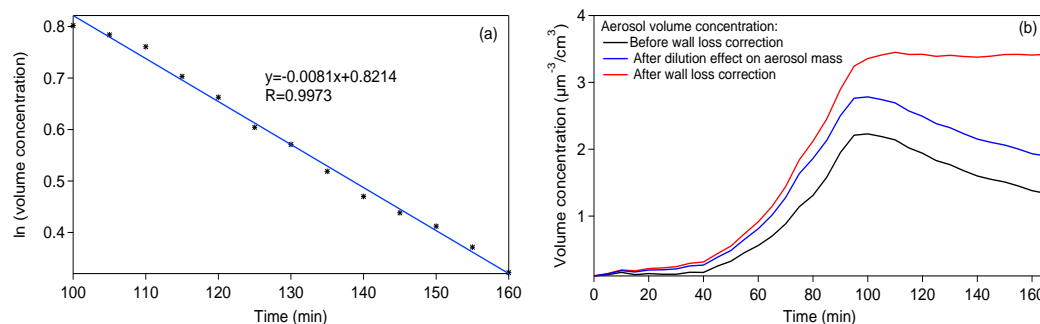
**Table 2.** SOA mass yields from OH and O<sub>3</sub> initiated oxidation of real emissions of two boreal forest trees. Reactivity fraction (*Rea. Fra.*) was calculated using Eq. (10).

Systems	Exp.	VOCs	ΔHC	$M_o$ ( $\mu\text{g m}^{-3}$ )	<i>Rea. Fra.</i> (%)		Yield (%)
	No.	(ppb)	(ppb)		OH	O <sub>3</sub>	
OH-dominated	S1019	217.4	43.4	32.8	91.5	8.5	13.6
	P1025	113.8	26.2	21.7	89.5	10.5	15.0
	P1023	28.8	7.45	4.62	89.2	10.8	11.2
	P1012	74.1	26.5	26.0	83.7	16.3	17.7
O <sub>3</sub> -initiated	R1024	159.2	49.2	79.1	42.1	57.9	28.9
	P1022	23.2	6.69	3.12	36.7	63.3	8.4
	S1017	28.2	6.67	0.69	36.1	63.9	1.9
	S1015	94.7	13.9	9.62	33.8	66.2	12.4
Ozonolysis dominated	P1026	100.3	22.6	12.6	0.9	99.1	10.0

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**Fig. 1.** (a) Logarithm of measured volume concentration as a function of time in smog chamber in experiment P1023. Aerosol wall loss rate was obtained from the fitting Eq. (2). (b) Aerosol volume concentration after taking into account the aerosol depositions on the chamber wall and dilution effects. Black curve is the directly measured aerosol volume concentration as a function of time in smog chamber. Blue curve is for the aerosol volume concentration after taking into account dilution effects arising from the ozone addition at  $40\text{ L min}^{-1}$  for 75 min. Red curve shows the corrected volume concentration by applying the wall loss factor derived in Fig. 1a.

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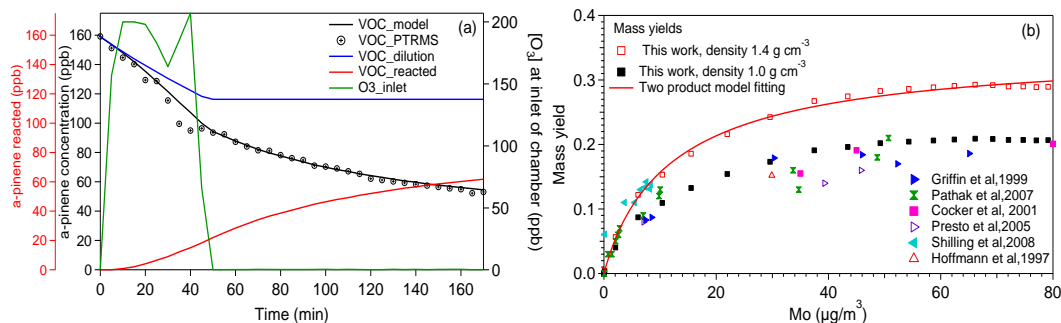
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**Fig. 2.** (a) The time evolution of  $\alpha$ -pinene concentration. Blue curve: change of  $\alpha$ -pinene concentration due to the dilution of ozone addition into the chamber; black curve:  $\alpha$ -pinene decay profile from the chemical kinetic model; black markers:  $\alpha$ -pinene decay profile from PTR-MS measurement; red curve: changes in  $\alpha$ -pinene concentration upon reaction (excluding the dilution effect); green line: ozone concentration at inlet of chamber. (b) SOA mass yields as a function of aerosol concentration. The red empty rectangles are shown from the experimental data by using the determined aerosol density  $1.4 \text{ g cm}^{-3}$  and the red dotted line were fitted by a two-product partitioning model with values 0.3326, 0.0760, 0.0129 and 2.6826 for  $\alpha_1$ ,  $K_{\text{om},1}$ ,  $\alpha_2$  and  $K_{\text{om},2}$ , respectively. The black compact rectangles shown are adjusted to  $\rho = 1.0 \text{ g cm}^{-3}$  to facilitate the comparison with other studies.

