Answers to the reviewer

We gratefully thank the reviewer for the comments. Please find the corresponding answers below. Changes in the manuscript are highlighted in blue.

Reviewer 1

Reviewer comment: Page 8, line 260-268. I do not agree with the reasoning that the inorganic nitrate is not higher under humid conditions. At <5 % RH, the ratio of DM:NO3-is 29.9:3.1 = 9.65. In contrast, at 75 % RH, the ratio is 16:3.5 = 4.65. A much larger fraction of the aerosol produced is nitrate at higher RH. Also, if any organic nitrates that are present in the SOA do hydrolyse, then they could appear as NO3-in the IC analysis, since this uses a water extractionstep.

Authors response:

We do agree to this comment. The absolute value of nitrate stayed constant under dry and humid conditions. While calculating the ratio of organics to nitrate under both conditions another conclusion can be found. The ratio is much lower under humid conditions indicating a high contribution of nitrate. The manuscript was changed accordingly and the new text now reads:

Page 8, line 262: *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 seems to be supported by the quantification of particulate inorganic nitrate as this shows a higher fraction in SOA under elevated RH (Table 1). Under dry conditions the ratio of produced organic mass:particulate inorganic nitrate is around 9.65 whereas under elevated RH this ratio decreases to 4.65. Therefore, a stronger contribution of particulate inorganic NO_3^- can be suggested.*

Reviewer comment:Page 10, line 340-345: What were the results of the blank tests? The a-pinene results are indeed very unexpected. Can you estimate the proportion of RO2reacting with HO2versus NO in these experiments? What is the temporal evolution of NO in the chamber, how quickly is it converted to NO2? Also, how much ozone is formed? Could you be seeing ozonolysis leading to SOA peroxides? Your values seem so much higher than previous studies. Could other species be giving a response? Needs more information in the experimental about the analysis method, not just giving a previous paper. For limonene, surely you could use the MS data to determine if high molecular weight peroxide dimers were present?

Authors response:

The reviewer here addresses important issues. The blank test was conducted to evaluate the formation of SOA by side reactions, in particular inorganic nitrate and to exclude a contribution of H2O2 used for OH-radical generation during the determination of SOA-bound peroxides. As it can be seen no SOA, nitrate could or SOA-bound peroxides could be detected from the blank runs.

An estimation of the formed amount of RO_2 and HO_2 would be very interesting. As the present study is solely focused on experimental measurements, modeling of the experimentally obtained data might well be a topic of a follow-up manuscript. The discussion on the branching ratio of RO_2+HO_2 and RO_2+NO is given at page 10, line 345-352.

Within a follow-up study an AMS could be connected to the chamber to monitor online the particle-phase composition. Unfortunately, AMS was not present during the measurements the results of which are presented here.

We certainly agree on reviewers comment that the fraction of peroxides is high for a-pinene/OH. Nevertheless, they are lower than values reported by Docherty et al., 2005. As the reviewer stated in a later comment, the peroxide level is very sensitive towards molar mass. Using a lower molar mass would lower the peroxide fraction. Compounds that might interfere with the peroxide test are peroxy acyl nitrates (PAN). A respective paragraph is added to the manuscript, i.e.:

Page 10, line 352: *Peroxy acyl nitrates (PAN-type compounds) would be potential candidates or the contribution of H_2O_2 partitioned from gas to the particle phase.*
Page 27, line 887: *Please note, according to Eq. 1-3 the peroxide fraction is highly sensitive towards the molar mass used for calculation.*

Reviewer comment: Page 11, section on Biogenic SOA markers: There is no comparison of the a-pinene SOA tracer data to previous studies. Are the levels observed in alignment with previous studies (especially when considering such high peroxide content)? There needs to be a better discussion here about the amount of liquid water content present at the different RH levels. Is there really less pinonic acid formed at 75 % RH or is there just more water in the SOA, leading to a more dilute aerosol?

Authors response:
To the authors' opinion the discussion on the LWC at page 11 is sufficient. Different routes how water can affect the partitioning behavior and also the formation of carboxylic acids are given. A dilution of the target compounds might be relevant while interpreting absolute concentrations. To avoid those effects, the fraction of marker compounds within the formed SOA is illustrated (Figure 6). While analyzing the mass fraction, effects such as dilution shouldn´t disturb. To highlight this fact, a sentence is added to the manuscript. Furthermore, as only mass fractions are illustrated comparisons to other available literature is not needed. Additionally, the yield and mass fraction highly depends on LWC, phase state, composition of the organic phase etc.

Page 28, line 892: *Please note that the fractions of marker compounds in the SOA formed SOA are illustrated.*

Reviewer comment: Line 406: Some of the dimers can be observed in negative ionisation ESI. Could you qualitatively determine whether this pathway increases at higher RH using the LC-MS data?
Authors response:
We agree on reviewer comments that a quantification of dimers is missing. Unfortunately, no standards are available and thus a quantification cannot be provided. The synthesis of those standards for quantification would be very beneficiary for the whole aerosol community but is out of scope for the present study. As it is stated in the manuscript, this is a suggestion based on literature findings.

Page 12, section on Anthropogenic SOA markers: I don't really understand why you are comparing the composition to an "ASOA marker" mixture, rather than using existing knowledge about cresol chemistry to use appropriate standards of oxidation products. Also, there is discussion here about biomass burning but you have called this an anthropogenic tracer. The Hoffmann paper (2007) calls this a method for biomass burning. How many of these compounds would you expect to form from m-cresol oxidation?Are there species you would have expected to see but don't? While the 3MNC shows a positive trend, I don't really feel that this data adds very much to our understanding of cresol SOA.
Authors response:
We do not agree on reviewer comment. As it was pointed out, cresols are important biomass burning marker compounds are often related to the described ASOA marker mixture. Many of these compounds have been described also in literature to be formed during cresol oxidation. Thus, the used mixture seemed to be representative. Furthermore, it should be clear that the present study was focused solely on SOA formation and thus particulate oxidation products were in the focus of the work. Even though

few studies exist on pure cresol-oxidation, the minority of them provides products identification in the particle phase using authentic standard compounds. 3MNC was the only compounds we could observe with applied technique. In the future other techniques than the one applied in the present study could provide better insight into the particle-phase composition (e.g. IC/MS for small functionalized organic acids)

Reviewer comment: Page 13, line 465: Have there been any studies of the OH yield from NO3+a-pinene? The formation route for pinonic acidis not obvious. Do you have any idea where it is coming from in the NO3 reaction? Is it similar to the norpinonic and a possible hydrolysis product? Or could it be from residual ozone or OH?

The formation of pinonaldehyde is described in Spittler et al., 2006 via formation of the nitrate-peroxy-radical. As pinonaldehyde is a potential pinonic acid precursor this pathway could be considered. A corresponding paragraph is added to the manuscript which reads:

Page 13, line 462: *The formation of pinonic acid might proceed via further reaction of pinonaldehyde that this described to be formed during NO_3-radical initiated reaction of a-pinene (Spittler et al., 2006).*

Reviewer comment: Page 13, line 478: I felt the last few lines made a very important comment that was not really discussed in the main paper. To me it seems very odd that so little SOA is formed from this route as such a large amount of m-cresolis reacted. In your table 1, there is a literature reference suggesting a 35-49 % yield, but I think perhaps this should be for OH chemistry? A recent paper on o-cresol +NO3indicated a SOA yield of 7-17%. There needs to be much more discussion about the reasons for this in the main paper on in the section on page 7. Sathiyamurthi Ramasamy, Tomoki Nakayama, Takashi Imamura, Yu Morino, Yoshizumi Kajii, Kei Sato, Investigation of dark condition nitrate radical-and ozone-initiated aging of toluene secondary organic aerosol: Importance of nitrate radical reactions with phenolic products, Atmospheric Environment, 2019, https://doi.org/10.1016/j.atmosenv.2019.11704

We agree that the reference by Nakao et al. belongs to OH-radical chemistry. Accordingly, we shifted it. We apologize for this mistake.

