Reply to reviewer #1

We thank the reviewer #1 for the helpful comments. We addressed all points raised.

Reviewer comment:

1. The paper concluded with increasing NOX HOM-ACC strongly decreases and consequently suppress SOA formation. While the experiments and analysis appear robust and in agreement with some literature, it is important to point out that some other literature such as Pye et al., (2015) and Marais et al. (2016), with specific representation of particulate organic nitrate predict the reduction in NOx emissions causes a considerable reduction in organic aerosol. Could authors comment on this discrepancy? In this regard, in Figure 2 authors showed HOM spectra with and without NOX addition. It might be worthwhile to mention total SOA or HOM mass for these two cases for easier comparison.

Reply:

In our paper Safrazadeh et al. (2016) we showed that the effect of NO_X on SOA yields is complex. NO_X can affect SOA formation by influencing the OH concentration (a variation of OH scavenging as described in McFiggans et al. (2019)) and by changing the product composition. How the product composition and the product properties are changing with NO_X has general components, such as NO reacting fast with RO_2, and is specific for the compound (class) under consideration.

Marais et al. (2016) propose an improved mechanism for isoprene oxidation and applied it in a regional model study. They showed that increasing NO_X (NO) is leading to decreasing *isoprene* SOA: “Isoprene SOA concentrations increase as NOx emissions decrease (favoring the low-NOx pathway for isoprene oxidation).” Herein the low-NO_X pathway leads to the formation of IEPOX, which in turn enter the particulate phase by reactive uptake. The reactive uptake of IEPOX is specific to isoprene reaction systems, and we don’t really see what could be learned from that comparison for our study of monoterpenes.

The work of Pye et al. (2015) is also a regional model study considering the role of NO and NO_3 in organic nitrate (ON) formation. The results of regional model studies depend on parametrization of the precursor chemistry (which is in this case lumped), while we describe specific observations in our chamber. Pye et al. find a decrease of 9% in SOA when NO_X emissions are reduced by 25%. The NO_X level was roughly of the order of one 1 ppb, the effect of the NO_X reduction on the NO_X concentration was not specified. Pye et al. attributed the monoterpene-SOA decrease with decreasing NO_X mainly to a decreasing NO_3 contribution. Effects of NO_3 are outside our observations, and we added a statement in the Introduction section, underling that our study focus on NO_X in daytime photochemical systems and that NO_3 reactions also lead to ON, but are not treated here (p.2, line 16-20, in the revised manuscript).

Since Marais et al. as well as Pye et al. address aspects different than our study, it is very difficult to say if their model results are in contradiction to ours or not. So, detailed specific comparisons with Marais et al. or Pye et al. do not make much sense to us. However, the referee is correct that our laboratory results, which address mechanistic aspects of SOA formation in the presence of NO_X especially under consideration of HON-ON, should not be generalized too quickly and blindly transferred to the atmosphere, where more aerosol precursors and SOA formation processes prevail. In order to prevent misleading interpretations of our specific results we will add a sentence in the concluding section (p.23, line 26-31):

“Note, that we considered the photochemistry of NO_X to SOA contribution for two major MT, α-pinene and β-pinene. We find that that SOA yields are fairly independent of NO_X, but drop significantly at the highest NO_X levels. Model studies show that increase of NO_X emissions may also lead to more SOA, when NO_3 is the oxidant (e.g. Pye et al. 2015) or when isoprene is involved (Marais et al. 2016). In the latter case NO directs the gas phase mechanism toward isoprene products with reactive uptake, while for compounds like α-pinene and β-pinene, which were investigated here, condensation is more important for SOA formation and thus vapor pressures controls SOA yields.”

