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 (**Fehler! Verweisquelle konnte nicht gefunden werden.**). 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 **Fehler! Verweisquelle konnte nicht gefunden werden.**, 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 (**Fehler! Verweisquelle konnte nicht gefunden werden.**).*

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 (**Fehler! Verweisquelle konnte nicht gefunden werden.**).*