In fact, the low SOA yield of m-cresol+NO_3 was very unexpected. But as all three cresol isomers have very different physical properties in terms of volatility, it seemed to be reasonable. o-cresol is less volatile than m-cresol, and, accordingly, the corresponding products might also be of lower volatility as well leading much faster to SOA formation. Therefore, both studies are not contradicting each other.

The reference Ramasamy et al. has now been included into the manuscript. Please note that this publication was not included into the orginial manuscript as it was published only after the present work was submitted.

Page 7, line 251*: In the literature, higher SOA yields for other cresol isomers have been reported. Due to the different volatilities of the cresol isomers, different SOA formation potentials are expected (Ramasamy et cl., 2019).*

Minor comments:

Abstract: why only give a-pinene peroxide levels here? Also, “pinonic acid as the most important particle phase constituent” What do you mean by “important”? Do you mean highest proportion based on the small subset of products measured?

The fraction of SOA-bound peroxides was added to the abstract. Pinonic acid was highlighted as most important product as it was found with 1-4 % which is a significant fraction for a single compound The abstract was changed accordingly and this text now reads:

Page 1, line 28: *The fraction of SOA-bound peroxides which originated from □-pinene varied between 2 – 80% as a function of RH and was found to be around 30% for limonene/Oh independent of the RH.*
Furthermore, SOA from α-pinene revealed pinonic acid as the most significant single particle-phase constituent under day- and night-time conditions with a SOA fraction of 1 – 4%.

Page 2, line 57 –is the uncertainty on the limonene + NO3 rate coefficient really a factor or almost 100? Seems very high.
Yes, the rate constants reported in the literature vary dramatically.

Page 2 -the introduction is very focussed on NO3chemistry and very little on OH. There is clearly much more literature information available for OH and I would like to see some of this incorporated here.
Authors response:
Certainly, more literature is available on OH radical chemistry. But the focus of the present manuscript is NO_3-radical chemistry and, accordingly, we highlighted the importance of NO_3 radical chemistry.

Page 2, line 69: Why is cresol used as the anthropogenic tracer? No explanation given for this choice, since itcan also be released from biomass burning.
Authors response:
Cresol is an important biomass burning tracer compound and only few studies are available that investigate cresol oxidation. Thus, it was included into the present study. The importance of cresol and the respective night-time chemistry is clearly stated in the atmospheric implication and conclusion section.

Page 3, line 96: "equals this a dilution" –consider rewording this sentence.
The sentence reads now:
Based on a reaction time of 90 minutes a dilution of 4.7 % (NO_3) and 2.4 % (OH) can be estimated.

Page 3, line 104: Can you explain how the pre-reactor was set up to avoid ozone entering the chamber. How much ozone did you detect in the chamber during NO3experiments?
The pre-reactor was described and characterised within a previous study (Iinuma et al., 2010.) from our laboratory. A detailed description can be found therein. The paper is now cited in the experimental description. As the pre-reactor was not newly developed for this study, a detailed characterisation was not included.

Page 3, line 86: *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 (Iinuma et al., 2010).*

Page 4, line 114: 1 g cm-3 seems a rather low value to use for density of SOA.
As the real density is unknown a standardized density of 1 g cm-3 is used. As we state clearly which density is used, one can use it and convert by factors to be able to compare to studies using another density.

Page 4, line 134: should this say micro L not milli L?
The manuscript was changed accordingly. *Page 4, line 134: 500 uL*

Page 5, section 2.3.4: The contents of the anthropogenic SOA mix need to be included here. The reader does not want to have to go and look this up. It is important to know whether you would expect to see any other tracers in the mix in the cresol experiment or not. If not, why not just use a 3MNC standard?

We agree and a list of compounds being present in the mixture is added now to the manuscript. The text now reads:
Page 5, line 157: *The composition of the anthropogenic SOA mix for biomass burning is described in detail in Hoffmann et al., 2007 containing 3,5-dimethoxy-4-hydroxy-acetophenone, 4-hydroxycinnamic acid; Sinapic acid; Ferulic acid; Vanillic acid; Vanillin; Homovanilic acid; Syringic acid; Syringaldehyde; Coniferyl aldehyde; Nitrocatechol; 4-nitrophenol; 4-nitroguaiacol; 2,4-dinitrophenol; 2-nitrophenol; 3-methyl-4-nitrophenol; 2,6-Dinitro-4-methylphenol; 2-methyl-4-nitrophenol; 2-methyl-4,6-dinitrophenol; 4-methyl-2-nitrophenol and 2,6-Dimethyl-4-nitrophenol.*

The used standard is a well-established mixture of atmospheric relevant compounds that are often observed from biomass burning events. Thus, it was worth evaluating if other compounds were formed as well. As this was not the case, no further discussion was provided.

Page 5, line 164: Reconsider this sentence. Im not sure how it can be “significantly or at least slightly higher”?
The manuscript was changed accordingly.
Page 5, line 168: *In general, α-pinene yielded higher SOA with NO_3 radicals ($Y_{NO3} \approx 6\%$) than with OH ($Y_{OH} \approx 3.5\ \%$).*

Page 6, line 190: This sentence doesn’t make sense. I think you are trying to say the yield from NO3 is higher than from OH. But this sentence seems to say the opposite. Only one a-pinene + OH reference is given in Table 1. I am sure there are many more than that.
The manuscript was changed accordingly to:
Page 6, line 190: *However, comparing the SOA formation from night-time chemistry with day-time, the yields from NO3 radical chemistry are higher.*
Yes, of course more literature is available. A selection is added to Table 1.

Page 6, Page 6, line 201: I don’t follow this sentence. Do you mean SOA is being formed from the oxidation of first generation products rather than the products themselves?
The strong contribution of first-generation oxidation products to SOA formation was developed and reported in detail by Ng et al., 2006. A delay time in growth curves often indicates that further reaction of oxidation products is able to yield condensable products. The sentence as changed.
Page 6, line 205: *Such a long induction period is most likely caused by further reaction of first-generation oxidation products leading to SOA formation as it was demonstrated in previous studies (Ng et al., 2006, Mutzel et al., 2016).*

Page 6, line 204: Please give structures for the non-standard named compounds like Myrtenal. Myrtenal is not a non-standard named compound. Myrtenal is the trivial name of **(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-carboxaldehyde. It has a CAS number 18486-69-6 and is commercially available.**

Page 6, line 216 –please give typical limonene ozonolysis SOA yields.
Yield from ozonolysis are added to the manuscript.

Page 6, line 217: *Those values are close to the lowest values reported for limonene ozonolysis with 29 – 69 % (Northcross and Jang, 2007, Chen and Hopke, 2010, Gong et al., 2018).*

Page 7, line 222 –is there no literature data for SOA from cresol for comparison? The start of this section is rather imprecise. Using cresol as a proxy for "anthropogenic" VOCs and comparing whether they form more SOA than biogenics is not accurate. Hildebrandt uses the parent hydrocarbons and so cannot simply be applied to the cresol.

