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Monoterpene chemical speciation in the Amazon tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO)

Combined document with detailed responses to the reviewer and a copy of the revised manuscript with all changes tracked.

Response to reviewers 1 and 2.

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 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 leafs 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 ~300 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 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 a-pinene mixing ratio? Or could be there more reasons for the model showing so high a-pinene in the night from the 17. to the 18.? Only if the source and the chemical sink of a-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 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, α-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_3, OH and NO_3 but this sink is relatively small compared to the dominant sink of α-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 α-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 a-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^{-1}, based on Henry law's constants on the order of ~1-3^{e-2} M atm^{-1}, 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_3 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.

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

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 cm3 and an order of 10-5 -10-6. 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^{-3} s^{-1}".These have been corrected in the revision. A particle growth would focus on size change per time i.e. nm h^{-1} 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 (RO2) from e.g. mono- and sesquiterpene reactions with OH or NO3 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 large organic RO2 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 ($1x10^{-5}$ to $5x10^{-5}$ cm^{-3} s^{-1} 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 $1x10^{-3}$ and $4.5x10^{-3}$ cm^{-3} s^{-1} 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/NOx 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 NOx at constant BVOC mixing ratio will decrease the BVOC/NOx 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:

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/NOx ratios. As the theory assumes contributions of larger organic peroxy radicals (RO2), which are destroyed by reactions e.g. with NO, increasing NOx at constant BVOC mixing ratio will decrease the BVOC/NOx 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 NOx 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^{-1} hr^{-1} (Guenther et al., 1995). Then we partitioned this emission flux over the different monoterpene species to see 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 mg C g^{-1} 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 µg C g^{-1} h^{-1} for α-pinene, 0.04 µg C g^{-1} h^{-1} for β-pinene, 0.11 µg C g^{-1} h^{-1} for α-terpinene, 0.9 µg C g^{-1} h^{-1} for limonene and 0.18 µg C g^{-1} 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" lead 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 percentages both in the graph and text.

1- line 286, first §: I suggest to define what you mean by reactivity. e.g. OH reactivity = kOH*[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-1]”, 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 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 beck. 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 α-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 <1s (not 30 s). It is also recently coupled with FastGC to characterise monoterpenes in < 2min. 1h GCFID 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 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^3 min^{-1} (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^2 g^-

^{1}) followed by 130 mg of Carbograph 5 (560 m^{2} g^{-1}) sorbents. The size of the Carbograph particles was in the range of 20–40 mesh. 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^{3} min^{-1} (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^{3} min^{-1} (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?

3. 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 – "2σ of the background" – 3σ it is more acceptable. Also briefly describe the blanks in each sampling systems.

2- We have modified the LOD to 3σ. A more detailed explanation of the blanks has been added as following:

3- L148: "Hourly background measurements with a catalytic converter (Supelco, Inc. with platinum pellets heated to >400ºC) 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 3σ 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 a-terpenene, 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 α-pinene (a), limonene (b), myrcene (c), ρ-cymene (d), β-pinene (e) and α-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."

1- L345– "..in previous campaigns.. earlier samples were collected using a GSA SG10-2 personal pump sampler. Adsorbent tubes were filled at 167 cm3 min-1 (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 cm3 min-1 (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 O3 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_3 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_3 mixing ratios were taken from the MLC-CHEM model simulations that predicted mixing ratios of ~0.4 ppt."

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 emis-sion 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 α-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 de-pendency 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 α-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.

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.

