

# ***Interactive comment on “Monoterpene chemical speciation in the Amazon tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO)” by Ana María Yañez-Serrano et al.***

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1- Comments from reviewers 2- Author's response 3- Change in the text

Reviewer #1 (Remarks to the Author):

General: The paper presents in-canopy, speciated BVOC measurements by GC-FID over a period of three days. These are compared PTR measurements and to longer time series of GC measurements in different seasons at the same site. The data is analyzed and discussed in terms of emission height, diurnal cycle, reactivity, and

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seasonality in comparison to the longer data series in different seasons. Observations are compared to a canopy model which contained detailed chemistry for some species and rudimentary chemistry for new others. The purpose of the comparison is to demonstrate speciated measurements are a good test if the overall key features and processes are captured by the model. The manuscript presents interesting data and data analysis. The text is well structured. The manuscript could be published in ACP after considering the following major and minor comments.

1- My major concern relates to the discussion of the role of deposition on wet leaf surfaces. From the presented material I do not see proof - from the model comparison that deposition on wet leaves is a significant process. This may be in parts owed to the fact that description and interpretation are not detailed enough. The authors may address the following questions and issues.

2- We understand the concern of the reviewer. We use a canopy exchange model which has been previously extensively evaluated for different ecosystems including tropical rainforest. We have further stressed this feature of model evaluation and have included some further references for more detailed information about some of the canopy model features relevant to the presented subject of BVOC exchange, e.g., estimating canopy wetness as a function of RH. We are not claiming that deposition to leaf wet surfaces is a significant process. One would actually indeed expect this sink to be of minor relevance for the terpenes included in this study given their low solubility's. However, the inferred wet vegetation uptake resistance following the widely-used Wesely (1989) approach of  $\sim 300 \text{ s m}^{-1}$  results in simulation of an apparent not ignorable sink also given the large area of potential wet surface. Using this inferred uptake rate we achieved a relative good agreement between model simulated and observed monoterpene mixing ratios, not only in magnitude (which is no surprise given the fact that the constant basal emission factor has been selected to reproduce the campaign average mixing ratios) but especially regarding the diurnal dynamics. The results point to a combined effect of the potential role of chemistry and deposition as monoterpene

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sinks pointing to the necessity to explore further this deposition to wet surface process.

1- (I think a paragraph should be started in line 406 where the leaf wetness is discussed.)

2- We have separated a paragraph for sink processes.

1. Did you observe the leaf surface wetness in the two nights? If yes, was it the same or was it different?

2- Unfortunately we did not have measurements of leaf surface wetness available for the site, and therefore we used relative humidity as a proxy for the calculation of leaf surface wetness. MLC-CHEM uses relative humidity as a proxy for the fraction of the wet leaf surface (Lammel, 1999). This results in smaller estimates of canopy wetness on 17 October 2015 compared to the following days. In the revised version, we now discuss that these estimates of canopy wetness cannot be corroborated without measured canopy wetness.

1. You suggest that the model has a strong missing sink in the night from the 17. to the 18. Is this the only possible explanation for the strongly overpredicted  $\alpha$ -pinene mixing ratio? Or could be there more reasons for the model showing so high  $\alpha$ -pinene in the night from the 17. to the 18.? Only if the source and the chemical sink of  $\alpha$ -pinene are about the same in the two nights then the depositions sink must have been also similar as the mixing ratios are about the same. Were source and chemical sink the same in both nights?

2. In response to this comment we modified the discussion about the comparison of the simulated and observed temporal variability in monoterpene mixing ratios and the role of canopy wetness. Rather than stressing these contrasts between the night of 17-18 October and the other nights we now contrast more generally the 17th and the other three days. This approach was chosen due to missing meteorological observations for the 18th. There is a significant change in the modeled canopy wetness conditions

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around midnight due to using a prescribed typical diurnal cycle in some meteorological parameters instead of the actual observations for the 17th. It provides though an interesting sensitivity analysis since as soon as the imposed canopy wetness increases to a value of 1,  $\alpha$ -pinene drops to much lower values. This strong dependence of the simulated temporal variability on changes in canopy wetness conditions is confirmed by an analysis of the process tendencies in the model which show that the emissions do not significantly change comparing the 17th with the other 3 days of the campaign. The contribution by chemical oxidation also shows some temporal variability due to differences in O<sub>3</sub>, OH and NO<sub>3</sub> but this sink is relatively small compared to the dominant sink of  $\alpha$ -pinene, canopy deposition. There the changes in canopy wetness contrasting the 17th with the other 3 days explains to a large extent the simulated temporal variability in mixing ratios of  $\alpha$ -pinene and the other terpenes and which generally agrees quite well with the observed temporal variability.