The respective sentence was deleted from the manuscript

Page 7, line 222 was deleted: *A study by Hildebrandt et al., 2009 raised the question about the low SOA yields and observed much higher yields by using artificial sunlight.*

Cresol is an anthropogenic VOC as well as a biomass burning tracer compound. The authers don´t think that this is contradicting. Biomass burning can be of anthropogenic origin. Available literature for cresol is cited many times throughout the manuscript.

A comparison of the SOA yields is done because biogenic VOCs are emitted during day-time. During evening biomass burning starts and compounds like cresol are emitted. This mixture of VOCs and OVOCs is subject to oxidation by OH and NO_3. This was exactly the objective of the present manuscript and is discussed in detail in section 3.5 Atmospheric implication.

Page 7, line 240 –there is no mention here about the impact of RH on aerosol phase and hence the uptake of SVOC.

Indeed, this investigation of SVOCs and their partitioning in the particle phase might be relevant and could be objective of a follow-up study. But it was no focus of the present study.

Page 7, line 250: You have not mentioned limonene + OH, which seems to have a different pattern to the others, with the highest yield at 50 % RH?

As it stated in the manuscript "According to Figure 2, 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)" these two cases were discussed in detail.

Page 8, line 277: can you really say this based on a SAR derived rate constant from the MCM?

As no experimental data are available, no other values can be provided. It clearly written, that this is a hypothesis. The SAR might be not completely accurate but the difference is at least two order of magnitude.

Page 8, line 280: Were these two sets of reactions done in this study? What is the "one study that investigated this reaction channel"?

This paragraph summarizes the study by Boyd et al., 2015. He investigated the reaction of RO_2+NO_3. To the authors best knowledge this hasn´t subject of other studies.

Page 8, line 297 –I don't understand what "the evolution in dependency on consumption" means.

This refers to the signal measured at *m/z* 123 which is illustrated as a function of the consumption. The sentence was changed accordingly.

Page 8, line 297: *Nevertheless, the increase of the signal in dependency on consumption does not show a significant effect of RH on the formation (Figure 2).*

Page 9, line 305: This whole section is really confusing, with long sentences with too many parts. There needs to be some more discussion about the data in the figure. Why are some values over 100 %? The proportion of OM also is much lower in limonene + NO3, why is this? I felt there was a lot of information in the figure, but very little discussion of what it means and the levels of uncertainty.

The authors do not agree on this comment. The discussion at page 9 "*Organic carbon and water-soluble organic carbon"* summarized the findings according to Figure 4. But in Figure 4 only sum parameters are provided. The break-down those sum parameters into smaller fractions, single discussions are provided regarding the peroxide content and single compound analysis. The following sentence is added to the manuscript to make it more clear:

Page 9, line 326: *To further investigate the fraction of organic material found in the formed SOA, discussions about SOA bound peroxides and single compounds is provided in the following sections.*

The level of uncertainty is given for each used technique (Figure 4). These uncertainties are the reason for values being slightly larger than 100%. Figure 3 illustrates the combination of three independent measurements, one online and two offline techniques. Small deviations are expected.

Also a discussion on the small fraction of water-soluble material in the case of limonene is provided. Although, the present work couldn´t find the reason for such a low fraction, feasible reasons are provided.

Page 9, line 321: What is the sensitivity of this analysis as a result of changing the molar mass? There is increasing evidence of auto-oxidation in some systems, which can occur in the presence of NO, which could shift the peroxide mass distribution.

The peroxide test gives an impression about the amount of hydroperoxides in the SOA. Acceding to Eq. 2-4 it can be seen that this analysis is very sensitive towards the molar mass. A molar mass of 300 g mol^{-1} is usually used as it refers to the original publication by Docherty et al., 2005 assuming that the majority of hydroperoxides are higher molecular weight compounds. This fact is clearly stated in the manuscript. While changing the molar mass, the fraction will change. As long as the identification of this fraction cannot be provided on a molecular level, it is valid to use those assumptions.

Page 10, line 355 to 360: can you make it clear that you are talking about HO2 concentrations in the GAS phase.

This information was added to the paragraph.

Page 10, line 360: *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 from the gas phase and ii) decomposition and/or hydrolysis of hydroperoxides. It has been reported that the gas phase 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 react 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).*

Page 11, line 415. I don't follow this sentence. To me the RH dependence looks very different –nowhere near as dramatic at 75 %

The sentence was changed accordingly.

Page 11, line 423: *Notably, pinonic acid was detected in comparable amounts from a-pinene/OH and a-pinene/NO_3 with the same RH dependency* (*Figure* 6).

Reviewer 2

Please use abbreviation consistently. It improves the readability of the manuscript greatly. E.g. RH and relative humidity.
L23 In average -> On average
The manuscript was changed accordingly and now reads:
Page 1, line 23: *On average, α-pinene yielded SOA with about 6 - 7% from* NO_3 *radicals and 3 – 4 % from OH radical reaction.*

L127: Please give the name of an IC-CD model and manufacturer.
Thermo Scientific Dionex ICS-3000 CD

L150: Please provide a reason for changing the chromatographic condition.
The chromatographic separation was done accordingly to Hoffmann et al., 2007. These authors figured out that these conditions are much better for separation. To emphasize that the method is taken from Hoffmann and co-workers (from our lab), the citation is added.
Page 5, line 149: *For anthropogenic SOA compounds, the separation was done as described above at 15°C and with 0.2 % acetic acid in water as described in Hoffmann et al., 2007.*

L186: Do the authors mean "The values obtained in this study did not agree with previously reported values because OH sources are different"?
Yes, this is correct. As the choice of OH-radical generation is crucial for product distribution (eg. Influence of RO_2/HO_2 ratio etc.), the OH source might have an effect on $\alpha_{1/2}$ and $K_{1/2}$ values.

L239: This should be 3.2. Please change all the section numbers accordingly.
The section numbers were changed accordingly:
Page 7, line 243: 3.2 *Influence of RH on SOA yield and growth*
Page 9, line 308: 3.3 *Characterisation of particle-phase chemical composition*
Page 13, line 456*: 3.4 Atmospheric implications and Conclusion*
Page 14, line 501: *4 Acknowledgment*
Page 14, line 508: *5 References*

Line 262: I am not too sure what the authors mean here by "a decreasing consumption when RH increases". Do the authors mean "a decreasing consumption of VOC when RH increases"? If so, this seems to contradict what Figures 1 and 2 (limonene/NO3) shows. Please clarify this sentence.
This description is not contradicting. As it can be seen in Figure 1, in the case of limonene/NO3 the consumption of limonene is lower under dry conditions ($\Delta HC = 193\ \mu g\ m^{-3}$) than under humid conditions ($\Delta HC = 107\ \mu g\ m^{-3}$). Thus VOC consumption decreases when RH is higher. Additional information is added to make it more clear. The text now reads:
Page 8, line 269: *As can be seen in Figure 1, in the case of limonene/NO3 the consumption of limonene is lower under dry conditions (*$\Delta HC = 193\ \mu g\ m^{-3}$*) than under humid conditions (*$\Delta HC = 107\ \mu g\ m^{-3}$*).*

L307: NPOM should be described in line 73.
Page 9, line 316: *Please note, water-soluble organic carbon was determined as NPOM.*
Page 1, line 72: *The chemical composition of formed SOA was characterized for their fraction of organic carbon (OC), non-purgeable organic carbon (NPOM), SOA-bound peroxides and SOA marker compounds.*

L315: It may well be that higher molecular weight compounds do not ionize well in negative ESI, and they aren't present in the LC/MS data. Just in case, do the authors have signals for them in LC/MS data? Signals were present but only few and difficult to interpret. As the ionization efficiency is unknown and matrix effects might play a role, an interpretation of those data were not done.