We did not modify Figure 2 as this illustrates how the effect of NO_X appears quite obvious in the mass spectra. Instead we modified Figure 3, which now shows mass concentrations of total HOM and of monomers and accretion products. These were derived from high resolution analysis of the mass spectra, as this allowed for a more detailed analysis. We replaced integration of mass spectra at UMR in certain ranges by analysis based on peak lists (Suppl. S6). We can thus resolve monomers and accretion products in the overlapping range. Identified peaks explain more than 90% of the observed signal. We also replaced mixing ratio by mass concentration as this allows for a better direct estimate how much mass monomers and accretion products potentially contribute to SOA. We limited the analysis to the mass range 230-550Da, which covers the compounds with sufficient functionalization to condense and form SOA. Therefore the numbers are somewhat lower compared to the original manuscript, but this did not affect any of the conclusions.
With new Figure 3 we also modified formulations in section 3.3 (p.12, line 26 – p.13, line12, in the revised manuscript).

2. Page 11, Line 2
a) The authors estimated a molar yield of ≈36% for the ON formed from β–pinene which is higher than the largest previously reported values (26 ±7% Rindelaub et al., (2016), while for similar condition of this study (acidic seed aerosol and RH ≈60%), they even estimated less (≈6%).
b) The authors mentioned at the Figure 9’s caption “The effect of hydrolysis of 80% of the organic bound nitrate has no substantial effect on the SOA mass.” However, Boyd et al. (2015) estimated particle phase hydrolysis of organic nitrates compose 45–74% of the organic aerosol. These discrepancies might be attributed to estimation of a slower aerosol hydrolysis in this study? and subsequently underestimation of importance of hydrolysis for explaining the SOA mass suppression with increasing NOX in the system?

Reply:
a) Our molar yield considers the sum of all organic nitrates formed from β-pinene in the gas-phase in absence of seed aerosol at RH = 60%. Our finding is commensurable with molar branching ratios of the reaction RO_2 + NO into RO and ON as implemented in MCMv3.1.1 for ß-pinene for the given conditions. Since we did not have seed aerosols in this experiment, the observed molar yield cannot be dependent on the pH of the seed aerosols. ON formation depends of course both on the VOC under investigation and on the VOC/NOX ratio. Therefore one cannot expect the same yields in different studies with different precursor starting conditions.

Rindlaub et al. (2015) investigated α-pinene and reported an apparent yield for ON of 26(±7)% by extrapolation to particle free conditions. Assuming that α-pinene and β-pinene have a similar ON/RO branching ratio in the reaction of RO_2 with NO/NO_2 this value is within the errors the same as our 36(±4)%. While Rindelaub et al. observed the integral ON by actively measuring the available ON by FTIR, we derive our value from the consumption of NO_2, more precisely from the excess of NO_2 in the absence of β-pinene at the same OH concentration. So, as long as the branching ON/RO does not much depend on RH, which is the case, we would observe by our method the same apparent ON yield at all RH, while Rindelaub et al. would miss the hydrolysed ON. It is not on us to judge Rindelaub's et al. work, but it was performed for another compound, α-pinene, at ppm initial concentrations and more than 100ppb of NO_X initially in the system. Moreover, there were several hundred to several thousand ug/m^3 particulate mass formed during their non-seeded experiments, so a substantial fraction of the ON, including semivolatile ON, must have resided in the particulate phase. In our interpretation of their Figure 4 they observed overall a yield of ON of 5-10% for a wide range of RH with strong excursions up to 23% in a narrow range around 15% RH. We reformulated a part of section 3.5 to include references proposed by the reviewer (p.17, line 8-13).

b) The intent of our study is clearly *not* to solve the question of hydrolysis of particulate ON. Our starting point of discussing HOM-ON hydrolysis is to find a rationale for the mismatch between observed $OrgNO_3$ (particulate organic bound nitrate) observed by AMS (up to 3%) and the $OrgNO_3$ which should be expected from the uptake/condensation of HOM, including HOM-ON, with more than 6 O (up to 10%). The mismatch indicated that more than 2/3 of the $OrgNO_3$ got somehow lost. Nevertheless, as shown in Figure 9, the role of hydrolysis for the impact of NO_X for SOA production is negligible. Since this has been proposed in the literature, we were merely wondering if hydrolysis of ON in the particulate phase may help to reconcile particulate phase observations and HOM-ON.