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 monoter-pene species abundance in aver-age 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.:

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Monoterpene chemical speciation in ~~the Amazon~~a tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO)

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Speciated monoterpene measurements in ~~the Amazon~~ rainforest air are scarce, but they are ~~important in order to understand their~~essential for understanding the contribution of these compounds to the overall reactivity of volatile organic compound (VOCs) emissions towards the main atmospheric oxidants, such as hydroxyl radical (OH), ozone (O_3) and nitrate radical (NO_3). In this study, we present the chemical speciation of gas phase monoterpenes measured in the tropical rainforest at the Amazon Tall Tower Observatory (ATTO, Amazonas, Brazil). Samples of VOCs were collected by two automated sampling systems positioned on a tower at 12 and 24 m height and analysed using Gas Chromatography Flame Ionization Detection (GC-FID). The samples were collected in October 2015, representing the dry season, and compared with previous wet and dry season studies at the site. In addition, vertical profile measurements (at 12 and 24 m) of total monoterpene mixing ratios were made using Proton-Transfer Reaction Mass Spectrometry (PTR-MS). The results showed a distinctly different chemical speciation between day and night. For instance, α-pinene was more abundant during the day, whereas limonene was more abundant at night. Reactivity calculations showed that higher abundance does not generally imply higher reactivity. Furthermore, inter- and intra-annual results demonstrate similar chemodiversity during the dry seasons analysed. Simulations with a canopy exchange modelling system show simulated

monoterpene mixing ratios that compare relatively well with the observed mixing ratios, but also indicate the necessity of more experiments to enhance our understanding of in-canopy sinks of these ~~monoterpenes~~compounds.

1. Introduction

Isoprenoids such as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) are considered to be key contributors to the production of biogenic secondary organic aerosol (SOA), which affects cloud condensation nuclei production (Engelhart et al., 2008; Jokinen et al., 2015; Pöschl et al., 2010). While isoprene ~~has been shown to be~~is a globally significant source of SOA (Claeys et al., 2004), it~~'~~s presence ~~has been also shown to~~can also inhibit SOA formation under certain conditions (Kiendler-Scharr et al., 2009). By virtue of their lower volatility and higher ozone reactivity, monoterpenes and sesquiterpenes are strong sources of secondary organic aerosol (SOA) through the generation of low-volatility oxidation products formed via ozonolysis and hydroxyl radical oxidation (Bonn and Moortgat, 2003; Zhao et al., 2015).

The main source of monoterpenes to the global atmosphere is emission from vegetation, with smaller contributions from soil (Kesselmeier and Staudt, 1999; Kuhn et al., 2002; Ormeno et al., 2007). Synthesis of the monoterpene species occurs via the non-mevalonate pathway within the plant chloroplast (Kesselmeier and Staudt, 1999; Lichtenthaler, 1999; Schwender et al., 1996), which explains the light dependency also known to determine isoprene synthesis and emission. These commonly emitted compounds have been identified as important signalling compounds through plant-to-plant, plant-insect or plant-microbe interactions (Gershenzon, 2007; Gershenzon and Dudareva, 2007; Kishimoto et al., 2006; Maag et al., 2015) and they are thought to protect photosynthetic membranes against abiotic stresses (Jardine et al., 2017; Penuelas and Llusia, 2002; Vickers et al., 2009).

Despite having a common sum formula, variations in the molecular structure of the various monoterpenes result in large variations (over two orders of magnitude) of their reaction rate coefficients with the hydroxyl radical (OH), ozone (O_3) and nitrate radical (NO_3). ~~Current quantification methods~~

~~for monoterpenes include the fast (ca. 30 seconds) but unspecific total monoterpene measurement by the proton transfer reaction mass spectrometer (PTR-MS) (Lindinger and Jordan, 1998) and the slower (ca. 1 hour) but chemically speciated gas chromatographic methods. In order to gauge the role of these species in atmospheric chemistry, chemical speciation needs to be provided by the gas chromatographic techniques while the on-line mass spectrometer can assess how the total mass changes over time. It should be noted that the structure and reactivity of the monoterpenes can also have~~This leads to different implications for the efficiency of SOA formation (Hallquist et al., 2009; Kiendler-Scharr et al., 2009; Mentel et al., 2009; O'Dowd et al., 2002). In most cases, SOA products are poorly characterized due to a scarcity of measurements (Martin et al., 2010).