L346: a-pinene/OH -> α-pinene/OH
The manuscript was changed accordingly and now reads:
Page 10, line 358: *In general, peroxide fractions of 10 - 80% of the organic mass have been detected from α-pinene/OH experiments.*

L346-347: Why do high peroxide fractions contradict the small SOA yields? Please provide the reason for this explanation.
The sentence is deleted from the manuscript.
Page 10, line 358: *The high peroxide fractions of 10 – 80% are contradicting to the small SOA yields from α-pinene/OH ($Y_{OH} \approx 3.5$ %)* is deleted

L376 Biogenic SOA marker compounds and Figure 6: Does the discussion take the water content of SOA? If not, it makes more sense to discuss data in terms of carbon mass fraction of marker compounds in OC to eliminate the effect of water content.
The effect of LWC on the partitioning behavior and formation processes is discussed in detail at page 11 and 12. As pointed out by the reviewer, the amount of marker compounds is expressed as mass fraction in formed OM. Thus, dilution effects are eliminated.

L865 Figure 4 Caption: non-purgeable organic material (OM) -> non-purgeable organic material (NPOM).
The manuscript was changed accordingly.
Page 26, line 885: *Comparison of organic mass calculated from SMPS with an offline determined concentration of organic material (OM) and non-purgeable organic material (NPOM).*

L415: Do the authors mean pinonic acid was detected in comparable fractions in both NO3 and OH oxidation of α-pinene? If so where do these 20-25% come from? For the 75%RH experiments, α-pinene/OH experiment shows much lower pinonic acid fraction. Can the authors clarify this?

Pinonaldehyde was detected from both systems and the amounts were comparable. To clarify, the sentence was re-written and now reads:
Page 12, line 427: *Notably, pinonic acid was detected in comparable amounts from α-pinene/OH and α-pinene/NO_3 with the same RH dependency (Figure 6).*

At this moment, it is unclear why pinonic acid is formed less at RH = 75%. As this was not observed for α-pinene/NO_3 system, water might affect the formation process of pinonic acid during OH-radical reaction. This fact remains still speculative and more work is needed to evaluate this observation.

Changes made to the manuscript

Page 1, line 23: "In average, α-pinene yielded SOA with about 6 - 7% from NO_3 radicals and 3 – 4 % from OH radical reaction" has been changed to "On average, α-pinene yielded SOA with about 6 - 7% from NO_3 radicals and 3 – 4 % from OH radical reaction."

Page 1, line 28: "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%." has been changed to "The fraction of SOA-bound peroxides which originated from a-pinene varied between 2 – 80% as a function of RH and was found to be around 30% for limonene/OH independent of the RH.

Furthermore, SOA from α-pinene revealed pinonic acid as the most significant single particle-phase constituent under day- and night-time conditions with a SOA fraction of 1 – 4%."

Page 1, line 72: 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. Has been changed to

"The chemical composition of formed SOA was characterized for their fraction of organic carbon (OC), non-purgeable organic carbon (NPOM), SOA-bound peroxides and SOA marker compounds."

Page 3, line 86: (Iinuma et al., 2010) was added

Page4, line 130: "Thermo Scientific Dionex ICS-3000 CD" was added

Page 4, line 134: "500 mL" was changed to "500 uL"

Page 5, line 149: "as described in Hoffmann et al., 2007" was added

Page 5, line 157: "containing 3,5-dimethoxy-4-hydroxy-acetophenone, 4-hydroxycinnamic acid; sinapic acid; ferulic acid; vanillic acid; vanillin; homovanilic acid; syringic acid; syringaldehyde; coniferyl aldehyde; nitrocatechol; 4-nitrophenol; 4-nitroguaiacol; 2,4-dinitrophenol; 2-nitrophenol; 3-methyl-4-nitrophenol; 2,6-dinitro-4-methylphenol; 2-methyl-4-nitrophenol; 2-methyl-4,6-dinitrophenol; 4-methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol." was added to the manuscript

Page 5, line 168: "In general, α-pinene yielded significantly or, at least, slightly higher SOA with NO_3 radicals ($Y_{NO3} \approx 6\%$) than with OH ($Y_{OH} \approx 3.5\%$)." was changed to "In general, α-pinene yielded higher SOA with NO_3 radicals ($Y_{NO3} \approx 6\%$) than with OH ($Y_{OH} \approx 3.5\ \%$)."

Page 6, line 190: "However, comparing the SOA formation from night-time chemistry with day-time, the yields are by a factor of two higher than with NO_3." Was changed to "However, comparing the SOA formation from night-time chemistry with day-time, the yields from NO_3 radical chemistry are higher."

Page 6, line 205: 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)." has been changed to "Such a long induction period is most likely caused by further reaction of first-generation oxidation products leading to SOA formation as it was demonstrated in previous studies (Ng et al., 2006, Mutzel et al., 2016)."

Page 6, line 217: "Those values are close to the lowest values reported for limonene ozonolysis (Northcross and Jang 2007, Chen and Hopke 2010, Gong et al. 2018)." has been changed to "Those values are close to the lowest values reported for limonene ozonolysis with 29 – 69 % (Northcross and Jang, 2007, Chen and Hopke, 2010, Gong et al., 2018)."

Page 7, line 222 "A study by Hildebrandt et al., 2009 raised the question about the low SOA yields and observed much higher yields by using artificial sunlight." was deleted

Page 7, line 243: "3.3" was changed to "3.2"

Page 7, line 251: "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." has been changed to "In the literature, higher SOA yields for other cresol isomers have been reported. Due to the different volatilities of the cresol isomers, different SOA formation potentials are expected (Ramasamy et al., 2019)."

Page 8, line 262: 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 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." has been changed to "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 seems to be supported by the quantification of particulate inorganic nitrate as this shows a higher fraction in SOA under elevated RH (Table 1). Under dry conditions the ratio of produced organic mass:particulate inorganic nitrate is around 9.65 whereas under elevated RH this ratio decreases to 4.65. Therefore, a stronger contribution of particulate inorganic NO_3^- can be suggested. "

Page 8, line 297: "Nevertheless, the evolution in dependency on consumption does not show a significant effect of RH on the formation (Figure 3)." has been changed to "Nevertheless, the increase of the signal in dependency on consumption does not show a significant effect of RH on the formation (Figure 3)."

Page 9, line 308: "3.4" was changed to "3.3"

Page 9, line 316: "Please note, WSOC was determined as non-purgeable organic carbon (NPOM)." Was changed to "Please note, water-soluble organic carbon was determined as NPOM."

Page 9, line 326: "To further investigate the fraction of organic material found in the formed SOA, discussions about SOA bound peroxides and single compounds is provided in the following sections." was added.

Page 10, line 352: “Peroxy acyl nitrates (PAN-type compounds) would be potential candidates or the contribution of H_2O_2 partitioned from gas to the particle phase.” was added

Page 10, line 358: The high peroxide fractions of 10 – 80% are contradicting to the small SOA yields from α-pinene/OH ($Y_{OH} \approx 3.5$ %) is deleted

Page 10, line 360: “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) 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).” was changed to “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 from the gas phase and ii) decomposition and/or hydrolysis of hydroperoxides. It has been reported that the gas phase 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 react 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).”

Page 12, line 427: “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).” has changed to “Notably, pinonic acid was detected in comparable amounts from α-pinene/OH and α-pinene/NO_3 with the same RH dependency (Figure 6).”

