# Importance of SOA formation of α-pinene, limonene and *m*-cresol comparing day- and night-time radical chemistry

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## Abstract

The oxidation of biogenic and anthropogenic compounds leads to the formation of secondary organic aerosol mass (SOA). The present study aims to investigate α-pinene, limonene and *m*-cresol with regards to their SOA formation potential dependent on relative humidity (RH) under night- ($NO_3$ radicals) and day-time conditions (OH radicals) and the resulting chemical composition. It was found that SOA formation potential of limonene with $NO_3$ significantly exceeds the one of the OH radical reaction, with SOA yields of $15 - 30$ % and $10 - 21$ %, respectively. Additionally, the nocturnal SOA yield was found to be very sensitive towards RH, yielding more SOA under dry conditions. On the contrary, the SOA formation potential of α-pinene with $NO_3$ slightly exceeds that of the OH radical reaction, independent from RH. In average, α-pinene yielded SOA with about 6 - 7% from $NO_3$ radicals and $3 - 4$ % from OH radical reaction. Surprisingly, unexpected high SOA yields were found for *m*-cresol oxidation with OH radicals (3 - 9%) with the highest yield under elevated RH (9%) which is most likely attributed to a higher fraction of 3-methyl-6-nitro-catechol (MNC). While α-pinene and *m*-cresol SOA was found to be mainly composed of water-soluble compounds, $50 - 68$ % of nocturnal SOA and 22 - 39% of daytime limonene SOA is water-insoluble. The fraction of SOA-bound peroxides which originated from α-pinene varied between $2 - 80$% as a function of RH.

Furthermore, SOA from α-pinene revealed pinonic acid as the most important particle-phase constituent under day- and night-time conditions with fraction of $1 - 4$%. Further compounds detected are norpinonic acid ($0.05 - 1.1$% mass fraction), terpenylic acid ($0.1 - 1.1$ % mass fraction), pinic acid ($0.1 - 1.8$ % mass fraction) and 3-methyl-1,2,3-tricarboxylic acid ($0.05 - 0.5$ % mass fraction). All marker compounds showed higher fractions under dry conditions when formed during daytime and almost no RH effect when formed during night.

## 1 Introduction

Large amounts of volatile organic compounds (VOC) are emitted into the atmosphere from both biogenic and anthropogenic sources with estimated source strengths of about 1300 TgC yr$^{-1}$ (Goldstein and Galbally, 2007). Once emitted, VOC undergo gas-phase reactions with ozone (O$_3$), hydroxyl (OH) or nitrate (NO$_3$) radicals (Atkinson and Arey 2003). Those reactions result in the formation of oxygenated products with a lower vapor pressure than the parent hydrocarbons which are subject to partitioning into the particle phase leading to the formation of secondary organic aerosol (SOA). The atmospheric degradation of BVOCs and subsequent SOA formation was subject of numerous studies during the last decades (Hallquist et al., 2009, Glasius and Goldstein 2016, Shrivastava et al., 2017). The majority of these studies examined the reaction initiated by the OH radical or ozone as they are considered as most dominating VOC sinks, although measurements indicated NO$_3$ radical reaction is the most important sink for several VOCs during nighttime (Geyer et al., 2001). It was demonstrated that NO$_3$-radical initiated oxidation contributes with 28% to the overall VOC conversion compared to 55 % for OH radical reaction and 17% for the ozonolysis (Geyer et al., 2001, Kurtenbach et al., 2002, McLaren et al., 2010, Liebmann et al., 2018, Liebmann et al., 2018). While NO$_2$ and O$_3$ serve as precursor for nitrate radicals, NO$_3$ is most dominating at night due to the fast photolysis and degradation with NO (Wayne et al., 1991, Brown and Stutz, 2012). The reaction of NO$_3$ with VOCs is suggested to be more important for VOCs of biogenic origin than for anthropogenic VOCs (Brown and Stutz, 2012) being the reason for studies developing mechanisms interconnecting NO$_x$ and BVOC emissions (Fry et al., 2009, Xu et al., 2015).

Even though the number of studies investigating the NO$_3$ radical-initiated SOA formation raised during the last few years increased (e.g., Pye et al., 2010, Fry et al., 2014, Boyd et al., 2015, Fry et al., 2018, Qin et al., 2018, Joo et al., 2019), there is still an enormous lack of data with respect to SOA yields, the influence of RH on SOA formation as well as the product distribution in gas and particle phase. Kinetic studies have shown rate constants for α-pinene and limonene with NO$_3$ in the range of 1.1 – 6.5 x 10$^{-12}$ and 1.1 – 94 x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively (Atkinson et al., 1984, Dlugokencky and Howard 1989, Barnes et al., 1990, Kind et al., 1998, Martinez et al., 1998, Martinez et al., 1999, Stewart et al., 2013). For *m*-cresol only two rate constants are reported in the range of 7.0 – 9.2 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Carter et al., 1981, Atkinson et al., 1984). Accordingly, at least at nighttime and on the regional scale, NO$_3$ reaction might lead to important contributions to VOC degradation and SOA formation. According to the comprehensive review by Ng et al., 2017, NO$_3$+VOC is worth investigating, because i) it can lead to anthropogenically influenced BSOA (Hoyle et al., 2007), ii) SOA yields might be higher than from OH and ozone (Ng et al., 2017), iii) it compromises an important source for organonitrates that serve as NO$_x$ and NO$_y$ reservoirs (von Kuhlmann et al., 2004, Horowitz et al., 2007) and iv) in few regions it was identified as most dominating SOA contributor (Hoyle et al., 2007, Pye et al., 2010, Chung et al., 2012, Kiendler-Scharr et al., 2016).

This study is aimed to investigate three selected precursor compounds, namely α-pinene and limonene as biogenic VOCs and *m*-cresol as anthropogenic VOC with regards to their SOA formation potential under nighttime (NO$_3$ radicals) and daytime conditions (OH radicals). SOA yield and SOA growth will be discussed in detail as well as the influence of the relative humidity. The chemical composition of formed SOA was characterized for their fraction of organic carbon (OC), water-soluble organic carbon (WSOC), SOA-bound peroxides and SOA marker compounds.

## 2 Experimental

### 2.1 Chamber experiments

75    Experiments were conducted in the aerosol chamber at the Leibniz Institute for Tropospheric Research in Leipzig. As a complete description of the chamber can be found elsewhere (Mutzel et al., 2016), only a brief description of the chamber will be given. The aerosol chamber is of cylindrical geometry with a total volume of 19 $m^3$ and a surface to volume ratio of 2 $m^{-1}$. The chamber is equipped with a humidifier to enable reactions at elevated RH

80    and a temperature-controlled housing to keep the temperature stable at T = 298 K throughout the experimental run. Experiments were conducted using ammonium sulfate/sulfuric acid seed (($NH_4$)$_2SO_4$/$H_2SO_4$) particles of pH = 4 at RH 50 %). Their RH-dependent pH-value was calculated by E-AIM (Clegg et al., 1998). OH-radical reactions were initialized by photolysis of hydrogen peroxide ($H_2O_2$) in the presence of NO (15 ppb). $H_2O_2$ was continuously injected into the chamber with a peristaltic pump at 100 uL $hr^{-1}$ and was photolyzed with UV-A-

85    lamps (Osram Eversun Super). $NO_3$ radicals were produced in a pre-reactor by the reaction of $NO_2$ and $O_3$. A fraction of the air flow (10 L $min^{-1}$) out of the total air flow in the flow tube (30 L $min^{-1}$) was directed to the chamber. After a reaction time of 90 min the reaction was stopped and samples were taken at 47 mm PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, US) and QF filter for 30 minutes at 30 L $min^{-1}$. PTFE filter were afterwards quantified for biogenic and

90    anthropogenic SOA marker compounds and QF to determine organic/elemental carbon (OC/EC), non-purgeable organic carbon (NPOC, former time: water-soluble organic carbon) and for selected experiments also concentration of inorganic nitrate ($NO_3^-$).

Experiments were conducted either under night time conditions with $NO_3$ radicals or with OH radicals to represent day-time chemistry. A complete overview of all experiments can be found in Table 1.