Considering the overall size of the Amazon rainforest (5.4 million km^2 in 2001; Malhi et al., 2008) and the significant contribution of BVOC emissions from this vast forest to the global VOC budget (globally 1000 Tg of carbon yr^{-1}; Guenther et al., 2012), measurements of total monoterpene emissions and mixing ratios from this ecosystem are scarce (Greenberg and Zimmerman, 1984; Helmig et al., 1998; Jardine et al., 2015, 2011, 2017; Karl et al., 2007; Rinne et al., 2002; Yáñez-Serrano et al., 2015). Speciated measurements are even more rare (Jardine et al., 2015, 2017; Kesselmeier et al., 2002; Kuhn et al., 2004). Yet, this information is essential for our understanding of the functioning of the Amazon rainforest in atmospheric chemistry-climate interactions. Knowledge of these processes also serves to improve predictions of future changes in atmospheric composition and to assess the impact of changes in regional emissions and land use on global climate caused by Amazon deforestation.

In this study, we evaluate measurements of speciated rainforest monoterpene mixing ratios as a function of height in the canopy, season and diel cycle. This evaluation includes a comparison with a canopy exchange modelling system (MLC-CHEM, Multi-Layer Canopy Chemistry Exchange model) to support analysis of the measured temporal variability in speciated rainforest monoterpene mixing ratios inside the tropical rainforest canopy. The MLC-CHEM model was also selected since it has been already extensively applied for site- to global-scale studies on atmosphere-biosphere exchange for tropical rainforests ~~ecosystems~~ (Ganzeveld et al., 2008, 2002; Ganzeveld and Lelieveld, 2004; Kuhn et al., 2010).

2. Methodology

2.1. Site

The site chosen for this study was the Amazon Tall Tower Observatory, ATTO (Andreae et al., 2015). This site is located in Central Amazonia (S 02° 08.647’ W 58° 59.992’), 150 km NE of the closest ~~populated~~ large city, Manaus, Brazil. Due to the prevailing north-easterly wind direction, the influence of the Manaus plume is negligible and the measurements at this site can be considered to reflect pristine tropical forest conditions affected by air masses that have passed over about 1000 km of undisturbed rainforest. The site is equipped with a 325 m tall tower as well as two smaller towers. This study was carried out on the INSTANT tower, an 80-m walk-up tower located 600 m from the tall tower in easterly direction. Sampling was performed on this tower below canopy top (mean canopy height 35 m) at two different heights (12 m and 24 m). For a comprehensive site description see Andreae et al. (2015).

2.2. Air sampling

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 height of the canopy is approximately 35 m (Andreae et al., 2015).~~ The adsorbent tubes used for VOC sampling were filled with 130 mg of Carbograph 1 (90 m^2 g^{-1}) followed by 130 mg of Carbograph 5 (560 m^2 g^{-1}) sorbents. The size of the Carbograph particles was in the range of 20–40 mesh. 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^3 min^{-1} (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^3 min^{-1} (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.

2.3. Instruments used for chemical analysis

2.3.1. Gas Chromatography –Flame Ionization Detector (GC-FID)

After collection, the adsorbent tubes were analysed at the Max Planck Institute for Chemistry (MPIC) using a Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID, Model Auto-System XL, Perkin Elmer GmbH, Germany) for identification and quantification of the monoterpene species. Helium was used as carrier gas, and ~~. S~~separation occurred on a 100 meter HP-1 column with 0.22 mm inner diameter, ~~and~~ coated with the non-polar dimethylpolysiloxane as stationary phase. The compound mixture collected in the adsorbent tubes was discharged into the gas stream with the help of a two-step desorption system (Model ATD400, Perkin Elmer, Germany). The samples were cryofocused in a cold trap at -30 °C filled with Carbograph 5, providing better defined peaks in the chromatograms. Afterwards the cold trap was ~~rapidly~~ heated to 280°C and the pre-concentrated sample injected onto the column. The following temperature programme was used: (-10 to 40 °C at 20 °C min^{-1}, 40 to 145 °C at 1.5 °C min^{-1}, and 145 to 220 °C at 30 °C min^{-1}). The separated compounds were quantified with a Flame Ionization Detector (FID). Identification was achieved through spiked injection of pure compounds. For a more detailed description see Kesselmeier et al., (2002).