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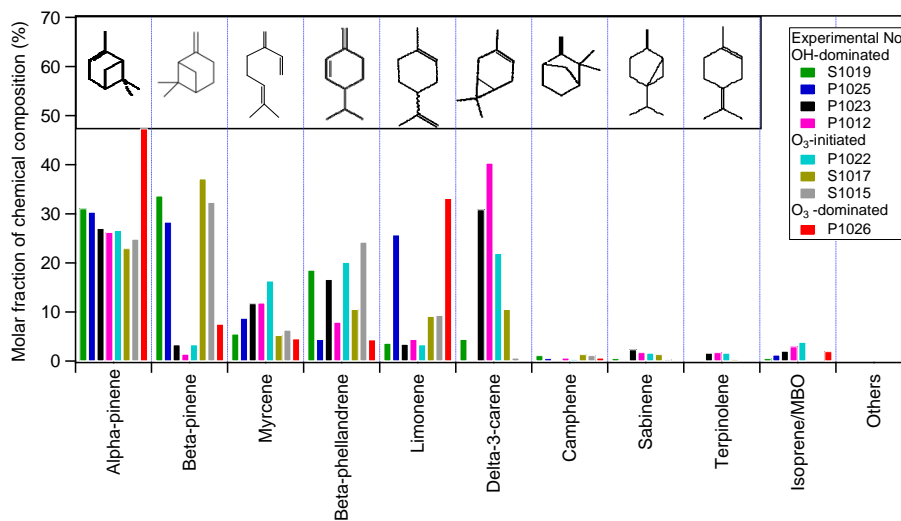
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**Fig. 3.** Percentage molar contributions of detected individual BVOC from plant emissions in different experiments and corresponding BVOC molecular structures.

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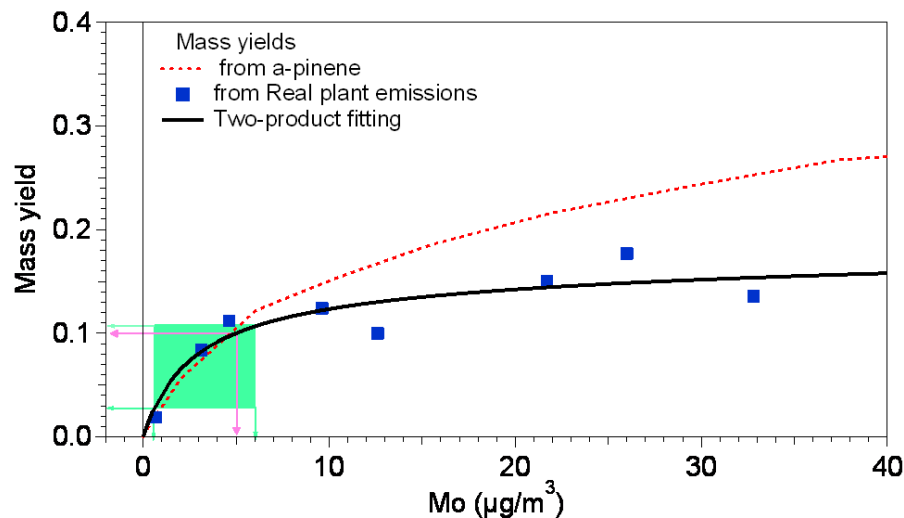
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**Fig. 4.** The SOA mass yield curve from real plant emissions compared to  $\alpha$ -pinene experiment. The blue rectangles are for SOA yields from each real plant emissions. The red dotted line is from the  $\alpha$ -pinene SOA mass yields. Black solid curve is fitted to the real plant SOA yields by a two-product absorptive partitioning model with parameters of 0.1462, 0.3850, 0.0531 and 0.0160 for  $\alpha_1$ ,  $K_{\text{om},1}$ ,  $\alpha_2$  and  $K_{\text{om},2}$ , respectively. The dark green bar shows the organic mass loadings in the aerosol phase observed in a boreal forest area, Hyytiälä (Raatikainen et al., 2010; Tunved et al., 2006a). The pink arrow points to an estimation of the average global biogenic SOA mass concentration ( $5 \pm 3 \mu\text{g m}^{-3}$ ), corresponding to a SOA mass yield of  $10 \pm 2\%$ .