Page 13, line 462: “The formation of pinonic acid might proceed via further reaction of pinonaldehyde that this described to be formed during NO_3-radical initiated reaction of a-pinene (Spittler et al., 2006).” was added.

Page 13, line 456: “3.5” has been changed to “3.4”

Page 14, line 501: “3” has been changed to “4”

Page 14, line 508: “4” has been changed to “5”

Page 26, line 885: “OM” has been changed to “NPOM”

Page 27, line 887: “Please note, according to Eq. 1-3 the peroxide fraction is highly sensitive towards the molar mass used for calculation.” Was added

Page 28, line 892: “Please note that the fractions of marker compounds in the SOA formed SOA are illustrated.” was added

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. On 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 and was found to be around 30% for limonene/OH independent of the RH.

Furthermore, SOA from α-pinene revealed pinonic acid as the most significant single particle-phase constituent under day- and night-time conditions with a SOA 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), non-purgeable organic carbon (NPOM), SOA-bound peroxides and SOA marker compounds.

2 Experimental

2.1 Chamber experiments

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 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. H_2O_2 was continuously injected into the chamber with a peristaltic pump at 100 uL hr^{-1} and was photolyzed with UV-A-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 (Iinuma et al., 2010). 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 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.

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 a dilution of 4.7 % (NO_3) and 2.4 % (OH) can be estimated. 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 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 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.

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 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

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 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 (Thermo Scientific Dionex ICS-3000 CD).

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 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 uL of methanol 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_3OH/H_2O (50/50, v/v).

2.3.3 Analysis with HPLC/(-)ESI-TOFMS

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 % 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 as described in Hoffmann et al., 2007.

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 for biomass burning is described in detail in Hoffmann et al., 2007 containing 3,5-dimethoxy-4-hydroxy-acetophenone, 4-hydroxycinnamic acid; sinapic acid; ferulic acid; vanillic acid; vanillin; homovanilic acid; syringic acid; syringaldehyde; coniferyl aldehyde; nitrocatechol; 4-nitrophenol; 4-nitroguaiacol; 2,4-dinitrophenol; 2-nitrophenol; 3-methyl-4-nitrophenol; 2,6-Dinitro-4-methylphenol; 2-methyl-4-nitrophenol; 2-methyl-4,6-dinitrophenol; 4-methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol.

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 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.

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.

α-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-time, the yields from NO3 radical chemistry are higher. 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 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 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 further reaction 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 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

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 with 29 – 69 % (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 ($Y_{OH} \approx 10$ – 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.

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.

3.2 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 %). In the literature, higher SOA yields for other cresol isomers have been reported. Due to the different volatilities of the cresol isomers, different SOA formation potentials are expected (Ramasamy et cl., 2019).

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 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. As can be seen in Figure 1 the consumption of limonene is lower under dry conditions ($\Delta HC = 60\ \mu g\ m^{-3}$) than under humid conditions ($\Delta HC = 20\ \mu g\ m^{-3}$). 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 seems to be supported by the quantification of particulate inorganic nitrate as this shows a higher fraction in SOA under elevated RH (Table 1). Under dry conditions the ratio of produced organic mass:particulate inorganic nitrate is around 9.65 whereas under elevated RH this ratio decreases to 4.65. Therefore, a stronger contribution of particulate inorganic NO_3^- can be suggested.

A second aspect to be considered is the contribution of first-generation oxidation products. According to 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 2.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1} can be found. According to k values taken from MCM and kinetic studies, limonene+NO_3 is by two orders of magnitude ($k_{lim+NO3}$: 1.2 6 x 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 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 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.

Under RH 0 % and 50 % conditions, aerosol production starts at $\Delta HC \approx 80 - 90\ \mu g\ m^{-3}$. Notably, at more elevated RH the SOA production starts immediately after initialization of the reaction ($\Delta HC \approx 5 - 10\ \mu g\ m^{-3}$). 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.

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 increase of the signal 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 products, such as methyl-nitro-catechol that showed a higher mass fraction under elevated RH (Figure 7).

3.3 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.

Organic carbon and water-soluble organic carbon

Pre-heated quartz fiber filter were analysed for OC/EC and WSOC content. Please note, water-soluble organic carbon was determined as NPOM. The obtained results were compared to the increase in organic mass (ΔM) 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 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 ΔM 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.

To further investigate the fraction of organic material found in the formed SOA, discussions about SOA bound peroxides and single compounds is provided in the following sections.

SOA-bound peroxides

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:

$$\mathrm{m}_{Perox} = n_{Perox} * 300\ g\ mol^{-1} \qquad (Eq.2)$$

$$M_{Perox} = \frac{\mathrm{m}_{\mathrm{perox}}}{\mathrm{V}_{\mathrm{sampling}}} \qquad (Eq.3)$$

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

where

$\mathrm{n}_{\mathrm{Perox}}$ is amount of substance in µmole (calculated from the iodometric peroxide test)

$\mathrm{m}_{\mathrm{Perox}}$ is mass of organic peroxides in µg

$\mathrm{M}_{\mathrm{Perox}}$ is mass concentration of organic peroxides in µg m^{-3}

$\mathrm{V}_{\mathrm{sampling}}$ is sampling volume of the filter in m^3

$\mathrm{F}_{\mathrm{Perox}}$ is mass fraction of SOA-bound peroxides in %

$\mathrm{M}_{\mathrm{org}}$ is amount of organic mass formed during experiment in µg m^{-3}

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 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. Peroxy acyl nitrates (PAN-type compounds) would be potential candidates or the contribution of H_2O_2 partitioned from gas to the particle phase. 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 partitioning of the injected oxidant. In general, peroxide fractions of 10 - 80% of the organic mass have been detected from α-pinene/OH experiments. 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 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 from the gas phase and ii) decomposition and/or hydrolysis of hydroperoxides. It has been reported that the gas phase 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 react 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).

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 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' 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 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. 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 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 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 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., 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 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 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.

Notably, pinonic acid was detected in comparable amounts from α-pinene/OH and α-pinene/NO_3 with the same RH dependency (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, 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 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*-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 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 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.

3.4 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 % (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 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 NO_3 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, NO_3 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 NO_3-initiated SOA formation. NO_3 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 NO_3- 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. The formation of pinonic acid might proceed via further reaction of pinonaldehyde that this described to be formed during NO_3-radical initiated reaction of α-pinene (Spittler et al., 2006). 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+NO_3 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 RO_2 radicals, leading to a lower conversion of limonene. Furthermore, *m*-cresol was found to yield only neglectable amounts with NO_3, 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 data from experiment at RH=50% (α-pinene/OH, α-pinene/NO_3, limonene/OH, limonene/NO_3, cresol/NO_3) are available at the EUROCHAMP webpage (https://data.eurochamp.org/).

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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Table 1. Experiments conducted for the NO_3- 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 $(NH_4)_2SO_4/H_2SO_4$ (pH = 4 at 50% RH).