Calibration for VOCs containing no heteroatoms was achieved by using a standard gas mixture of isoprene and several n-alkanes (n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane) (Apel-Riemer Environmental Inc., USA). In this case, it is assumed that the “effective carbon number” (Sternberg et al., 1962) is equal to the real carbon number of the molecules (Komenda, 2001), yielding a signal response that is proportional to the real carbon number. The monoterpenes identified and quantified were α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α-terpinene, ρ-cymene, limonene and γ-terpinene. Isoprene was also quantified. The detection limit for the GC-FID was 2 ppt (Bracho-Nunez et al., 2011).

2.3.2. Proton Transfer Reaction - Mass Spectrometer (PTR-MS)

Online total monoterpene mixing ratios were determined by a quadrupole Proton Transfer Reaction - Mass Spectrometer, PTR-MS (Ionicon Analytic, Austria). The PTR-MS was operated under standard conditions (2.2 mbar drift pressure, 600 V drift voltage, with an E/N of 142 Townsend (Td)). In addition to weekly humidity dependent calibrations, hourly background measurements were performed with a catalytic converter (Supelco, Inc. with platinum pellets heated to >400ºC). A gravimetrically prepared multicomponent standard for calibration was obtained from Apel & Riemer Environmental, USA. The measurements were carried out at two different heights (~~0.05, 0.5, 4,~~ 12 and~~,~~ 24~~, 53 and 79~~ m) with the PTR-MS switching sequentially between each height at 2 min intervals~~ and only data from 12 and 24 m is shown~~. The inlet lines were made of PTFE (9.5 mm OD), insulated and heated to 50 ºC, and had PTFE particle inlet filters at the intake end. The compounds of interest for this study were ~~the~~ isoprene (*m/z* 69) and the sum of monoterpenes (*m/z* 137)~~ and isoprene (in *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 3σ of the background noise. More information about the gradient system and PTR-MS operation at ATTO can be found elsewhere (Nölscher et al., 2016; Yáñez-Serrano et al., 2015).

2.4. Multi-Layer Canopy Chemistry Exchange model (MLC-CHEM)

To analyse the magnitude and temporal variability ~~in~~of the observed monoterpene concentrations inside and above the forest canopy, we applied the Multi-Layer Canopy Chemistry Exchange Model (MLC-CHEM), driven by the observed micro-meteorology and ozone surface layer mixing ratios. MLC-CHEM was originally developed and implemented in a single-column model (SCM). It is ~~originally~~ set up ~~as well as~~also in a global chemistry and climate-modelling system to assess the role of canopy processes in local- to global-scale atmosphere-biosphere exchange of nitrogen oxides (Ganzeveld et al., 2008, 2002; Kuhn et al., 2010). The model's generalized representation of chemistry, dry deposition, emissions and turbulent mixing allows ~~to~~ studying the role of canopy interactions in determining atmosphere-biosphere exchange fluxes and in-canopy and surface layer mixing ratios of, e.g., ozone (O_3), nitrogen oxides (NO_x) and biogenic volatile organic compounds (BVOCs). The BVOC emissions are calculated according to MEGAN (Guenther et al., 2006), considering the vertical distribution of biomass and direct as well as diffuse radiation to calculate leaf-scale BVOC emissions. The current implementation of canopy chemistry in MLC-CHEM considers, in addition to standard photo-chemistry involving O_3, NO_x , methane (CH_4) and carbon monoxide (CO), the role of non-methane hydrocarbons including isoprene, and a selection of hydrocarbon oxidation products such as formaldehyde, higher aldehydes and acetone. Oxidation of the monoterpenes by OH, O_3 and NO_3 is taken into account, but the role of the monoterpene oxidation products in photo-chemistry is not considered in the current implementation of the chemistry scheme in MLC-CHEM. For this study, we have extended MLC-CHEM to consider, besides the already included compounds α-pinene and β-pinene, the observed monoterpene species, α-terpinene, limonene and myrcene. The monoterpene basal leaf-scale monoterpene emission factors have been selected 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 comparison of 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 µg C g^{-1} h^{-1} for α-pinene, 0.04 µg C g^{-1} h^{-1} for β-pinene, 0.11 µg C g^{-1} h^{-1} for α-terpinene, 0.9 µg C g^{-1} h^{-1} for limonene and 0.18 µg C g^{-1} h^{-1} for myrcene. Note the selected relative high basal emission flux for limonene is required to arrive at simulated mixing ratios comparable to the observed ones. Regarding the physical sinks; dry deposition of gases including the BVOC compounds depends on their uptake resistances calculated according to Wesely's (1989) parameterization, which estimates these uptake resistances based on the compounds' solubility and reactivity.