1- How can deposition on wet leaves affect so strongly the mixing ratio of non-water soluble compounds like  $\alpha$ -pinene?

2- What we present here, relies on application of inferred uptake efficiencies for these monoterpenes not only commonly being used in any model study following the Wesley (1989) approach to consider dry deposition but also recently being applied in a detailed study on Boreal forest canopy exchange of BVOCs (Zhou et al., 2017). The inferred monoterpene wet-surface uptake resistances on the order of 300 s m<sup>-1</sup>, based on Henry law's constants on the order of  $\sim 1\text{-}3\text{e-}2$  M atm<sup>-1</sup>, suggest a potentially still quite efficient uptake by leaf wetness. Note that this seems to be similar to the observed removal of ozone by wet canopies where, despite its low solubility, there is actual experimental evidence that canopy wetness enhances O<sub>3</sub> deposition potentially due to aqueous-phase chemical interactions. Clearly, this feature on leaf wetness in monoterpene removal has to be corroborated by further experimental evidence.

3- I understand there was no RH data for the 18. How could the model derive a reliable surface wetness then?

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2- See also our response to the previous points about missing canopy wetness observations and the impact of the imposed meteorological data for the 18th of October.

1- Why do the different MT respond so differently to the ill predicted surface wetness on 17.: a-pinene and b-pinene too high, limonene ok, myrcene in between, and terpinolene too low. Insofar I think the statement in line 527 is not justified by the presented material and analysis.

2- In the revised version we have excluded the respective statement.

Major comments:

1- line 514-518: I do not understand what the authors are discussing here. I cannot understand how a “potential” aerosol growth could have a dimension of molecules per cm<sup>3</sup> and an order of 10<sup>-5</sup> -10<sup>-6</sup>. Moreover, I did not find such notations in Bonn et al. 2014. This part must be clarified or deleted.

2- Our aim was to discuss the effects of mono- and sesquiterpenes as classified in the Amazon on particle formation rates i.e. not aerosol growth rates. Admiringly, the reviewer is correct as the wrong wording was used. The units provided are wrong as the unit needs to be “cm<sup>-3</sup> s<sup>-1</sup>”. These have been corrected in the revision. A particle growth would focus on size change per time i.e. nm h<sup>-1</sup> for a certain initial size but not change concentrations per time as provided. In general, we used the word “potential” as no direct measurements of particle growth or of particle size distribution were available and calculations are based on the transfer of results from elsewhere to Brazil. With respect to the aerosol formation and growth rate, it has been shown (for example by Wolf et al. (2009; 2011) and by Hummel (2010) and included in Bonn et al. (2014)) that the initial growth of (smaller) particles is determined by organic peroxy radicals as one of two processes. Those processes are (a) the reactive interaction of large organic peroxy radicals (RO<sub>2</sub>) from e.g. mono- and sesquiterpene reactions with OH or NO<sub>3</sub> and (b) in case sufficient organic mass has been acquired already uptake by partitioning of oxidized VOCs with a reduced volatility. Both processes can be simulated and

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large organic RO<sub>2</sub> concentrations approximated assuming steady-state conditions for radicals which is a common assumption. For clarification the text has been changed to:

3- L388 (please refer to supplement for correct location of line number): “Following the equation established by Bonn et al. (2014) (Equation number 5 in text), we were able to estimate the potential aerosol particle number formation rate initiated by monoterpene species only ( $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  cm<sup>-3</sup> s<sup>-1</sup> at 24 m) assuming steady state conditions for radicals. Those were found to be approximately two orders of magnitude smaller than the calculated potential new aerosol particle formation rate caused by oxidation products of sesquiterpenes. Our calculations assume mixing ratios of sesquiterpenes of 0.2 ppb revealing potential formation rates of  $1 \times 10^{-3}$  and  $4.5 \times 10^{-3}$  cm<sup>-3</sup> s<sup>-1</sup> at 24 m) based on previous measurements in the Amazon (Jardine et al., 2011) which are remarkably smaller than observed at mid-latitude conditions (Bonn et al., 2014).”