95    Dilution rates and wall losses were considered as following: $NO_3$ radicals and $H_2O_2$ were injected into the chamber with a bypass air of 10 L $min^{-1}$ and 5 L $min^{-1}$, respectively. Based on a reaction time of 90 minutes, equals this a dilution of 4.7 % ($NO_3$) and 2.4 % (OH). These values are within the measurement uncertainty of the PTR-TOFMS (± 10 % according to Romano and Hanna, 2018) according to and were thus not considered. Wall losses of VOCs were determined to be 2.5 x $10^{-5}$ $s^{-1}$ (α-pinene), 7.9 x $10^{-5}$ $s^{-1}$ (limonene) and 2.2 x $10^{-5}$ $s^{-1}$ (m-cresol). The

100    consumption recorded by PTR-MS is corrected for those additional sinks. Particle wall losses were determined from the blank experiments at RH=50%. Time-dependent particle losses were used to correct the SMPS measurements.

An ozone monitor was connected for all experiments. During $NO_3$ radical reaction conditions in the pre-reactor were set to avoid ozone entering the chamber. Thus for this reaction type ozonolysis as side reaction can be

105    excluded. During $H_2O_2$ photolysis small amounts of $O_3$ are always formed, which might lead to ozonolysis. It should be noted, that OH radical reaction was conducted in the presence of $NO_x$. Thus, formed $O_3$ will rapidly react with NO, rather than with α-pinene and limonene. Due to low reaction rate constant and the low concentration, ozonolysis occurs to a very small extent and can thus, not be excluded. A maximum $O_3$ concentration of 5 ppb was observed.

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### 2.2 Online instrumentation

The consumption of precursor compounds (ΔHC) was monitored by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOFMS, Ionicon, Lindinger et al., 1998). The particle size distribution was measured by a scanning mobility particle sizer (SMPS, Wiedensohler et al., 2012). An average density of 1 g cm$^{-3}$ was used to

115 convert the SMPS measurement data into the increase in organic mass (ΔM). Monitors for ozone (49c ozone analyzer, Thermo Scientific, USA) and NO$_x$ (42i TL, Trace level NOx analyzer. Thermo Scientific, USA) were connected to the chamber as well.

### 2.3 Offline measurements

#### 2.3.1 OC/EC, NPOC, inorganic nitrate and SOA bound peroxides

120 The quartz filter was cut into halves. One half was used for OC/EC quantification and second for water-soluble organic carbon. The content of OC/EC was determined with a C-mat 5500 carbon analyser applying a two-step thermographic method (Neusüß et al., 2002). The fraction of water-soluble organic carbon was determined as non-purgeable organic carbon with a TOC-V$_{CPH}$ analyser (van Pinxteren et al., 2009). To do so, the second half of the QF was extracted in 25 mL ultrapure water for 30 minutes with an orbital shaker. The resulting extract was filtered

125 through a 0.45 μm syringe filter (Acrodisc 13, Pall, USA). 250 μL of the extract was used for NO$_3^-$ analysis. After acidification and sparging with N$_2$, the remaining extract was injected into the TOC-analyzer. The amount of NO$_3^-$ was determined by IC-CD using an AS18 column combined with AG18 guard column.

For SOA bound peroxides, half of the PTFE filter was used. One quarter of the filter was used for the peroxide test and the second quarter filter to determine the blank value. The method is described in detail elsewhere (Mutzel

130 et al., 2013).

#### 2.3.2 Sample preparation for LC/MS

*Biogenic and anthropogenic marker compounds*

The sample preparation follows the method described in the literature (Hoffmann et al., 2007, Mutzel et al., 2015). Briefly, half of the PTFE filter was cut into small pieces and transferred into an extraction vial. 500 mL of methanol

135 was added and the vial was placed in an orbital shaker for 15 min at 1000 rotations min$^{-1}$. Insoluble material was removed by a syringe filter (0.2 mm, Acrodisc Pall, USA). Afterwards, the extraction was repeated with 500 mL of MeOH. The combined extracts were dried under a gentle stream of nitrogen and reconstituted in 250 mL of CH$_3$OH/H$_2$O (50/50, v/v).

#### 2.3.3 Analysis with HPLC/(-)ESI-TOFMS

140 An HPLC (Agilent, 1100 Series, Santa Clara, CA, USA) connected to a electrospray ionization time of flight mass spectrometer (microTOF, Bruker Daltonics, Bremen, Germany) was used for separation and quantification of marker compounds. For the separation an Agilent ZORBAX C18 column (3.0 x 150 mm, 5 μm particle size) at a temperature of 25°C and a flow rate of 0.5 ml min$^{-1}$ was used with 0.1 % acetic acid in ultrapure water (A) and 100 % methanol (B) as eluents. The gradient was as follows: 10 % B for 2 minutes, increased from 10 % B to 100

145 % B in 20 minutes, held constant for 3 minutes and re-equilibrated for 5 minutes to the initial conditions. The quantification was done in the negative ionization mode with a mass range between *m/z* 50 and 1000 applying a

series of sodium acetate clusters to calibrate mass accuracy. Quantification was done using authentic standard solutions within a 7-point calibration with three repetitions of each calibration point.

For anthropogenic SOA compounds, the separation was done as described above at 15°C and with 0.2 % acetic acid in water.

### 2.3.4 Chemicals

The following chemicals were used as received: α-pinene, limonene and *m*-cresol (Sigma-Aldrich, St. Louis, USA), terebic acid (Sigma-Aldrich, St. Louis, USA) and pinic acid (Sigma-Aldrich, St. Louis, USA).

The following compounds were synthesized according to procedures given in the literature: norpinonic acid, terpenylic acid (Claeys et al., 2009), 3-methyl-1,2,3-butanetricarboxylic acid (Szmigielski et al., 2007), diaterpenylic acid acetate (DTAA; Iinuma et al., 2009). The composition of the anthropogenic SOA mix is described in detail in Hoffmann et al., 2007.

### 3 Results and Discussion

### 3.1 SOA formation and yield

The SOA formation from the reaction of α-pinene, limonene and *m*-cresol with $NO_3$ radicals has been investigated within the present study with emphasis on SOA yields, the chemical composition in the particle phase, the influence of the RH and finally comparison to daytime chemistry with OH radicals. A complete overview about all experiments, the obtained results as well as the comparison to literature values is given in Table 1.

In general, α-pinene yielded significantly or, at least, slightly higher SOA with $NO_3$ radicals ($Y_{NO3} \approx 6\%$) than with OH ($Y_{OH} \approx 3.5\%$). In the case of limonene the difference is not as well pronounced but still observable ($Y_{NO3} \approx 15 - 30\%$; $Y_{OH} \approx 10 - 21\%$). Contrary, *m*-cresol yielded a neglectable amount of SOA with $NO_3$ radicals and moderate amounts with OH radicals ($Y_{OH} \approx 3 - 9\%$). Thus, the highest SOA formation potential for $NO_3$ radical reaction was found for limonene and the lowest for *m*-cresol.

The SOA yield curves were parameterized according to Odum et al., 1996 following Eq. (Eq. 1):

$$Y = \sum Y_i = M_0 \sum \frac{\alpha K_{OM,i}}{1 + K_{OM,i} M} \qquad \text{(Eq. 1)}$$

where

α is mass yield of compound i

$K_{OM,i}$ is the partitioning coefficient of compound i

By applying the one-product model approach, the fit resulted in very good results with $R^2 > 0.99$. Yield curves without any effect of RH, result in comparable α and K values. Those yield curves with a distinct RH influence, show a higher partitioning coefficient for higher SOA yields together with increasing mass yields. All α and K values are depicted in the respective yield curves (Figure 1).

Only a limited number of studies provided parameterisation of yield curves for VOC/OH/NOx and VOC/NO3 according to Odum et al., 1996 which highlights the need for the present data set. Spittler et al., 2006 reported based on a two-product model for limonene/$NO_3$ $\alpha_{1/2}$ and $K_{1/2}$ values of 0.1249/0.3128 and 0.0348/0.0181, respectively. The reported values for α correspond well to values obtained in this study whereas K values are by

one order of magnitude smaller. This might be caused by different seed particles as Spittler and co-workers used a pure organic seed and in the present study inorganic seed was used.

185    Iinuma et al., 2010 reported based on a two-product model for cresol/OH $\alpha_{1/2}$ and K values of 0.1231/0.0004 and 0.0753. These values are in no agreement to reported values which might be caused by different OH sources used.