The simulations with MLC-CHEM were constrained with the observed surface layer net radiation (above the canopy only), wind speed, relative humidity and O_3 mixing ratios as well as the temperatures measured above and inside the canopy (8 different heights including 12 and 24m) from 17 to 20 October 2015, coinciding with the measurement dates. These simulations represent a set-up of MLC-CHEM distinguishing six canopy levels with a canopy height of 30 m, implying canopy layers with a thickness of 5 m. Furthermore, we assumed a Leaf Area Index (LAI) of 5 m^2 m^{-2} and a Leaf Area Density (LAD) profile such that about 70% of this biomass is present in the top 15 m of the canopy, as previously observed ~~in~~at other tropical rainforest sites (Nölscher et al., 2016). Monoterpene emissions by vegetation were simulated using a temperature-only dependent emission flux as a function of the amount of biomass in each layer and the measured canopy temperature profiles interpolating between the 0.4 m and 26 m temperature sensors. Meteorological observations for 18 October were missing and therefore MLC-CHEM was constrained for this day by first-order estimates of the diurnal cycles in radiation, air and surface temperatures, relative humidity and wind speed comparable to the previous and ~~posterior~~subsequent day's meteorological conditions.

3. Results and discussion

3.1. Time series and diel cycles

The c~~C~~ontinuous online PTR-MS measurements were compared with off-line GC-FID samples over the course of 3 days in October 2015 (Figure 1). The close agreement between the two measurement techniques provides confidence that almost all monoterpenes present ~~at~~ in ambient air ~~in~~ at the site were being measured. Note that in this comparison, ρ-cymene (an aromatic monoterpene) was removed from the calculations as the PTR-MS does not detect it on *m/z* 137. The observed differences in the monoterpene chemodiversity ~~at~~in the ~~ATTO~~ rainforest canopy atmosphere were regarded to be driven by differences in emission, reactivity with~~to~~ the oxidizing species, physical removal processes and turbulent mixing conditions.

The total monoterpene mixing ratios were higher during the day, when temperature and solar radiation were at their maxima. Most of the observed distinct diurnal cycle in total monoterpene mixing ratios could~~an~~ be attributed to α-pinene, which was the dominant species during ~~the~~ daytime (0900h to 1700h) with mixing ratios as large as (average ± standard deviation) 0.33±0.04 and 0.38±0.21 ppb at 12 and 24 m respectively, and 0.15±0.05 and 0.11±0.06 ppb for the night (2000h to 0500h) at 12 and 24 m. The second most abundant monoterpene species was limonene, with observed average daytime mixing ratios of 0.18±0.09 and 0.19±0.12 ppb at 12 and 24 m, respectively, and 0.18±0.01 and 0.14±0.07 ppb for the night time at 12 and 24 m.