Precursor compound		RH [%]	ΔHC [µg m^{-3}]	ΔM [µg m^{-3}]	SOA yield [%]	NO_3^- [µg m^{-3}]	Literature reference[a]
α-pinene	NO_3	<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)
	NO_3	50	125	7	5.9		
	NO_3	75	129	8	6.4	0.27	
	OH	<5	126	5	4.1		6.6 - 21.2 % (Ng et al., 2007); 7 – 18 % (Eddingsaas et al., 2012); 3 – 4 % (Zhao et al., 2018); 0.1 – 8.6% (Friedmann and Farmer, 2018)
	OH	50	115	6	3.4		
	OH	75	139	6	4.3		
limonene	NO_3	<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
	NO_3	50	156	41	26.1		
	NO_3	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	NO_3	<5	115	<1	<1	< DL	4.9 % (Iinuma et al., 2010)[b];
	NO_3	50	102	<1	1.0		
	NO_3	75	100	<1	1.7	< DL	
	OH	<5	133	4	2.9		35 – 49% (Nakao et al., 2011)
	OH	50	114	8	6.2		
	OH	75	84	10	9.1		
Blanks	NO_3	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 H_2O_2/NO as OH source; [b] due to the lack of data all available literature is shown

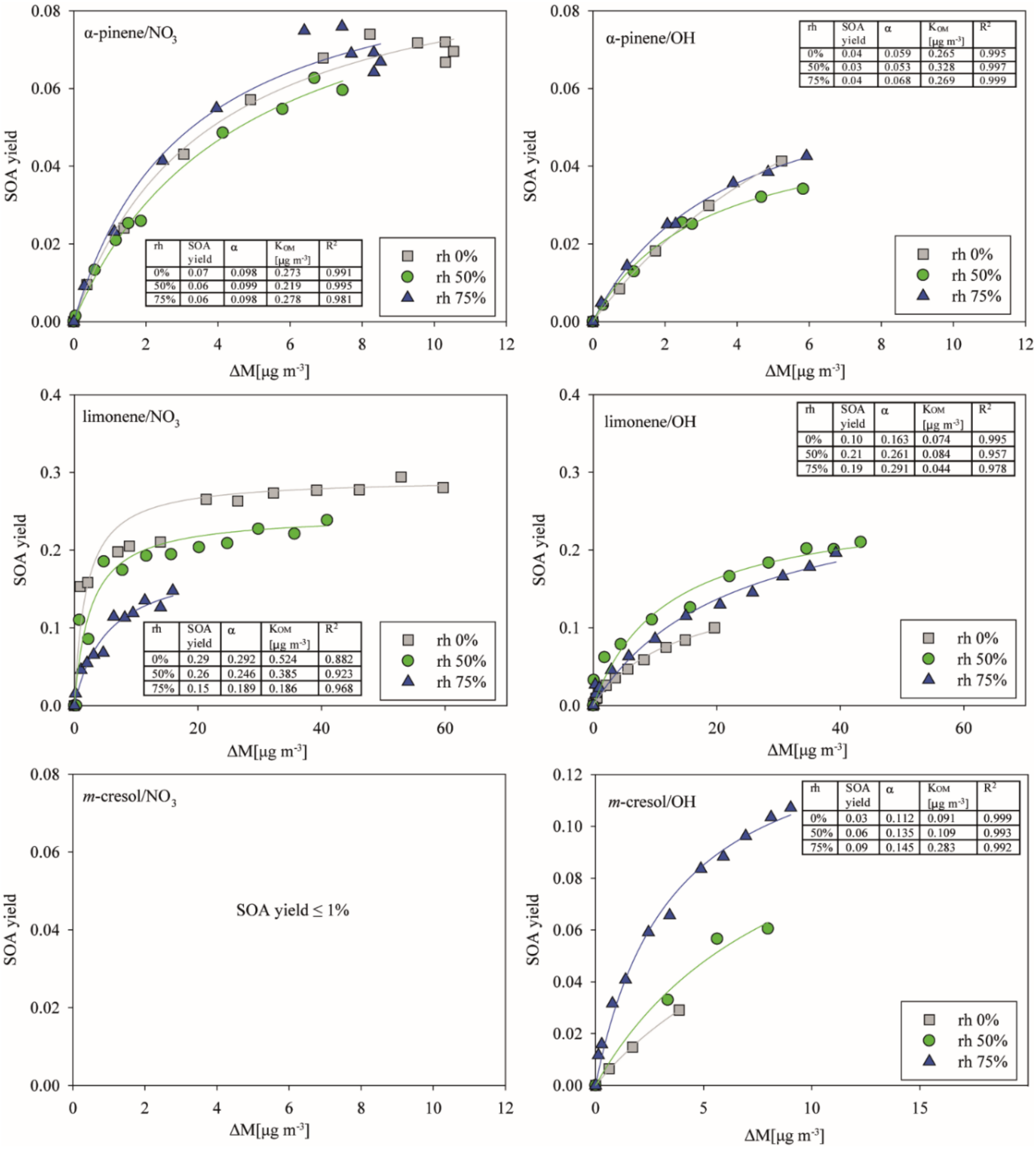

Figure 1. Yield curves for α-pinene, limonene and *m*-cresol with NO_3 and OH radicals for RH 0%, 50% and 75%. Yield curves were parametrised with the one-product approach (Odum et al., 1996). The obtained values for α (mass yield) and K_{OM} (partitioning coefficient) are included as well. Please note,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