*a-Pinene*

SOA yields for α-pinene with $NO_3$ radicals ranged from $Y_{NO3} \approx 5.9$ to 6.4 % in reasonable agreement with the literature data (0 – 16 %; Table 1). However, comparing the SOA formation from night-time chemistry with day-

190    time, the yields are by a factor of two higher than with $NO_3$. The SOA yield in the present study is very close to those that have been reported by Moldanova and Ljungstrom, 2000 ($Y_{NO3} \approx 0.3 - 6.9$ %) and Nah et al., ($Y_{NO3} \approx 1.7 – 3.6$ %). Although the values agree very well to the majority of the studies, it is still unclear that Fry and co-workers reported no SOA formation from α-pinene/$NO_3$ in the presence of seed particles. Although small SOA yields were observed within our present investigation, α-pinene/$NO_3$ yielded always SOA. The initial conditions

195    in the study of Fry et al., and in the present study are very similar, with the exception of the work flow. Fry and co-workers injected the BVOCs into a chamber that was filled with $NO_3$ radicals whereas for the present study the BVOC was injected at first and afterwards the reaction was initialized. Further studies are needed to reveal the reasons for the discrepancies in the SOA yields from $NO_3$-radical reaction.

Furthermore, comparing the growth curves for OH and $NO_3$ radical reaction with α-pinene and limonene, a clear

200    difference in the curve shapes can be seen (Figure 2). The SOA formation from the OH-radical initiated reaction starts later than in the case of $NO_3$ for both systems, α-pinene and limonene. Such a long induction period is most likely caused by the contribution of first-generation oxidation products leading to SOA formation as it was demonstrated in previous studies (Ng et al., 2006, Mutzel et al., 2016). As it has been reported by Mutzel et al., 2016, the SOA formation of α-pinene /OH and limonene/OH most likely proceeds via further reaction of myrtenal

205    and limonaketone/endolim, respectively. The reaction of these first-generation oxidation products is the limiting factor for SOA formation and explains the delay in SOA growth (Mutzel et al., 2016). In contrast, SOA originated from $NO_3$ starts immediately after 30 ug m$^{-3}$ are consumed. Thus, condensable oxidation products are directly produced and partition into the particle phase. Potential candidates of those products might be organonitrates.

*Limonene*

210    Limonene for both oxidation regimes (day and night) yielded the highest SOA yields, compared to α-pinene and *m*-cresol. The SOA yield from limonene ($Y_{NO3} \approx 16 – 29$ %) is by a factor of 3 - 5 higher than α-pinene and by a factor of 10 higher than *m*-cresol. Those values are close to the lowest values reported for limonene ozonolysis (Northcross and Jang, 2007, Chen and Hopke, 2010, Gong et al., 2018). Furthermore, according to the present data set, limonene+$NO_3$ ($Y_{NO3} \approx 16 – 29$ %) is also more efficient in SOA production than the OH radical reaction ($Y_{OH}$

215    $\approx 10 – 21$ %).

Consequently, nocturnal oxidation of limonene with $NO_3$ yields more SOA than ozonolysis and OH radical reaction. This additional SOA source should be considered in future studies, in particular under less humid conditions. In addition to the strong SOA formation potential, the organic mass production of limonene+$NO_3$ seems to be highly humidity dependent. This will be discussed separately in the corresponding section below.

220

*m-Cresol*

In contrast to α-pinene and limonene, *m*-cresol yielded only negligible amounts of SOA with $NO_3$ radicals while the OH radical reaction seems to be more efficient than α-pinene. This observation was unexpected because anthropogenic VOCs are often suggested to form less SOA than biogenic once. SOA production from anthropogenic VOCs has often been investigated but usually led to inconsistent results and very low yields (e.g. Izumi and Fukuyama 1990, Healy et al., 2009, Emanuelsson et al., 2013). A study by Hildebrandt et al., 2009 raised the question about the low SOA yields and observed much higher yields by using artificial sunlight. The present study also demonstrates higher SOA yields than expected and supports the hypothesis of Hildebrandt and co-workers about a higher importance of SOA production from anthropogenic VOCs.

It should be noted that due to the low SOA yields from $NO_3$ radical reaction, no parameterization of the yield curves can be provided (Figure 1). In general, the SOA yields ($Y_{OH} \approx 2.9 - 9.1$ %) for OH radical reaction with *m*-cresol are in good agreement to Iinuma and co-workers ($Y_{OH} \approx 4.9$ %), although the photolysis of methylnitrite was used. Compared to the study by Nakao et al., 2011 ($Y_{OH} \approx 35 - 49$%) the values are much lower. This is not surprising, as Nakao et al., conducted experiments in the absence of $NO_x$ whereas in the present study $NO_x$ was always present. The effect of $NO_x$ lowering SOA yields has often been described in the literature (e.g. Presto et al., 2005, Ng et al., 2007, Zhao et al., 2018).

Furthermore, the yield curved clearly indicated a strong effect of relative humidity which can also be seen from the growth curves (Figure 2). This effect will be discussed in the following section.

**3.3 Influence of RH on SOA yield and growth**

Within the present study, experiments were conducted under RH <5 %, at 50% and at 75% to investigate the effect of humidity on SOA yield, growth and composition. As discussed before, relative humidity has been suggested to affect the competition between VOC+$NO_3$ and heterogenous uptake of $N_2O_5$. Furthermore, the limited number of studies investigating the effect of RH on the OH radical reaction often contradicts each other (Cocker et al., 2001, Bonn and Moortgat 2002). Only a very limited number of studies is available investigating the influence of RH on SOA formation originating from VOCs+$NO_3$ – as to the authors' knowledge this is only Spittler et al., 2006, Fry et al., 2009 and Bonn and Moortgat 2002, Boyd et al., 2015. According to Figure 1, a significant effect can be observed for two systems, i.e. limonene/$NO_3$ and *m*-cresol/OH while α-pinene/$NO_3$ and *m*-cresol/$NO_3$ were not affected by RH in good agreement with the literature studies by Bonn and Moortgat 2002, Fry et al., 2009, Boyd et al., 2015). Only Spittler and co-workers observed lower SOA yields under humid conditions (RH 20 % vs. 40 %). Notably, in the case of limonene/$NO_3$, the SOA yield varies by a factor of two between 29.1 % (at RH <5 %) and 14.8 % (at RH 75 %). Contrary, in the case of *m*-cresol/OH the SOA yield increases with humidity by a factor of 5. Thus far, no study has investigated the role of RH on the SOA formation from limonene/$NO_3$ and *m*-cresol/OH and the dataset for α-pinene /$NO_3$ is small and inconsistent. As an effect was only observed for limonene/$NO_3$ and *m*-cresol/OH, these systems will be discussed in more detail.

*Limonene+$NO_3$*

The SOA yield was found to decrease with increasing relative humidity from 29 down to 14.8 %. This pronounced effect could be a result of a direct effect of RH on the partitioning of condensable products. Organonitrates (ON) are well known oxidation products of VOC+$NO_3$ and are often related to SOA formation and growth (e.g. Day et al., 2010, Rollins et al., 2010, Zaveri et al., 2010). ON are reported to be very prone to hydrolysis which might

260 explain the lower SOA yields under humid conditions (e.g. Darer et al., 2011, Hu et al., 2011, Jacobs et al., 2014, Rindelaub et al., 2015). This hypothesis cannot be supported, as the growth curves (Figure 2) clearly demonstrate a decreasing consumption when RH increases as a potential reason for lower SOA yields at higher RH. One might assume that lower consumptions are caused by an enhanced partitioning of $NO_3$ radicals into the particle phase due to an enhanced aerosol liquid water content (ALWL). This can be excluded as the quantification of particulate

265 inorganic nitrate does not show higher values under elevated RH (Table 1). Therefore, a stronger contribution of particulate inorganic $NO_3^-$ can be excluded. As this approach does only cover inorganic $NO_3$, compounds formed by the reaction of $NO_3$ with organic compounds are not considered and a possible contribution of such compounds cannot be excluded.

A second aspect to be considered is the contribution of first-generation oxidation products. According to

270 theoretical investigations, endolim is the most favored product formed during limonene+$NO_3$ (Jiang et al., 2009). It could be speculated that endolim reacts faster with $NO_3$ than limonene, scavenging $NO_3$ radicals. As no rate constants are available for endolim+$NO_3$, the values from master chemical mechanism (MCM, version 3.3.1, Jenkin et al., 1997, Saunders et al., 2003) were taken for comparison. For the reaction of endolim with $NO_3$ (LIMAL) a rate constant of $2.6 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ can be found. According to k values taken from MCM

275 and kinetic studies, limonene+$NO_3$ is by two orders of magnitude ($k_{lim+NO3}$: $1.2\ 6 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) faster compared to endolim. Consequently, a competition between limonene and the respective first-generation oxidation product can be excluded.