Our Figure 6 shows that vapor pressures of HOM do not depend much on the type of the termination group. It seems realistic to us that only HNO_3 will escape the particulate phase on hydrolysis of multi-functionalized HOM-ON, while the multi-functionalized organic moieties remain. Under this specific case/assumption we calculated the change of the expected mass as shown in Figure 9; it assumes in fact instantaneous, thus fast hydrolysis. The release of HNO_3 can explain the mismatch between gas phase $OrgNO_3$ that is expected to condense on particles and realized $OrgNO_3$ in the particulate phase. Figure 9 is supposed to show that this type of hydrolysis will not much affect the SOA mass thus our finding of a low dependence of SOA yield on NO_X, if *OH concentration is kept stable*. The somewhat lower yields at high NO_X in our case can be solely accounted for by less mass formation due to HOM by suppression of dimers with increasing NO_X. Overall, our interpretation is not in contradiction with field and model studies which detected that about 2/3 of the particulate ON hydrolyze and release HNO_3 from the particulate phase (Zare et al., 2019, Fisher et al., 2016). Like Takeuchi and Ng (2019), these studies leave the fate of the organic moieties open, but they are likely alcohols (Hu et al. 2011) and thus have the same or lower vapor pressures as the mother ON (Zare et al., 2019).

We are aware of and appreciate the study by Boyd et al. 2015. However here must be a misunderstanding. First of all, Boyd et al. investigated the oxidation of β-pinene by NO_3. Herein NO_3 is the primary oxidant forming nitrate groups directly by first attack on the double bond. This is different from our study where we oxidize the MT by OH and (HOM-)ON are formed by peroxy radicals terminating with NO and NO_2. Boyd et al. found 45-74% contribution of particulate ON of which 90% survived hydrolysis, due to a lower fraction of tertiary ON in NO_3 oxidation compared to photooxidation and termination by NO_X (our case).

Browne et al. (2013) suggested that photooxidation of α-pinene and termination by NO_X produces about 60% tertiary ON that easily hydrolyze, but they considered ON hydrolysis only for HNO_3 budget. The suggestion by Browne et al. would be perfectly in line with our interpretation, that about 2/3 of the $OrgNO_3$ is lost as HNO_3. Takeuchi and Ng (2019) stated in a recent paper that they cannot determine for sure the “fate of the organic moiety of the hydrolysis product (i.e., stay in the particle phase or repartition back to the gas phase)”. The hydrolysis was observed by Takeuchi and Ng for about the same relative humidity. The hydrolyzable fraction FH for α-pinene +OH + NO system was 32%, if one assumes no loss of the organic moiety. A hydrolyzed fraction of 32% is about half what we determined, but regarding our only rough estimates it is within the errors. The hydrolysis was fast and we are able to easily observe it within the residence time of 1h in our chamber. Taken all together the findings of the Boyd et al, Browne et al. (2013), and Takeuchi and Ng l. are supportive or at least not in contradiction to our findings. Furthermore, the experiment of Zhao et al. (2018) showed that expected $OrgNO_3$ and observed $OrgNO_3$ agree in a dry environment. These experiments were made in another context but with the same instruments and analysis methods. Together with most of the literature data this all is in favor of our interpretations. However, we would like to note that hydrolysis of ON and pON is not the focus of the paper and our data are not suited to solve inconclusive findings in the literature.

3) Page 18, Line 11-24 The authors discussed higher humidity in their chamber and hydrolysis as the key for less estimation of $OrgNO_3$ fraction in the particulate-phase than as determined by AMS and also finding (≈11%) by Zhao et al. (2018). It is important to point out not only Zhao et al. but also many recent measurements (e.g., Romer et al., 2016) and modeling studies (e.g., Pye et al., 2015; Fisher et al., 2016; Zare et al., 2019) estimated a higher fraction of organic nitrates in the particle phase (≈10%-20%). As they also considered a rather fast hydrolysis for organic nitrate aerosols it might be worthwhile to compare the result here to their results as well. However, it might be useful to mention Zare et al. show that at a more humid condition (similar to this study with higher RH) heterogeneous uptake to particle water tends to form less particulate organic nitrates against uptake to dry organic aerosols. Considering the impact of humidity at the aerosol formation together with the impact on the loss process of hydrolysis for particulate organic nitrates could help reconcile the discrepancy?