1- line 519f: This a strong statement. Do you have proof for that or a reference? Moreover, potential aerosol growth and formation rate are not the same. Indeed NO suppresses nucleation (Wildt et al. ACP, 2014) but not so much the yield (Sarrafzadeh et al. ACP, 2016)

2- We kindly refer the reviewer to Sarrafzadeh et al. (2006) and the respective Figure 1 that illustrates how SOA yield depends on the BVOC/NO<sub>x</sub> ratio (see attached figure 1). For Amazonian conditions (in contrast to smog chamber measurement conditions) the typical BVOC mixing ratios are smaller than 3 ppb and most of the time around 1 ppb. If we apply Fig. 1 of Sarrafzadeh et al. (2016), the situation is located on the very left of the plot. Increasing NO<sub>x</sub> at constant BVOC mixing ratio will decrease the BVOC/NO<sub>x</sub> ratio and lead to a decline in SOA yield. The unaffected region of the same figure is not applicable for the Amazon region because of present concentrations. This is in line with the findings of Wildt et al. (2014) for smaller particles indicating similar processes responsible for the growth. For clarification we provide with a more detailed explanation as below:

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3- L396: “Furthermore, the level of present NO (nitric oxide) also affects the potential aerosol growth (Wildt et al., 2014) and yield (Sarrafzadeh et al., 2016) at low BVOC/NO<sub>x</sub> ratios. As the theory assumes contributions of larger organic peroxy radicals (RO<sub>2</sub>), which are destroyed by reactions e.g. with NO, increasing NO<sub>x</sub> at constant BVOC mixing ratio will decrease the BVOC/NO<sub>x</sub> ratio and lead to a decline in SOA yield. Our calculations showed this effect, with a change of NO from 0.2 ppbv to 1 ppbv leading to a decrease in the formation rate at a diameter of 3 nm. This interdependence calls for a consistent consideration of the BVOC and NO<sub>x</sub> exchange in aerosol formation and growth studies.”

Minor comments:

1- Starting with line 219 the authors give errors/uncertainty ranges/standard deviations in form of “+/-yx” at many instances (including Table 1) without explaining the specific meaning.

2- We have added averages +/- standard deviation where corresponded in the text.

1- line 156: “142 Td”, Td is not explained

2- This is now explained in the text.

1- line 186f: The formulation “selected” suggests to me that the initial EA and the fractional EA for individual compounds were used as adaptable parameters. Is this case? If so, then the overall good agreement between modelled and observed concentrations in section 3.5 (line 398f) and Figure 6 is not surprising. If not, explain the in more detail the rationale for these selections.

2- The emission factors from the selected monoterpenes were indeed adaptable parameters. We used selected constant basal emissions for terpenes for the plant ecosystem class, in this case tropical rainforest. We used initially basal emission factor for monoterpenes for tropical rainforest of 0.4 ug C g<sup>-1</sup> hr<sup>-1</sup> (Guenther et al., 1995). Then we partitioned this emission flux over the different monoterpene species to see

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how well the model would reproduce the observed mixing ratios. Following, we adjusted the value for each species until the observed 4-day average mixing ratios were reasonably well reproduced. Given the daily changes in the processes potentially involved in explaining the observed temporal variability, the presented analysis gives you information about the role of the different processes, as these have different dominating effects at different times of the day and depend, at the same time, on many other drivers. In the text we have chosen to show the basal emissions in  $\text{mg C g}^{-1} \text{ h}^{-1}$ , rather than emission factor constant, and we have modified the text as follows in order to better explain this issue.