A last sink of $NO_3$ radicals, is the reaction of $RO_2$ radicals with $NO_3$ as it has been investigated by Boyd et al., 2015 for α-pinene. Conducting two different sets of reactions with "$RO_2$+$NO_3$ dominant" and "$RO_2$+$HO_2$

280 dominant" no effect on SOA yield of α-pinene was found. Nevertheless, taking into account that α-pinene contains only one double-bond, formed $RO_2$ radicals are saturated whereas limonene as a diene forms $RO_2$ radicals with one remaining double bond which could be expected to be more reactive than saturated $RO_2$ radicals. Therefore, limonene-originated $RO_2$ radicals are more reactive and might represent an important sink for $NO_3$ which is in competition to limonene+$NO_3$. Thus-far only one study exists investigating this reaction channel. Thus, this

285 competitor for limonene with $NO_3$ seems to be likely and should be systemically investigated in the future.

*m-Cresol+OH*

In contrast to limonene/$NO_3$, the OH radical initiated oxidation of *m*-cresol showed higher SOA yields with increasing RH (Figure 1). Even though the consumption also decreases under humid conditions, the particulate OM is increasing (Figure 2). Analyzing the respective growth curves, a delay in aerosol production can be seen.

290 Under RH 0 % and 50 % conditions, aerosol production starts at ΔHC ≈ 80 - 90 μg $m^{-3}$. Notably, at more elevated RH the SOA production starts immediately after initialization of the reaction (ΔHC ≈ 5 - 10 μg $m^{-3}$). According to Ng et al., 2006, such a difference in mass production can be cause by two reasons, first a delay in mass transfer from gas into particle phase and/or secondly, condensable products are only formed from second-generation oxidation products and thus the formation of those products is the limiting parameter for SOA formation.

295 According to a study by Coeur-Tourneur et al., 2006, methyl-1,4-benzoquinone (MBQ) is the most dominating oxidation product with up to 12 % molar yield. MBQ was also detected in the present study by means of the PTR-TOFMS at *m/z* 123. Nevertheless, the evolution in dependency on consumption does not show a significant effect of RH on the formation (Figure 3). Therefore, a strong contribution due to further reactions of MBQ can be

excluded. Thus, the delay might be caused by the effect of relative humidity on the partitioning of condensable
300    products, such as methyl-nitro-catechol that showed a higher mass fraction under elevated RH (Figure 7).

### 3.4 Characterisation of particle-phase chemical composition

The filter collected after each experiment were analysed with regards to their content of organic carbon (OC),
water-soluble organic carbon (WSOC), SOA-bound peroxides and SOA marker compounds. The results are
summarised in Figure 4 - 7.

305    *Organic carbon and water-soluble organic carbon*

Pre-heated quartz fiber filter were analysed for OC/EC and WSOC content. Please note, WSOC was determined
as non-purgeable organic carbon (NPOM). The obtained results were compared to the increase in organic mass
($\Delta M$) obtained from the SMPS (Figure 4). In general, the values agree well, meaning the increase in organic mass
corresponds to organic carbon and secondly, the majority of this mass is water-soluble, except mass originated
310    from limonene.

In general, limonene is the only compound showing hints for water-insoluble material with 22 – 36 % of organic
mass is composed of water-insoluble organic material. From both systems, limonene/$NO_3$ and limonene/OH, the
WSOM fraction ranges between 32 – 50 % and 61 – 78 %, respectively. In the case of limonene/$NO_3$ the fraction
of water-soluble carbon decreases dramatically when the relative humidity decreases. Only one third (32 %) of
315    $\Delta M$ is composed of water-soluble carbon, although the SOA yield was highest under dry conditions. Thus, under
reduced RH more water-insoluble compounds partition into the particle phase leading to an enhanced SOA growth.
Potential candidates might be higher-molecular weight compounds which seem to be involved in SOA growth for
the $NO_3$ and OH system.

*SOA-bound peroxides*

320    Organic peroxides in SOA were quantified according to a method published from our laboratory before (Mutzel
et al., 2013) applying a molar mass of 300 g mol$^{-1}$ (Figure 5) as it recommended by Docherty et al., 2005, assuming
that the majority of organic peroxides are higher-molecular weight compounds (e.g. dimers). The fraction of SOA-
bound peroxides is always expressed as a fraction of organic mass formed during the experiment and was
calculated as follows:

325
$$m_{Perox} = n_{Perox} * 300 \; g \; mol^{-1} \qquad (Eq. 2)$$

$$M_{Perox} = \frac{m_{perox}}{V_{sampling}} \qquad (Eq. 3)$$

$$F_{Perox} = \frac{M_{perox}}{M_{org}} \qquad (Eq. 4)$$

where

$n_{Perox}$ is amount of substance in µmole (calculated from the iodometric peroxide test)

330    $m_{Perox}$ is mass of organic peroxides in µg

$M_{Perox}$ is mass concentration of organic peroxides in µg m$^{-3}$

$V_{sampling}$ is sampling volume of the filter in m$^3$

$F_{Perox}$ is mass fraction of SOA-bound peroxides in %

$M_{org}$ is amount of organic mass formed during experiment in µg m$^{-3}$

335

Organic peroxides were detected from α-pinene and limonene, but not from *m*-cresol. The absence of organic peroxides for *m*-cresol might be a result of the aromatic structure. Notably, in the case of α-pinene, organic peroxides were only detected from the OH radical reaction, albeit in very high fractions. This observation was unexpected as $NO_x$ was present in the system, usually suppressing ROOH formation. Considering the reaction of

340    alkylperoxy radicals ($RO_2$) with hydroperoxy radicals ($HO_2$) as the most important source for ROOH, this source decreases with increasing $NO_x$ level due to the competition with $RO_2+NO$ (Presto et al., 2005). Thus, other processes than $RO_2+HO_2$ should have yielded organic peroxides and thus, other compounds of peroxidic nature are detected by the applied test. As day-time experiments were done with $H_2O_2$ as OH source, blank filter were carefully checked to exclude the contribution of $H_2O_2$ present in the particle phase due to gas-to-particle

345    partitioning of the injected oxidant. In general, peroxide fractions of 10 - 80% of the organic mass have been detected from a-pinene/OH experiments. The high peroxide fractions of 10 – 80% are contradicting to the small SOA yields from α-pinene/OH ($Y_{OH} \approx 3.5$ %). While the organic peroxide formation from the ozonolysis of α-pinene and limonene has been studied in the past (Docherty et al., 2005, Mertes et al., 2012, Epstein et al., 2014, Krapf et al., 2016, Gong et al., 2018), peroxide fractions from the OH-radical induced oxidation are rare (Mertes

350    et al., 2012). Mertes and co-workers reported peroxide fractions between 5 – 17 % (low $NO_x$ at RH 50 %) and 5.5 - 6.4 % (high $NO_x$ at RH 75 %). Those values are slightly lower than observed in the present study with 34 % (medium $NO_x$ at RH 50 %) and 13 % (medium $NO_x$ at RH 75 %). Differences between both studies are most likely caused by usage of other OH radical sources. Anyway, the observed trend of lower peroxide fractions under elevated RH is consistent in both studies and might be a result of two facts, i) the uptake of $HO_2$ radicals and ii)

355    decomposition and/or hydrolysis of hydroperoxides. It has been reported that the $HO_2$ radical concentration is significantly suppressed by three orders of magnitude when a liquid phase is present (Herrmann et al., 1999). Thus, the $HO_2$ uptake might increase under elevated RH and therefore $HO_2$ in the gas phase is only available to a lesser amount to with $RO_2$ radicals (Herrmann et al., 1999). Furthermore, under high RH decomposition and/or hydrolysis occur to a larger extent lowering the peroxide fraction (Chen et al., 2011, Wang et al., 2011).