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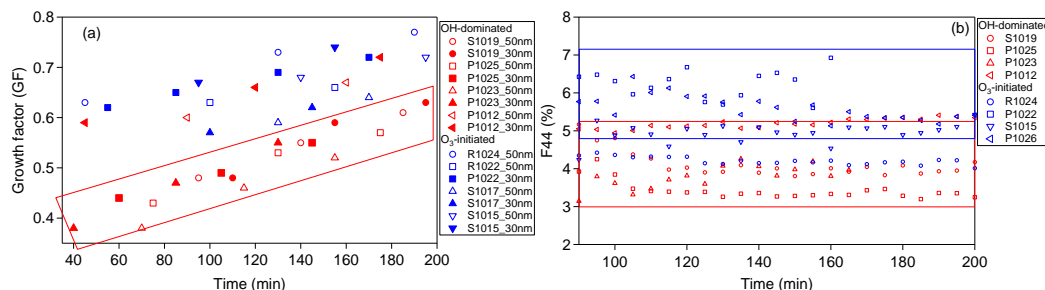
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**Fig. 5.** (a) Volatility growth factor determined by V-TDMA for 30 nm and 50 nm SOA at a temperature of 150 °C. (b) The fraction of  $m/z$  44 to total organic mass (F44), a proxy for oxidation state, as measured by the Q-AMS. Red markers are presented for the OH-dominated chemistry and blue markers are for O<sub>3</sub>-initiated systems. No V-TDMA measurement was made in P1026. F44 from S1017 is noisy due to the low aerosol mass (Table 2) and are not shown in Fig. 5b.

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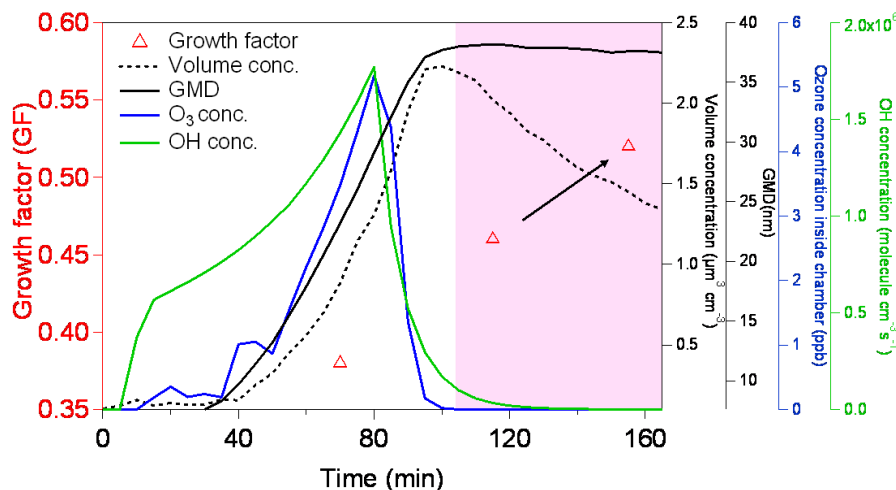
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**Fig. 6.** Evolution of volatility of 50 nm SOA determined at temperature 150 °C formed in P1023, as an example of the OH-dominated chemistry in this study. Blue curve shows the measured ozone concentration inside the chamber; solid black curve is for Geometric Mean Diameter (GMD) from FMPS measurement; green curve is the simulated OH concentration inside the chamber from the model prediction; dashed black curve is for the measured aerosol volume concentration inside the chamber. No oxidants were observed in the pink bar area.

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