3- L179: “The monoterpene basal leaf-scale emission factors have been selected as such that the model simulates monoterpene mixing ratios of comparable magnitude compared to the campaign average observed mixing ratios. In the evaluation of simulated and observed mixing ratios we mainly focus on the comparison between the simulated and observed temporal variability being determined by the differences in canopy processes for contrasting nocturnal and daytime conditions. For the model simulation, the basal emission factors were  $0.18 \mu\text{g C g}^{-1} \text{ h}^{-1}$  for  $\alpha$ -pinene,  $0.04 \mu\text{g C g}^{-1} \text{ h}^{-1}$  for  $\beta$ -pinene,  $0.11 \mu\text{g C g}^{-1} \text{ h}^{-1}$  for  $\alpha$ -terpinene,  $0.9 \mu\text{g C g}^{-1} \text{ h}^{-1}$  for limonene and  $0.18 \mu\text{g C g}^{-1} \text{ h}^{-1}$  for myrcene. Note the selected relative high basal emission flux for limonene is required to reach simulated mixing ratios comparable to the observed ones.”

1- line 386f: Similar is true for the formulation about the “assumed” leaf area index and leaf area density. What is the rationale for these choices? Did you estimate it from observations on the site?

2- LAI was previously measured at the site, and we have included this reference in the methodology.

1- line 256, first §: These percentages are averages over day and night hours and three measurement days? They should have standard deviations.

2- We agree with the reviewer and have added the standard deviations of the percent-

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ages both in the graph and text.

1- line 286, first §: I suggest to define what you mean by reactivity. e.g. OH reactivity =  $k_{OH} \cdot [MT]$ .

2- We have added this clarification in the text.

1- line 303, Table 2: The header of the third column is misleading. It should read “normalized reactivity for 1 ppb [s<sup>-1</sup>]”, or so. Otherwise confusion with the use of reactivity later in the text.

2- We have modified this in Table 2 accordingly.

1- line 489: Is Hallquist 2009 (a review) a good reference for this statement?

2- We agree this is not the most appropriate reference and we have excluded it.

1- line 542f: That is not new and with the given formulation the conclusion in its generality does not make sense. The authors did not show that there is no suited representation of MT, which considers also their reactivity. Moreover, the degree of tolerable simplification depends also on the purpose of the model calculation.

2- We have reformulated the sentence, and we believe the point of the sentence was not well stated before.

1- L502 “Furthermore, reactivity calculations demonstrated that higher abundance of MT does not automatically imply higher reactivity as the most abundant compounds may not be the most atmospheric chemically relevant compound or the relative contribution of different monoterpenes may change. Our calculations support the view to that the role of canopy exchange may be erroneously estimated when not taking into account speciation based reactivity in models. Moreover, simulations with a canopy exchange modelling system to assess the role of canopy interactions compared relatively well with the observed temporal variability in speciated monoterpenes, but also indicate the necessity of more experiments to enhance our understanding of in-canopy

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sinks of these monoterpenes.”

Reviewer #2 (Remarks to the Author):

General comments:

1- The manuscript “Monoterpene chemical speciation in the Amazon tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO)” is a suitable and in the scope of “Atmosphere Chemistry and Physics”, shading light on the importance of monoterpene characterisation. Although, the manuscript is interesting it requires a major revision as it lacks the clear structure. The reader is often forced to go forward and back. Many discussions are found in Results (e.g. L230-232, L241-242, L267-270, L276-278, L280-281 etc.). Many statements are started with not suitable paragraph context (e.g. L306: “The most abundant species are  $\alpha$ -pinene, limonene and myrcene”). Some statements and discussion are out of context or even incorrect as mentioned in the Specific comments below. It is also too long for the scientific content. I suggest the following: Restructure the text in order to join Results and Discussion into one section with adequate subsections, redo the figures as suggested below and delete the repetitions in the text. Please also find specific and technical comments.

2- We thank the reviewer for the fruitful feedback. As suggested, we have now merged the results and discussion sections, removed repetitive sentences and redid the figures.

Specific comments:

1- L60-63. Not entirely true. PTR-MS could have a time resolution  $<1$ s (not 30 s). It is also recently coupled with FastGC to characterise monoterpenes in  $<2$ min. 1h GC/FID is a bit too much for “current” method. Please update the references for all this.

2- We agree with the reviewer and therefore we have removed that part from the text.

1- L103 and 125 – Not indicated sampling frequency, 30 min mentioned in L125, is not in agreement with the resolution presented in the Figure 1b and c. A detailed but

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structured description of the methods used is needed.

2- The sampling frequency was every hour for 30 minutes. We agree with the reviewers this is not clear in the text and we have modified this paragraph for better explanation.