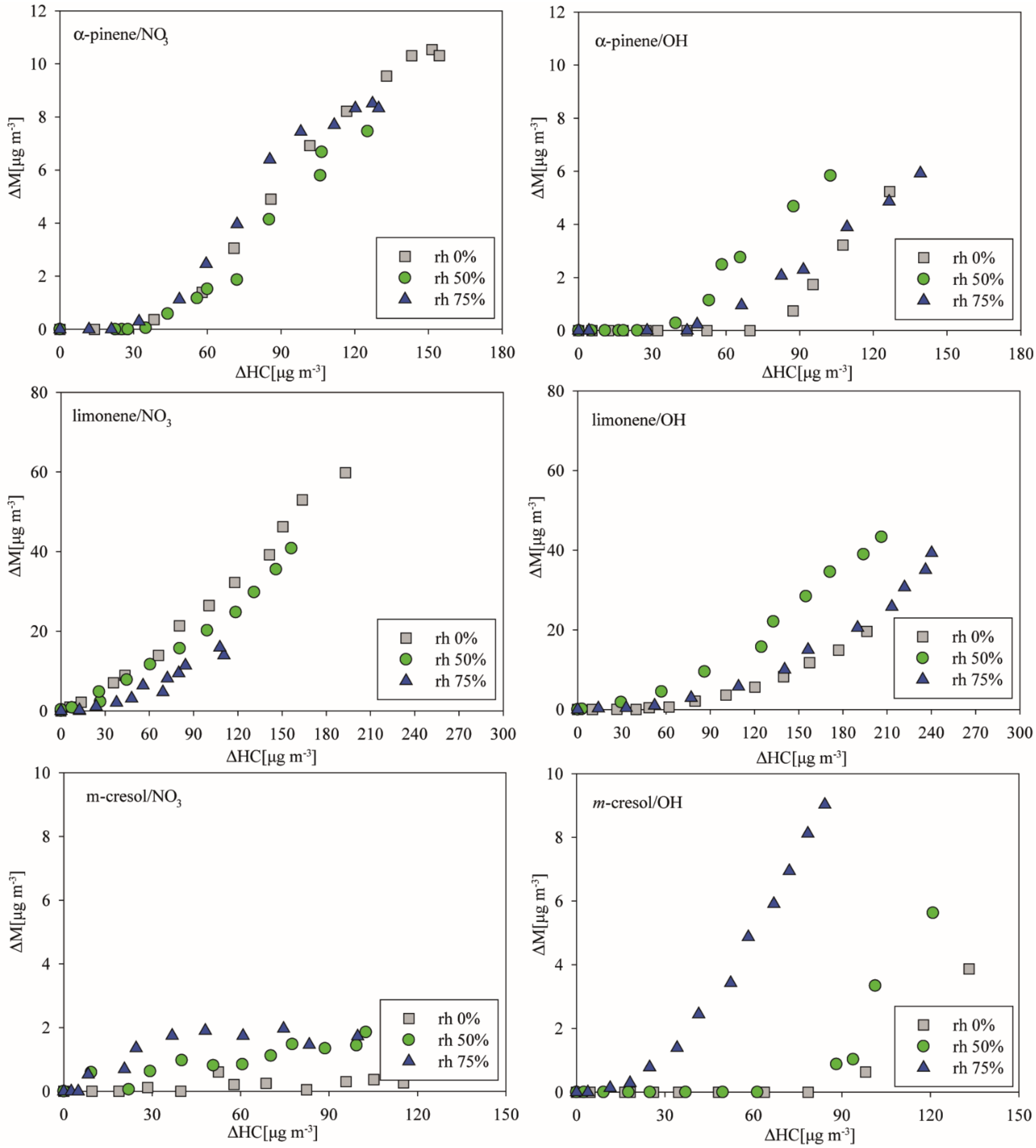

Figure 2. Growth curves for α-pinene, limonene and *m*-cresol with NO_3 and OH radicals for RH 0%, 50% and 75%.

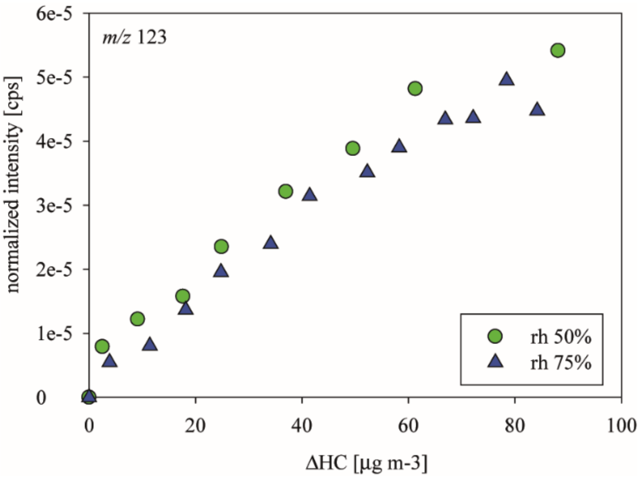

Figure 3. Evolution of *m/z* 123 as a function of consumption of *m*-cresol (ΔHC). The signal at m/z 123 can be attributed to methyl-1,4-benzoquinone.

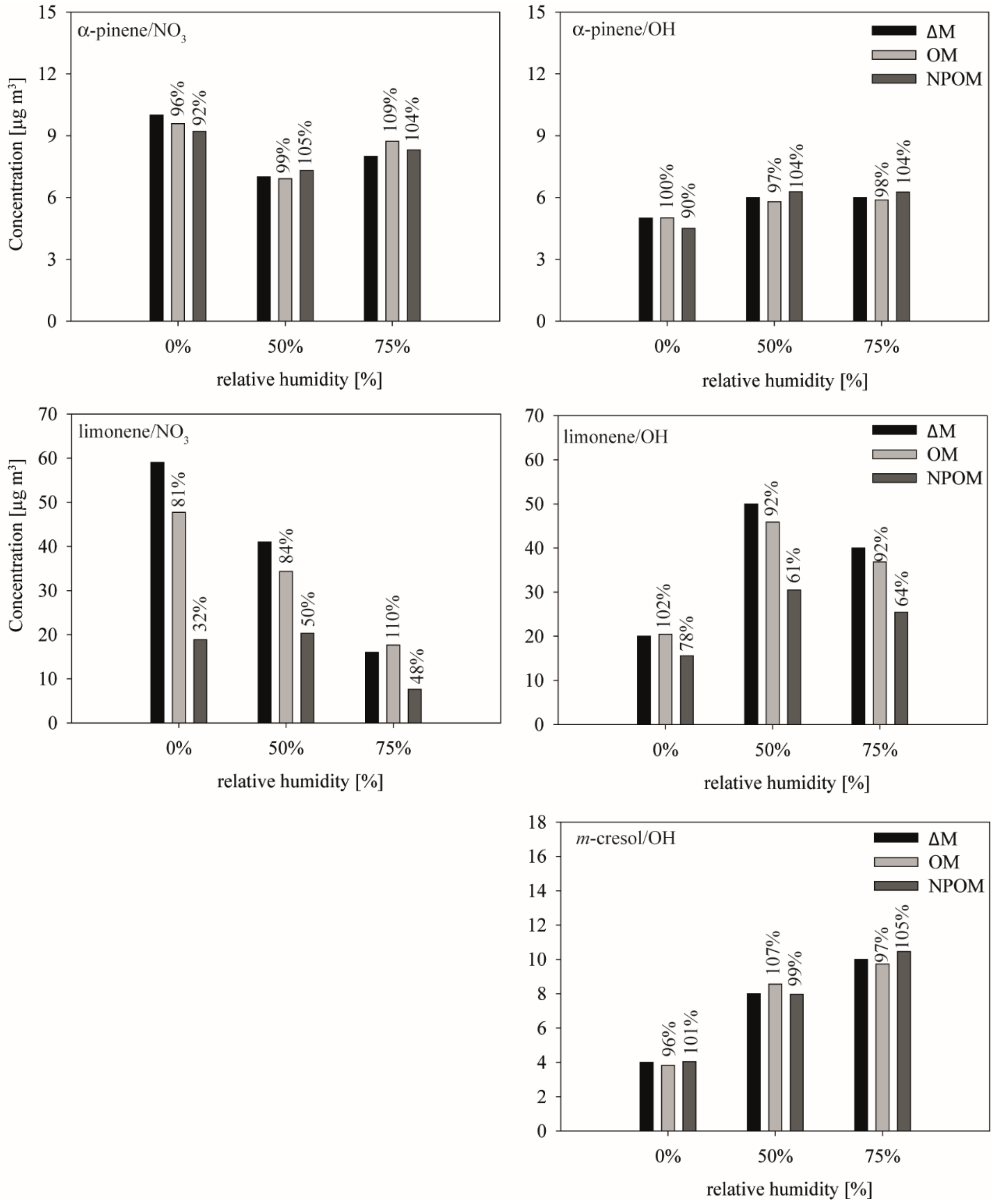

Figure 4. Comparison of organic mass calculated from SMPS with an offline determined concentration of organic material (OM) and non-purgeable organic material (NPOM). Measurement uncertainties are given as follows 10% for SMPS measurements (Wiedensohler et al., 2012), 5% for OC/EC measurements (Spindler et al., 2004) and 10% for WSOC measurements (Timonen et al., 2010). Please note, no values can be given for m-cresol/NO$_3$ as the produced organic mass was too small to be beyond the detection limits of the different techniques.