360    In contrast, limonene yielded SOA-bound peroxides from both oxidation regimes, $NO_3$ and OH. From OH radical reaction, no difference between the respective fractions can be observed, leading to an average organic peroxide fraction of about 30 % without a dependency towards RH, indicating organic peroxides i) are of other nature than formed from α-pinene and/or ii) they originate from other reactions. The almost stable content might indicate that those peroxides and their respective formation pathways are not affected by humidity. Thus, it could be speculated

365    that peroxides of higher molecular weight, i.e. dimers with peroxyhemiacetal structure are formed. Due to the lack of data, no comparison to other studies can be provided.

The reaction of limonene with $NO_3$ radicals yielded peroxides as well, in fractions comparable to those measured for the OH reactions for the two lower RH. Under higher RH (75 %), the peroxide fraction decreases dramatically to almost 0.5 %. The formation of organic peroxides in $NO_3$-initiated reactions was, to the best of the authors'

370    knowledge, not a subject of VOC studies oxidation studies up to now. Only few studies examined the fate of nitrooxy alkyl peroxy radical formed during $NO_3$-radical reaction. For isoprene it has been shown that the reaction of nitrooxy alkyl peroxy radical with other $RO_2$ and $HO_2$ is able to form peroxidic compounds, such as ROOR $C_{10}$-dimers and nitrooxyhydroperoxide (Kwan et al., 2012, Schwantes et al., 2015). As the detected fraction of SOA-bound peroxides decreases with RH the reaction of $RO_2 + HO_2$ seems to be the major source of these

375    peroxides

*Biogenic SOA marker compounds*

The quantification of biogenic marker compounds was performed using a BSOA standard containing norpinonic acid, terpenylic acid, pinonic acid, pinic acid and MBTCA (Figure 6). These compounds were detected from night- and day-time chemistry of α-pinene while limonene, due to its different structure, does not form these compounds.

380 Thus, the discussion about the fraction of those BSOA marker compounds refers to those formed in the α-pinene oxidations.

The most important SOA marker compounds formed from the OH-radical reaction of α-pinene are pinonic acid < pinic acid < norpinonic acid and terpenylic acid < MBTCA. For all compounds a significant dependency on RH was observed in the same manner as for the organic peroxides (Figure 5): Increasing RH leads to decreasing SOA

385 fractional contributions while the SOA yields themselves remain about constant (Figure 1).

This observation might be caused by three main factors: (i) the uptake behaviours of the SOA marker compounds or their precursor compounds change as a function of the experimental conditions; (ii) the formation processes of SOA marker compounds are directly affected by the experimental conditions; (iii) further reactions take place within the particle phase. It remains a challenge to differentiate between all these factors because the observed

390 dependency is most likely the result of a combination of all the factors. However, it should be noted that earlier studies suggested that the LWC does influence the partitioning behaviour of carboxylic acids such as pinic acid and pinonic acid (Seinfeld et al., 2001, Ma et al., 2007). As a higher RH corresponds to a higher ALWC, enhanced partitioning should result. This hypothesis is not supported by the experimental results of this study because higher fractions of the SOA marker compounds were observed under almost dry conditions, thus factor i) seems to be

395 unlikely. Factor (ii) may play a partial role in the formation of carboxylic acids; In the literature, the formation of carboxylic acids is often described via OH attack at a respective precursor compound and the subsequent mechanisms usually involve the reaction of a formed acylperoxy radical with $HO_2$ radicals (Niki et al., 1985, Moortgat et al., 1989, Lightfoot et al., 1992, Larsen et al., 2001). For both reactions, water is most likely to have a direct effect on the OH radical and the $HO_2$ radical, however, in opposite directions. Vöhringer-Martinez et al.,

400 2007 suggested that water molecules catalyse the attack by OH radicals (in the gas and particle phases) due to the formation of hydrogen bonds that can lower the reaction barrier. This catalytic effect could lead to higher fractions of specific markers under elevated RH, which was not observed in the dataset obtained from this study. Contrary, the reaction of the acylperoxy radical with $HO_2$ might be RH-dependent because, as discussed before, $HO_2$ tends to partition into the particle phase at elevated RH and is thus not sufficiently available in the gas phase (Herrmann

405 et al., 1999). This might explain the low fractions of marker compounds at elevated RH.

The last pathway iii) to be considered involves further reactions of the SOA marker compounds to yield HMWCs in the particle phase as it has been often described in the literature (e.g. Gao et al., 2004, Tolocka et al., 2004, Müller et al., 2008, Yasmeen et al., 2010). It was suggested that compounds such as terpenylic acid and pinic acid can react further in the particle phase to form dimers (Yasmeen et al., 2010). Thus, under elevated RH, the

410 formation of higher-molecular weight compounds might be enhanced lowering the fraction of individual monomeric compounds. Nevertheless, based on the experimental results of this study and the literature data, the combination of two factors appears to be important for the formation of carboxylic acids. First the suppression of carboxylic acid formation due to enhanced partitioning of $HO_2$ into the particle phase under elevated RH and second, the further reaction of particulate marker compounds yielding HMWCs.

415 Notably, pinonic acid was detected in comparable fractions from $NO_3$-radical reaction of α-pinene with the same RH dependency ($20 - 35\%$) although to a considerably lower extent (Figure 6). The reasons for such a pronounced

RH dependency have been discussed intensively above. In addition to the described factors, in the case of $NO_3$-radical reactions, the central role of organonitrates needs to be considered. It cannot be ruled out that ON act as potential precursors for the detected marker compounds. Under elevated RH, ON, dependent on their structure,

420    are prone to undergo hydrolysis and thus the respective products should show higher fractions under elevated RH. This observation seems to be the case for norpinonic acid, leading to the hypothesis that it might be the hydrolysis products of respective organonitrates. As more data are needed, the hypothesis that norpinonic acid is a hydrolysis product of ON remains speculative at this time.

The other remaining marker compounds observed following the $NO_3$ reactions, terpenylic acid, pinic acid and

425    MBTCA do not show a significant variation with RH and are thus not affected by water or ALWC. Nevertheless, the fractions of all compounds except pinonic acid are significantly lower compared to the OH radical reaction. This is most likely caused by an enhanced formation of ON.

*Anthropogenic SOA marker compounds*

A well-established analytical method was applied to identify and quantify ASOA marker compounds from *m*-

430    cresol oxidation (Hoffmann et al., 2007). Despite the larger number of standards present in the authentic standard mixture, only 3-methyl-6-nitro-catechol (MNC) was detected and quantified (Figure 7). This compound was only detected from the OH-radical reaction. Quantification of marker compounds in samples after night-time processing cannot be provided due to the very small SOA yields.

For MNC, a very strong RH dependency was found with higher values under humid conditions and lower values

435    under dry conditions (1.5 %). In particular, under elevated RH the fraction of 3-methyl-6-nitro-catechol reached 6 % of overall formed SOA mass highlighting the importance of this particular oxidation product. Methyl-nitro-catechols (MNC) are of special interest as they are important biomass burning tracer compounds and their ambient concentrations can reach up to 29 ng m$^{-3}$ (Iinuma et al., 2010). Additionally, such a high fraction of MNC could also affect the phase state of the particles as it has been shown that MNC particles adsorb water under elevated

440    RH leading to a change in the phase state of the particles (Slade and Knopf, 2014). This effect is connected to a decreasing uptake of OH radicals into the particle phase by a factor of 4 when RH increases from 15 to 30 %. The lower fractions under dry conditions might be a result of stronger OH uptakes into the particles, though to a greater extent of heterogenous reaction of MNC in the particle phase.

445    **3.5 Atmospheric implications and Conclusion**

The examination of the oxidation of atmospherically relevant compounds and the resulting SOA formation is of large importance for a better understanding of atmospheric chemistry, and its response to future climate change. Several studies predict an increase in BVOC emissions as a response to a warmer climate (e.g. Sanderson et al., 2003, Lathière et al., 2005, Heald et al., 2008). The increase in monoterpenes emission is estimated to be up to 50

450    % (Lathière et al., 2005). Such a dramatic increase might lead to an enhanced formation of reactive organic species (ROS) as determined here as peroxides and SOA. ROS are suggested to cause oxidative stress that influences human morbidity and mortality (Squadrito et al., 2001, Schwartz et al., 2002, Xiao et al., 2003, Ayres et al., 2008). The current knowledge is limited to predict the global SOA burden with large uncertainties (see review by Hallquist et al., 2009, Glasius and Goldstein 2016, Shrivastava et al., 2017). With an expected increase in VOC

455    emissions the knowledge about SOA formation processes and their response to changes in parameters investigated in the present study will become more important. The present study provides important data concerning SOA

formation potential of OH and NO₃ radical oxidation of biogenic and anthropogenic VOCs, the influence of relative humidity on the SOA yield and its resulting chemical composition.