3- L111 “The samples were collected from 17 to 20 October 2015 at an hourly frequency. Samples were collected for 30 min every hour at a flow of 200 cm<sup>3</sup> min<sup>-1</sup> (STP), leading to a collection of 6 L of air in each cartridge.”

1- L106 – Air sampling section needs structure improvement. You first open with your sampler giving the reference, then you describe your sampling dates/times and then you come back to the sampler, and again back to the sampling procedure.

2- We thank the reviewer for this comment, as it is true that section needed improvements. Therefore, we have restructured this section following:

3- L97: “Collection of ambient air samples on adsorbent tubes, for subsequent analysis by Gas Chromatography – Flame Ionization Detector (GC-FID), was made with two automated cartridge samplers described earlier (Kesselmeier et al., 2002; Kuhn et al., 2002, 2005) positioned at 12 and 24 m on the INSTANT tower. The samplers consist of two main units, a cartridge magazine that holds the adsorbent-filled tubes and the control unit timing the process and recording the data. This latter unit also houses the pumps (Type N86KT, KNF Neuberger, Freiburg, Germany), pressure gauges, mass flow controllers and power supply. The cartridge magazine is equipped with solenoid valves controlling the inlet and outlet of up to 20 individual sampling adsorbent tubes. The system is a constant-flow device, with one cartridge position per loop used as a bypass for purging the system. Due to the compact weatherproof housings and the low power consumption, we were able to position one sampler at 24 m and the other one at 12 m, attached to the INSTANT tower booms with commercially available 50 mm aluminium clamps. The adsorbent tubes used for VOC sampling were filled with 130 mg of Carbograph 1 (90 m<sup>2</sup> g<sup>-1</sup>) followed by 130 mg of Carbograph 5 (560 m<sup>2</sup> g<sup>-1</sup>) sorbents. The size of the Carbograph particles was in the range of 20–40 mesh.

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Carbographs 1 and 5 were provided by L.A.R.A s.r.l. (Rome, Italy) (Kesselmeier et al., 2002). The samples were collected from 17 to 20 October 2015. Samples were taken for 30 min every hour at a flow of 200 cm<sup>3</sup> min<sup>-1</sup> (STP), leading to a collection of 6 L of air in each cartridge using the automatic sampler. Additional sampling was performed at 24 m with a GSA SG-10-2 personal sampler pump during the years 2012-2014. These earlier samples were collected in the same type of adsorbent tubes as for the automatic sampler, and were filled at 167 cm<sup>3</sup> min<sup>-1</sup> (STP) air flow for 20 min. These additional measurements took place on 19 and 28 November 2012; 1, 3 and 4 March 2013; 11 to 14 June 2013; 22, 25 and 26 September 2013 and on 17 and 21 August 2014.”

1- L224 – In Table 1 it is not clear what the tolerance is.

2- We have added this information to the table legend.

1- L128 – The “Instrument for chemical analysis”. Are you intent to describe the instruments or the methods used?

2- We intent to describe the methods used, therefore we have changed the name of this section to “Instruments used for chemical analysis”.

1- L137 – What is “rapidly” in this context?

2- We wanted to say that the temperature increased at a high rate. We have removed this term from the text.

1- L160 – Why just 12 and 24 if all the data are available?

2- We only wanted to use 12 and 24m data of the PTR-MS as these were the only heights were GC-FID sampling took place in parallel.

1- L164 – “ $2\sigma$  of the background” –  $3\sigma$  it is more acceptable. Also briefly describe the blanks in each sampling systems.

2- We have modified the LOD to  $3\sigma$ . A more detailed explanation of the blanks has

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been added as following:

3- L148: “Hourly background measurements with a catalytic converter (Supelco, Inc. with platinum pellets heated to  $>400^{\circ}\text{C}$ ) and weekly humidity dependent calibrations of the PTR-MS were performed” L153: “The compounds measured were monoterpenes (m/z 137) and isoprene (m/z 69). The limit of detection (LOD) of the PTR-MS for total monoterpenes was 0.1 ppb and 0.2 ppb for isoprene, determined as  $3\sigma$  of the background noise.”

1- L239 - Isoprene! Not mentions in material and methods. How is this measured?

2- We understand we missed this part in the materials and methods. Isoprene was measured by the PTR-MS and by GC-FID. We have added this to the text.