Reply:

We think here is a misunderstanding. As was shown in Figure 8 (blue and orange circles) the molar fraction of particulate ON expected from HOM condensation ranges up to 40% for both MT with increasing NO_X. In the new Figure 4 we show now that the mass fraction of HOM-ON mounted up to 50%. From this point of view we are cum granis sale in agreement with the other lab, field and model studies which find similar fractions of particulate ON from MT. The diagnostic link between HOM-ON and particulate phase analysis by AMS was organic bound nitrate ($OrgNO_3$), a terminus used by the AMS community. We discuss $OrgNO_3$, i.e. the mass fraction of $–NO_3$ groups attached to ON. In Figure 8 we showed the $OrgNO_3$ mass fraction expected from condensable HOM-ON and compare it with the $OrgNO_3$ fraction observed by AMS. We tried to clarify the difference between $OrgNO_3$ and particulate ON throughout the manuscript, e.g. we added a note to section 2.3 (p.8, line 16-17, in the revised

manuscript), reformulated large parts of section 4.1. (p.18, line 2-15, in the revised manuscript) and (p.18, line 22-23, in the revised manuscript).
We attributed the discrepancy between $OrgNO_3$ in the gas-phase HOM and in the particle phase to plausible hydrolysis of ON in the particulate phase (as discussed in the previous reply). Since we are missing organic bound NO_3 in the system and *not* SOA mass, we assumed that only HNO_3 is released to the gas-phase. As shown in Figure 9 this effect is small, because $OrgNO_3$ contributed only about 20% to HOM-ON mass and HOM-ON contributes a few times 10% percent to SOA mass.
The HOM-ON hydrolysis in the particulate phase must occur on times scales of less than one hour at 60%RH. The time scale is in accordance with the findings of Romer et al. (2016), however they linked ON hydrolysis to isoprene oxidation, which we don't have. We choose Zhao et al. as an example for expected $OrgNO_3$ and observed $OrgNO_3$ being in agreement in a dry environment, because they used the same instruments and analysis methods.
We determined effective uptake rates for HOM-ON and the $OrgNO_3$ content in the particulate phase at only one relative humidity. We did not determine effective uptake rates for HOM ON at different humidity and therefore our data do not allow statements on the effects of humidity on particle formation by condensation of HOM.
Although hydrolysis of ON is very interesting and the most plausible explanation for the loss of $OrgNO_3$, it is not a central point of out studies and we prefer to refrain from further discussion in the manuscript.

We modified Figure 4 substantially in order to show the mass fraction of HOM-ON.

We added the references (see below) for discussion here to manuscript.

Minor comments
We are sorry for that many mistakes and typos. We thank the reviewer for the careful reading of the manuscript and for the corrections. We went through the manuscript in order to improve language and grammar.

Page 3, for less confusion and similar to the other relevant papers, it is better to give a same reaction number for reactions with similar reactants, e.g. (R4) and (R4a) should be "(R4a)" and "(R4b)", and also for R5 and R7 should change as "(R5a)" and "(R5b)".
done

Page 6, Line 1-4, multiplication sign for reaction rates are missed.
dots replaced by x

Page 6, Line 2, References should be lined up in the proper sequence.
done

Page 13, Line 13, remove spare space before parentheses.
done

Page 15, Line 1-4, remove redundant parentheses.
We could not find redundant parenthesis. The parenthesis being there were set by purpose to indicate a side remark.
No action.

Page 15, Line 21, remove extra “was”
done

Page 15, line 24, “estimated to be”
done

Page 32, Figure1, for better readability write axis label on the right-hand side from
done, for consistency also applied to Figure 7

Page 37, Line4, the brown bars look like more “orangeish” than brown in my eyes.
color tuned to brown

Page 40, Line 5-6 used different font.
corrected

References

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