During the night and at early morning hours, the RH near the surface is high, NO₃ radical chemistry is competitive with those of other oxidants and, accordingly, RH starts to play a crucial role. The investigation of the effect of RH on the SOA formation and chemical composition shed light on various aspects, especially for NO₃-initiated SOA formation. NO₃ radical reaction can form SOA more efficiently than OH radical reaction in the presence of $NO_x$, at least for α-pinene and limonene, highlighting the importance of this atmospherically relevant nighttime sink. Furthermore, pinonic acid was found to contribute significantly with up to 4 % to for NO₃- and OH-originated α-pinene SOA indicating that this compound might play a key role both under day- and night-time conditions and not just at daytime. It should be also noted that huge amounts of organic peroxides were found from α-pinene/OH which are an important part of ROS and can be associated with oxidative stress after inhalation of such particles. The peroxide fraction was found to be higher under dry conditions, and, somewhat surprisingly, decreases with RH.

Relative humidity was found to affect SOA growth and composition, in particular the formation of MNC during *m*-cresol oxidation. While day-time chemistry of α-pinene and limonene is RH independent ($Y_{OH} \approx 6$ and 20 %), SOA yields from *m*-cresol+OH increased with elevated RH ($Y_{OH} \approx 3 - 9$ %). This observed effect is most likely to be attributed to the huge fraction of MNC with up to 6% under high RH, lowering the uptake of OH radicals and changing the phase state. Additionally, the reaction of limonene+NO₃ pointed out to be very sensitive towards RH, yielding the highest SOA ($Y_{NO3} \approx 29$ %) under dry conditions. This observation is suggested to be caused by a competition reaction between limonene and formed RO₂ radicals, leading to a lower conversion of limonene. Furthermore, *m*-cresol was found to yield only neglectable amounts with NO₃, thus producing a highly reactive gas phase as almost all oxidation products stay in the gas phase. The concentration of reactive species in the gas phase could act as a reservoir for compounds with a much higher SOA formation potential.

*Data availability.* All data presented in this study are available from the authors upon request (mutzel@tropos.de and herrmann@tropos.de). In addition, all data from experiments at RH = 50 % (α-pinene/OH, α-pinene/NO₃, limonene/OH, limonene/NO₃, m-cresol/OH and m-cresol/NO₃) are available at the EUROCHAMP webpage (https://data.eurochamp.org/).

485 *Authors contribution.* AM, OB, HH have planned the experiments. AM, YZ, MR, AK, OB have performed the chamber experiments. AM, YZ, AK have analysed the data. AM and HH have written the manuscript. YZ, MR, AK, XW, and HH have edited the manuscript.

*Competing interests.* The authors declare that they have no conflict of interest.

*Special Issue statement.*

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845  **Table 1. Experiments conducted for the NO₃- and OH-radical initiated oxidation of α-pinene, limonene and *m*-cresol. All reactions were conducted with 60 ppbv initial hydrocarbon concentration, at T = 293 K and in the presence of (NH₄)₂SO₄/H₂SO₄ (pH = 4 at 50% RH).**

| Precursor compound | | RH [%] | ΔHC [µg m⁻³] | ΔM [µg m⁻³] | SOA yield [%] | NO₃⁻ [µg m⁻³] | Literature reference[a] |
|---|---|---|---|---|---|---|---|
| α-pinene | NO₃ | <5 | 154 | 10 | 6.7 | 0.30 | 0.2 - 16% (Hallquist et al., 1999); 4 or 16% (Spittler et al., 2006); 1.7 – 3.6% (Nah et al., 2016); 0% (Fry et al., 2014); 9% (Perraud et al., 2010); 0.3 - 6.9 % (Moldanova and Ljungstrom 2000) |
| | NO₃ | 50 | 125 | 7 | 5.9 | | |
| | NO₃ | 75 | 129 | 8 | 6.4 | 0.27 | |
| | OH | <5 | 126 | 5 | 4.1 | | 21.2 % (Ng et al., 2007) |
| | OH | 50 | 115 | 6 | 3.4 | | |
| | OH | 75 | 139 | 6 | 4.3 | | |
| limonene | NO₃ | <5 | 193 | 59 | 29.9 | 3.1 | 14 - 24 % (Moldanova and Ljungstrom 2000); 21 – 40% (Spittler et al., 2006); 25 – 40% Fry et al., 2011); 44 – 57% (Fry et al., 2014 |
| | NO₃ | 50 | 156 | 41 | 26.1 | | |
| | NO₃ | 75 | 107 | 16 | 14.8 | 3.5 | |
| | OH | <5 | 196 | 20 | 10.0 | | 4.3% (Larsen et al., 2001) |
| | OH | 50 | 236 | 50 | 21.0 | | |
| | OH | 75 | 240 | 40 | 19.6 | | |
| *m*-cresol | NO₃ | <5 | 115 | <1 | <1 | < DL | 4.9 % (Iinuma et al., 2010)[b]; 35 – 49% (Nakao et al., 2011) |
| | NO₃ | 50 | 102 | <1 | 1.0 | | |
| | NO₃ | 75 | 100 | <1 | 1.7 | < DL | |
| | OH | <5 | 133 | 4 | 2.9 | | |
| | OH | 50 | 114 | 8 | 6.2 | | |
| | OH | 75 | 84 | 10 | 9.1 | | |
| Blanks | NO₃ | 50 | - | <1 | <1 | | |
| | OH | 50 | - | <1 | <1 | | |

[a]only those studies are reported for OH radical reaction of limonene and α-pinene that apply also H₂O₂/NO as OH