1- L253 – Figure not clear. E.g. isoprene 24m not visible after 12:00. Legend not descriptive, not explained what are the error bars. Some error bars below zero and yet, above LOD? Explain?

2- This figure has been modified (see attached figure 2) Now isoprene mixing ratios as measured by the GC-FID can be better seen. Furthermore, and particularly for the low mixing ratio compounds, it is possible that the measurement is 0, as it can be seen for  $\alpha$ -terpinene, but it is not always 0. The data expressed here is an hourly average over three days and samples were collected every hour for 3 days, so having this in mind, standard deviations may be high. On the other hand, LOD for the GC-FID system is around 0.2 ppt, and this is generally way below than measured mixing ratios of the monoterpene species.

3- L737: “Figure 2: Average diel cycles for  $\alpha$ -pinene (a), limonene (b), myrcene (c), -cymene (d),  $\beta$ -pinene (e) and  $\alpha$ -terpinene (f) mixing ratios for 24 m (dashed line) and 12 m (thick line). In the back, average diel cycle of isoprene mixing ratios as measured by the GC-FID are shown for 24 m (light green) and 24 m (dark green). Error bars represent the standard deviation of the averages.”

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1- L345– “..in previous campaigns.. earlier samples were collected using a GSA SG10-2 personal pump sampler. Adsorbent tubes were filled at 167 cm<sup>3</sup> min<sup>-1</sup> (STP) air flow for 20 min”. This is again an example of poor structure. This need to be in the Material and Methods section.

2- We agree with the reviewer this explanation was not well structured. We have put this information in the methods paper and have removed this from the results.

3- L113: “Furthermore, additional sampling was performed at 24 m with a GSA SG-10-2 personal sampler pump during the years 2012-2014. These earlier samples were collected in the same type of adsorbent tubes as for the automatic sampler, and were filled at 167 cm<sup>3</sup> min<sup>-1</sup> (STP) air flow for 20 min. These additional measurements took place on 19 and 28 November 2012; 1, 3 and 4 March 2013; 11 to 14 June 2013; 22, 25 and 26 September 2013 and on 17 and 21 August 2014.”

1- L380 - How the above-canopy O<sub>3</sub> concentrations used in the model and for the reactivity calculation represent real situation in the canopy (between 12 and 24m)?

2- We have used measured ozone mixing ratios at 12 and 24m for our calculations and not the above canopy ozone mixing ratios. We have removed this part from the results as it was already specified in the methodology and we clarified that the ozone mixing ratio levels used for reactivity calculations were at 12 and 24m. The revised text reads as:

3- L191: “The simulations with MLC-CHEM were constrained with the observed surface layer net radiation (above the canopy only), wind speed, relative humidity and O<sub>3</sub> mixing ratios as well as the temperature measured above and inside the canopy (8 different heights including 12 and 24m) from 17 to 20 October 2015, coinciding with the measurement dates.” L310: “For ozone reactivity calculations, 12 ppb was used, as this mixing ratio was observed during the measurement period. NO<sub>3</sub> mixing ratios were taken from the MLC-CHEM model simulations that predicted mixing ratios of ~0.4 ppt.”

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1- L439 and on – “The emission of monoterpenes has generally been thought to be from storage glands in specialized structures like resin ducts, glandular trichomes or related structures (Schürmann et al., 1993; Steinbrecher, 1989).” This generalization and discussion based further in the text are related only to conifer type or monoterpene emitters (see also in your references). Thus, this is irrelevant (and incomparable) for the tropical forest as the physiology (and chemotypes) for monoterpene emission in broadleaf tree species is different to the pool emitters.

2- We agree with the reviewer that this is an unspecific generalization and we have revised the text accordingly:

3- L260: “In contrast to plant species of cooler climates, such as spruce, which emit terpenes from pools (Ghirardo et al., 2010; Lerdau et al., 1997), Amazonian plant species have been found to show an emission dependency on light and temperature (Bracho-Nunez et al., 2013; Jardine et al., 2015; Kuhn et al., 2002, 2004). This could partly explain the diurnal pattern of  $\alpha$ -pinene mixing ratios, which exhibit some relation to a light and temperature dependent emission flux (Kuhn et al., 2002; Rinne et al., 2002; Williams et al., 2007). However, this behaviour is not observed for all monoterpene species. Therefore, the observed diurnal cycles of some monoterpene species might be related to a stronger temperature response. While monoterpenes are stored in leaves and their release from these pools is governed by leaf temperature (Monson et al., 1995), Amazonian plant species have been found to show an emission dependency on light and temperature (Bracho-Nunez et al., 2013; Jardine et al., 2015; Kuhn et al., 2002, 2004). This could partly explain the diurnal pattern of  $\alpha$ -pinene mixing ratios, which exhibit some relation to a light and temperature dependent emission flux (Kuhn et al., 2002; Rinne et al., 2002; Williams et al., 2007). However, this behaviour is not observed for all monoterpene species. Therefore, the observed diurnal cycles of some monoterpene species might be triggered by stronger temperature dependencies.”

1- L502 and 522 – Any leaf level experiments to address this? Needs a brief discussion.

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2- We assume that the reviewer is referring to L520-522. Unfortunately, we do not have any leaf level experiments to address this. We have performed these calculations which give an estimation of the possible role of NO in SOA growth indicating the need for further studies. We only want to point out the necessity of assessing this role when studying SOA growth from monoterpene species in the Amazon region.

Technical corrections:

1- L1 – Two words “Amazon” in a title are not needed.

2- We have removed Amazon from the title.

1- L19 – Why just in Amazon rainforest? You may just say “a rainforest”.

2- We have changed it accordingly.

1- L24 – “automatic” - automated?

2- We have changed it accordingly.

1- L31 – “may not be the most atmospheric chemically relevant compounds”. Although it might be grammatically correct, this is a bit odd and does not read well. This is repeated later in the text.

2- We have changed this sentence to: “Reactivity calculations showed that higher abundance does not imply higher reactivity”

1- L74-76 – “scarce” – a bit over-repetition of this word throughout the manuscript and here.

2- We have modified the wordings accordingly.

1- L230 – The is a discussion in the “Result” section.

2- We have now merged results with discussion.

1- L253 – Figure 2 legend and axes text too small.

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2- We have modified this figure and increased legend and axes.

1- L283 – Figure 3 – figure caption above not needed. Description needs to be extended.

2- We have modified this figure and elaborated further in the description:

3- “Pie charts representing the day (a and c) and night (b and d) day and night averaged monoterpene species abundance in average percentage with standard deviation at 24 (a and b) and 24 (c and d) m. Day period was from 0900h to 1700h and night period was from 2000h to 0500h.”

1- L289 – “O1D” ?!

2- We agree with the reviewer this was not specified in the text and we have removed it.

1- L312 – Figure 4 out of margins, figure caption not needed. Use a) b): : : to refer to the individual figures with a clear description. Also, check all the figures to meet this standard.

2- We agree with the reviewer and we have modified the graph and footnote accordingly.

1- L381-384 - Repetition

2- We have deleted this part in the results sections to avoid repetition.

Ref.: Bonn, B., Bourtsoukidis, E., Sun, T. S., Bingemer, H., Rondo, L., Javed, U., Li, J., Axinte, R., Li, X., Brauers, T., Sonderfeld, H., Koppmann, R., Sogachev, A., Jacobi, S. and Spracklen, D. V.: The link between atmospheric radicals and newly formed particles at a spruce forest site in Germany, *Atmos. Chem. Phys.*, 14, 10823–10843, doi:10.5194/acp-14-10823-2014, 2014.

Hummel, M.: Laborstudie zum Beitrag organischer Peroxyradikale (RO<sub>2</sub>) bei der Par-

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tikelneubildung während der Ethen–Ozon–Reaktion, Master's thesis, J. W. Goethe-University, Frankfurt (Main), 2010.

Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S.H., Wu, C., Mentel, T.F., Zhao, D., Hastie, D.R., and Kiendler-Scharr, A.: Impact of NO<sub>x</sub> and OH on secondary organic aerosol formation from  $\alpha$ -pinene photooxidation. *Atmos. Chem. Phys.*, 16, 11237–11248, 2016

Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., M $\ddot{u}$ sgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R., and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NO<sub>x</sub>. *Atmos. Chem. Phys.*, 14, 2789–2804, doi:10.5194/acp-14-2789-2014, 2014.