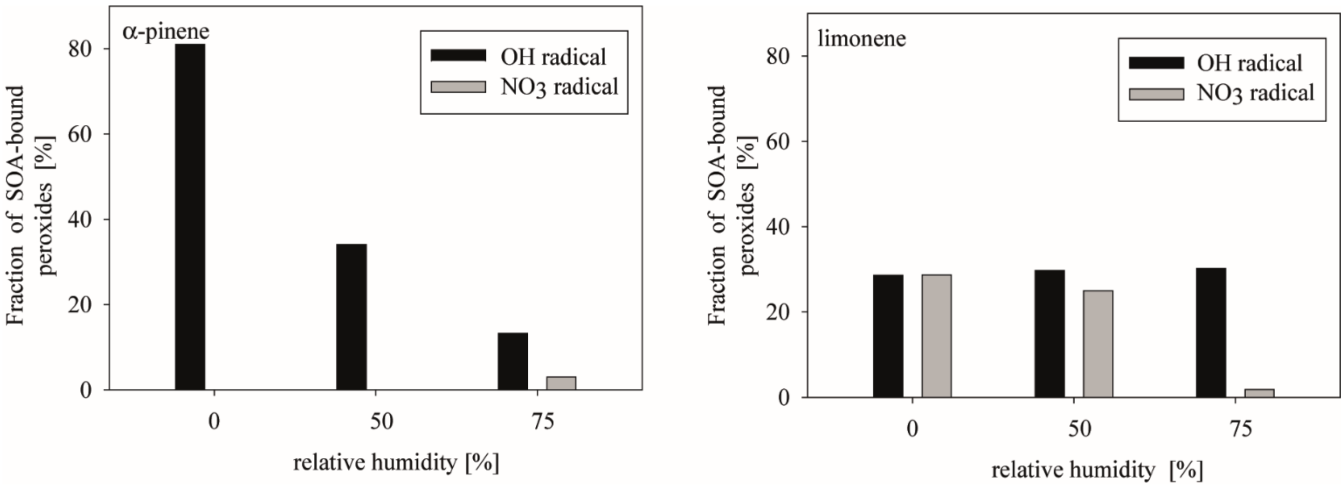

Figure 5. Fraction of SOA-bound peroxides from α-pinene (left) and limonene oxidation with OH radicals (black) and NO_3 radicals (grey). Quantification was done following the method described by Mutzel et al., 2013 assuming a molar mass of 300 g mol^{-1} (Docherty et al., 2005). Please note, according to Eq. 2-4 the peroxide fraction is highly sensitive towards the molar mass used for calculation.

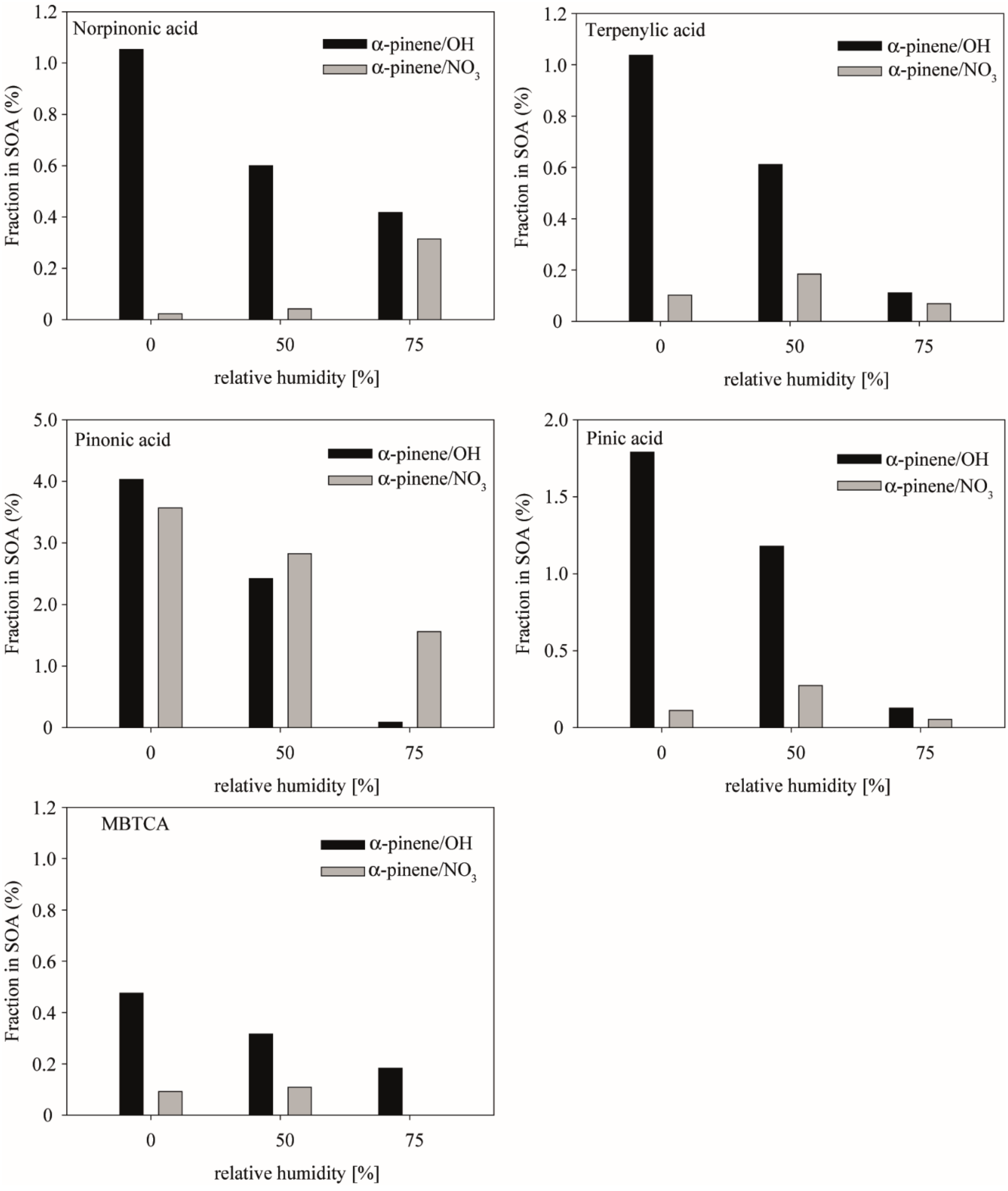

Figure 6. Fraction of α-pinene marker compounds norpinonic acid, terpenylic acid, pinonic acid, pinic acid and MBTCA for OH- radical reaction (black) and NO_3-radical reaction (grey). Please note, that fraction of marker compounds in formed SOA is illustrated.

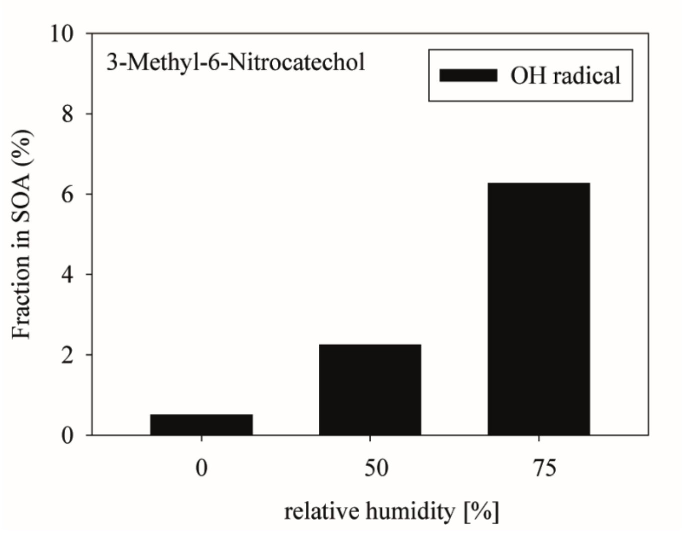

Figure 7. Fraction of 3-methyl-5-nitrocatechol from the oxidation of *m*-cresol with OH. Please note, other compounds from the ASOA standard (Hoffmann et al., 2007) were not identified and due to the low SOA yield from NO_3-radical reaction, the concentration might be below the detection limit.