source; [b] due to the lack of data all available literature is shown

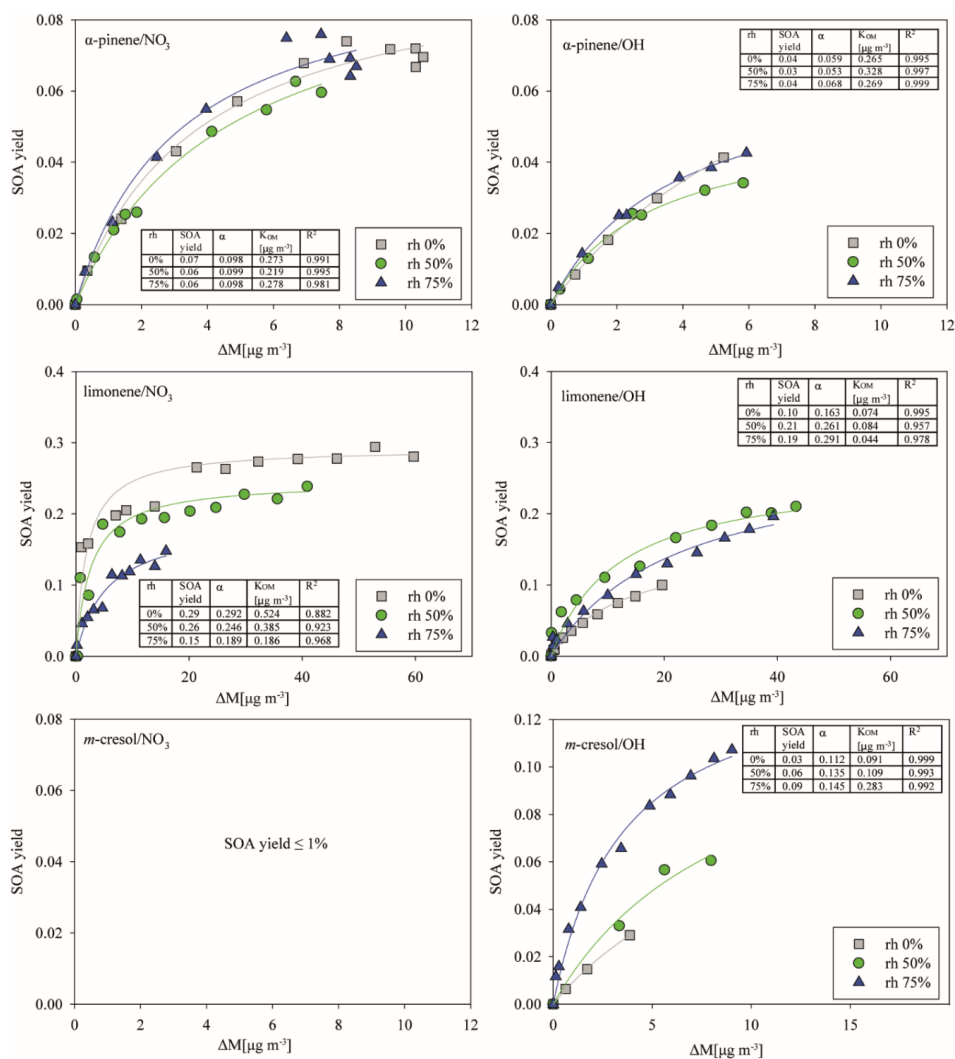



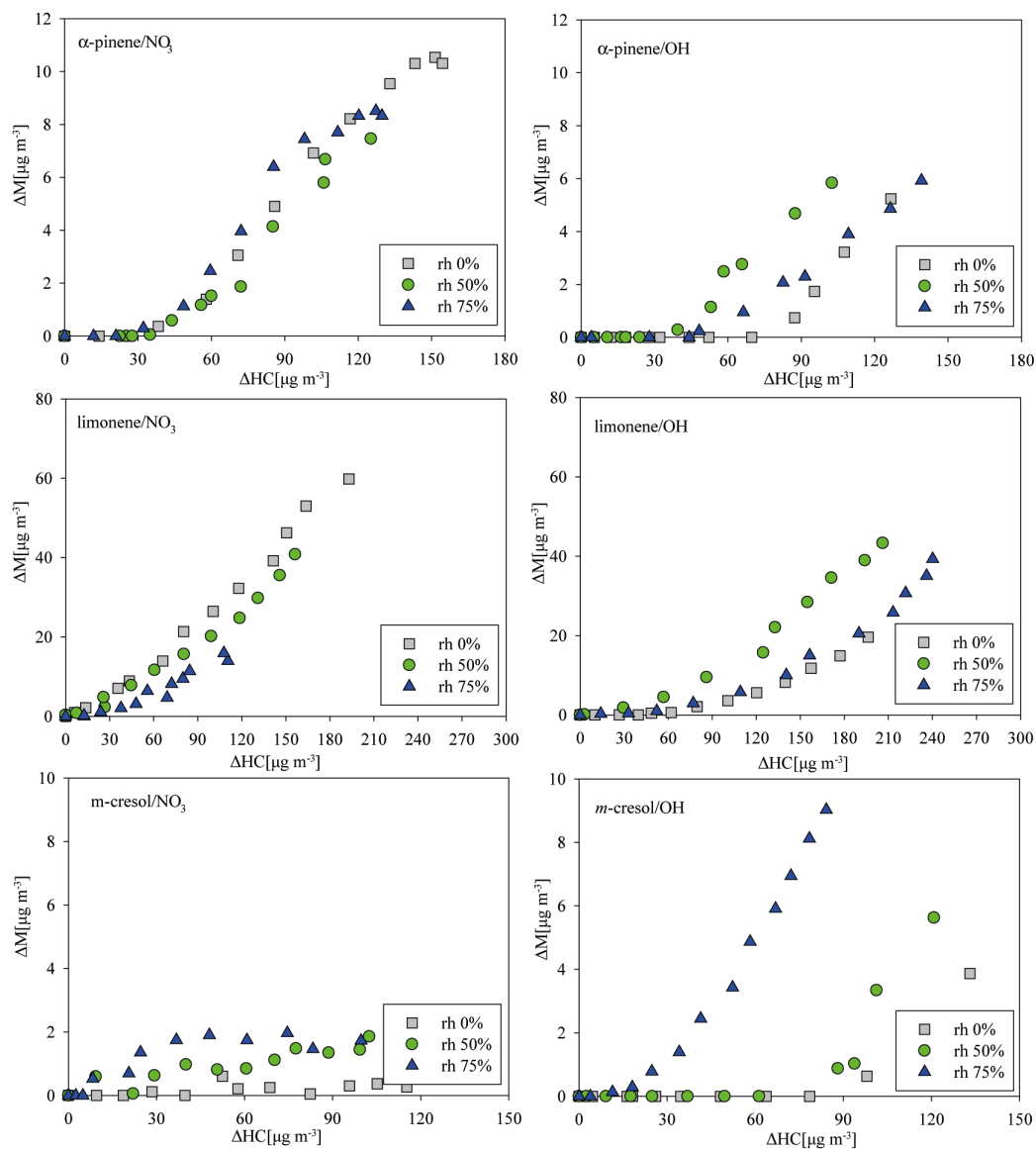
**Figure 1.** Yield curves for α-pinene, limonene and *m*-cresol with $NO_3$ and OH radicals for RH 0%, 50% and 75%. Yield curves were parametrised with the one-product approach (Odum et al., 1996). The obtained values for α (mass yield) and $K_{OM}$ (partitioning coefficient) are included as well. Please note, the SOA yield of m-cresol/$NO_3$ was below 0.01%. Therefore, no parameterisation can be provided.

855

**Figure 2. Growth curves for α-pinene, limonene and *m*-cresol with NO$_3$ and OH radicals for RH 0%, 50% and 75%.**

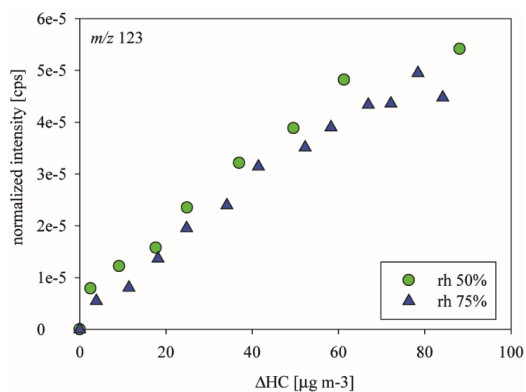



**Figure 3. Evolution of *m/z* 123 as a function of consumption of *m*-cresol (ΔHC). The signal at m/z 123 can be attributed to methyl-1,4-benzoquinone.**