Wolf, J. L., Suhm, M., and Zeuch, T.: Suppressed particle formation by kinetically controlled ozone removal: revealing the role of transient-species chemistry during alkene ozonolysis, *Angew. Chem.*, 48, 2231–2235, 2009.

Wolf, L., Richters, S., Pecher, J., and Zeuch, T.: Pressure dependent mechanistic branching in the formation pathways of secondary organic aerosol from cyclic-alkene gas-phase ozonolysis, *Phys. Chem. Chem. Phys.*, 13, 10952–10964, 2011.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-817>, 2017.

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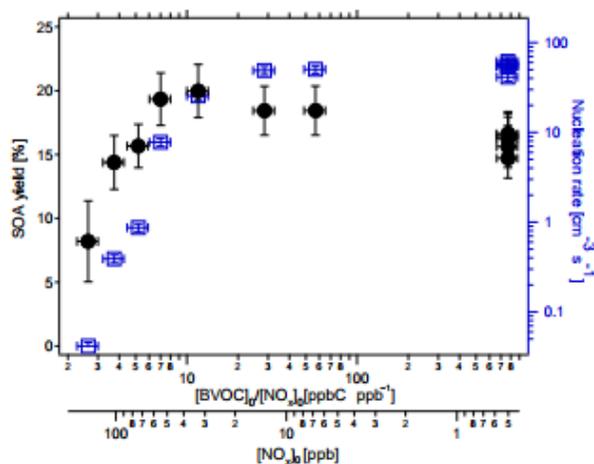


M. Sarrafzadeh et al.: Impact of  $\text{NO}_x$  and OH on SOA formation

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**Figure 1.** Measured SOA yield from  $\text{PM}_{\text{max}}$  (black circles) and rates of new particle formation (blue squares) for the  $\beta$ -pinene photooxidation as a function of the ratio of the initial hydrocarbon to the initial  $\text{NO}_x$  concentration and as a function of the initial  $\text{NO}_x$  concentration. Each point corresponds to one experiment. The errors in nucleation rate and  $[\text{NO}_x]$  were estimated to be  $\pm 10\%$ . The error in SOA yield was estimated from error propagation using the sum of the systematic error, correction procedure error and error in BVOC data. Note that the horizontal error bars are associated with the BVOC/ $\text{NO}_x$  axis.

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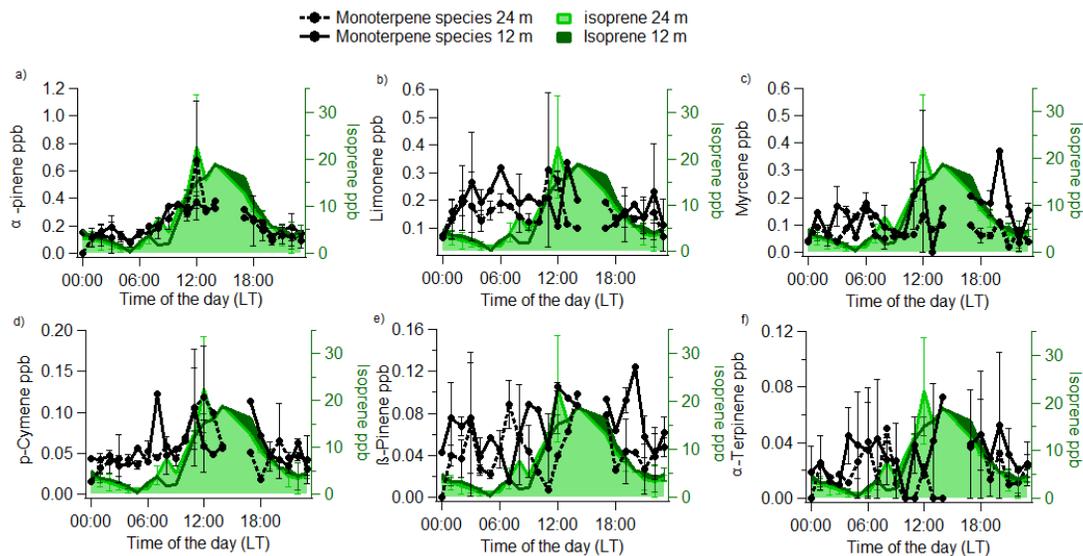


Fig. 2.

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