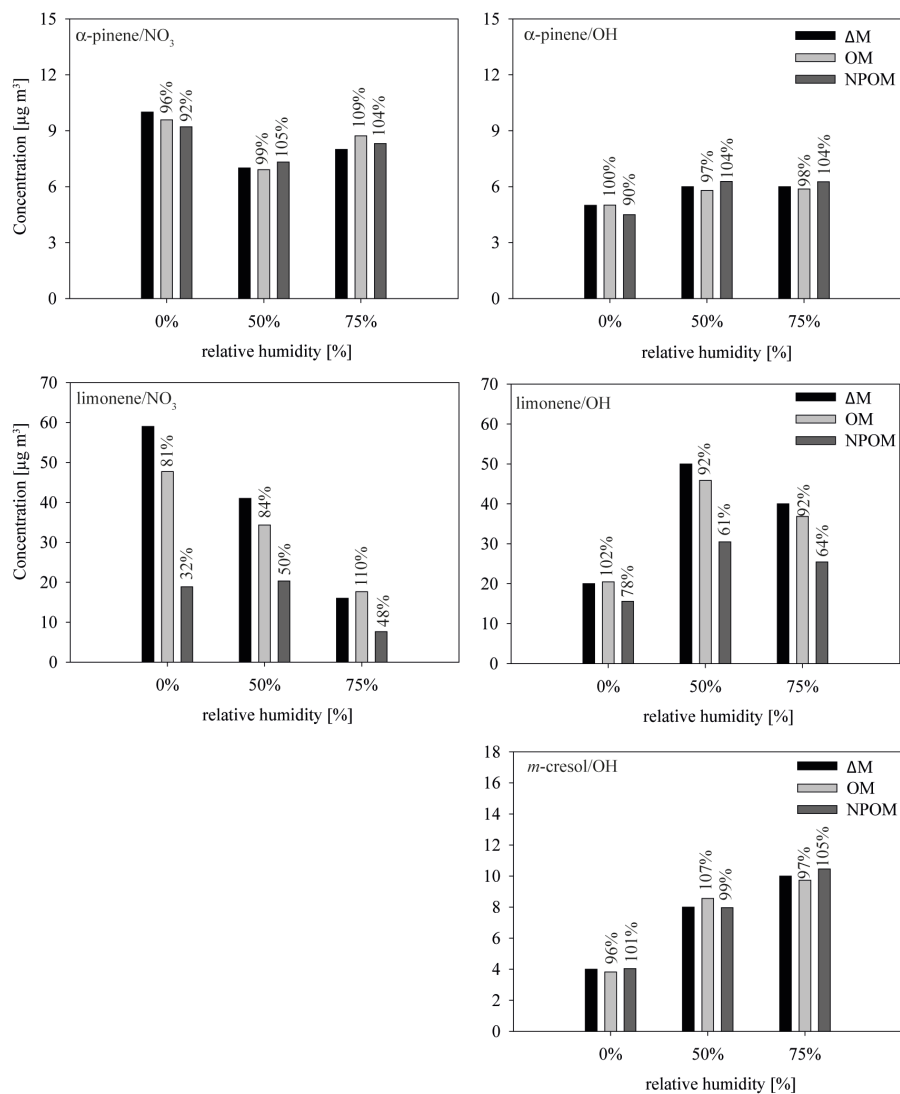



**Figure 4. Comparison of organic mass calculated from SMPS with an offline determined concentration of organic material (OM) and non-purgeable organic material (OM). Measurement uncertainties are given as follows 10% for SMPS measurements (Wiedensohler et al., 2012), 5% for OC/EC measurements (Spindler et al., 2004) and 10% for WSOC measurements (Timonen et al., 2010). Please note, no values can be given for m-cresol/NO₃ as the produced organic mass was too small to be beyond the detection limits of the different techniques.**

870

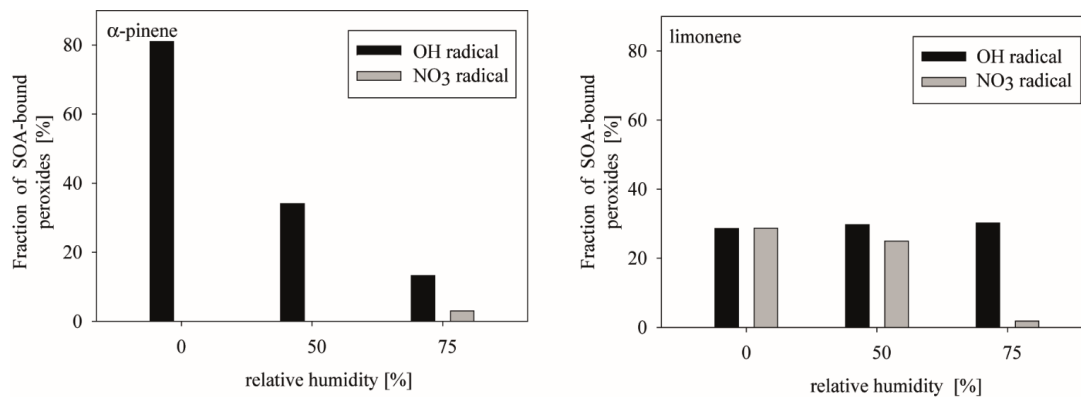



**Figure 5. Fraction of SOA-bound peroxides from α-pinene (left) and limonene oxidation with OH radicals (black) and NO$_3$ radicals (grey). Quantification was done following the method described by Mutzel et al., 2013 assuming a molar mass of 300 g mol$^{-1}$ (Docherty et al., 2005).**

875

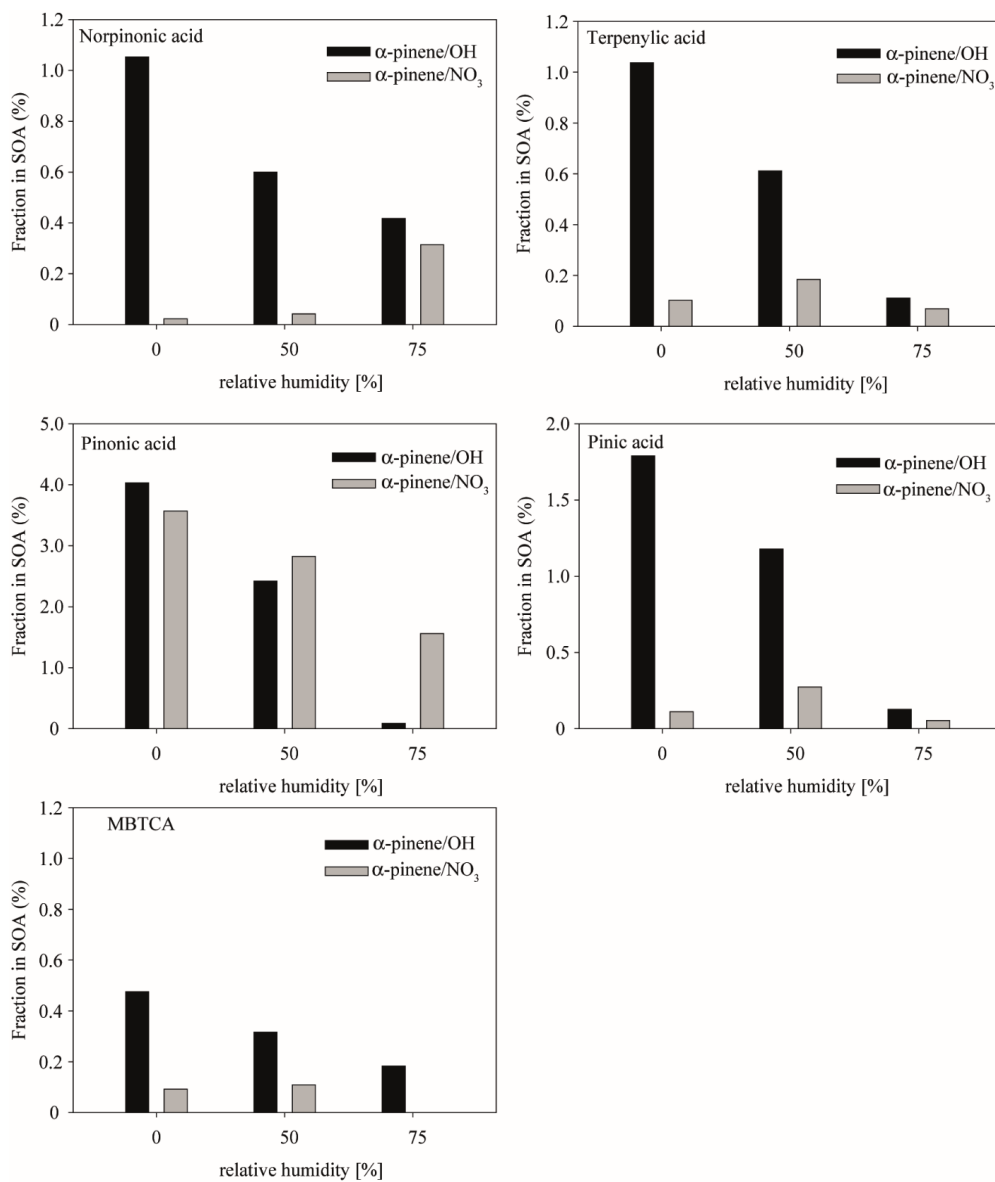



**Figure 6. Fraction of α-pinene marker compounds norpinonic acid, terpenylic acid, pinonic acid, pinic acid and MBTCA for OH-radical reaction (black) and NO₃-radical reaction (grey).**

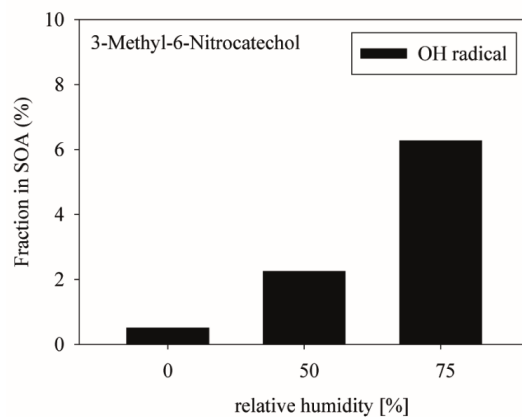



**Figure 7. Fraction of 3-methyl-5-nitrocatechol from the oxidation of *m*-cresol with OH. Please note, other compounds from the ASOA standard (Hoffmann et al., 2007) were not identified and due to the low SOA yield from NO$_3$-radical reaction, the concentration might be below the detection limit.**