When comparing our results to previously published studies, we observed consistent differences with other regions of the Amazon rainforest. For instance, Kesselmeier et al. (2002)~~,~~ studied the seasonal monoterpene speciation in the Rondonia rainforest in southern Amazonia. Even though they found the same monoterpene species as presented in this study, their individual abundances were very different compared to the mixing ratios for the dry season at the ATTO site. α-~~pi~~pine~~ne~~ne and limonene were much higher at ATTO than in Rondonia, whereas camphene was substantially lower. In the case of β-pinene, the abundance measured at ATTO was much lower than at other Amazonian sites (Andreae et al., 2002; Karl et al., 2007). ~~Despite~~Given that emission patterns are highly dependent on species, environmental conditions and stresses, these differences ~~show~~underline that it cannot be assumed that the same speciation and emission rates of monoterpenes exist throughout the vast Amazon basin.

Furthermore, the difference between the 12 and 24 m height total monoterpene mixing ratios was~~is~~ minor given the variance of the measurements, but there was~~is~~ a tendency for the difference to be more pronounced during night time (Table 1). These more pronounced differences between the measurement heights could be also due to an enhanced sensitivity of nocturnal mixing ratios to small changes in source and sink terms for the suppressed mixing conditions prevailing during the night time.

The continuous online measurements by the quadrupole PTR-MS indicated a clear diurnal cycle in the measured mixing ratios of the sum of monoterpenes, which has been reported previously from this site (Yáñez-Serrano et al., 2015). In order to assess the effect of each individual monoterpene species, we further investigated their diurnal cycles as obtained by the off-line GC-FID samples. The measured diel cycles for the most relevant monoterpene species at the ATTO site were very similar at both heights. We also compared the measured diel cycle~~s~~ of isoprene as measured by the GC-FID with the observed diel cycle for the different monoterpene species for 12 and 24 m. The compounds that showed a diurnal cycle similar to isoprene were α-pinene and ρ-cymene (Figure 2). This could be due to the emission of α-pinene and ρ-cymene being dependent on light and temperature, analogous to isoprene. However, during the night both monoterpenes were also present, albeit at lower mixing ratios, and the nocturnal mixing ratios of the monoterpenes did not decrease as much as isoprene. This has also been noted in previous studies (Yáñez-Serrano et al., 2015).

Despite the higher mixing ratios of limonene compared to other monoterpene species (other than α-pinene), it was not possible to distinguish any clear diel pattern in the average data for this species (see Figure 2). β-P~~p~~inene and α-terpinene likewise showed no obvious diel pattern in the rainforest air, but were found to be ~~greater than~~above the detection limit of the GC-FID of 2 ppt.

~~On the contrary~~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 α-P~~p~~inene 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 was~~is~~ not observed for all monoterpene species. Therefore, the observed diurnal cycles of some monoterpene species might be ~~triggered by~~related to a stronger temperature ~~affects~~response.

3.2. Chemodiversity

The chemical speciation (or chemodiversity) of monoterpenes relates to the relative abundances of the different monoterpene species in the sampled air. α-Pinene, limonene, myrcene, ρ-cymene and β-pinene represented more than 85% of the total monoterpene~~MT~~ mixing ratio (Figure 3). During the day (0900h to 1700h) α -pinene had an average abundance (average~~-~~±standard deviation) of 46±25% and 36±4% of the total monoterpene mixing ratios at 24 and 12 m, respectively, and was the dominant monoterpene in this study overall. However, during the night (2000h to 0500h), its relative abundance dropped to 25±13% and 25±9% at 24 and 12 m, respectively. In contrast, limonene made up 23±15% and 20±10% of the monoterpenes at 24 and 12 m, respectively, by day, and increased during night time to 33±15% and 26±16% at 24 and 12 m. Thus, there was~~is~~ a tendency ~~of~~towards some differences in monoterpene species abundances between day and night. These were~~are~~ mainly due to the nocturnal decreases in α-pinene and the nocturnal relative increase in limonene. It is plausible that the observed decrease in α-pinene mixing ratios could be due to~~ a~~ decreased vegetation emission, as reduced chemical destruction due to very low OH concentrations at night~~,~~ would lead to an increase in the nocturnal α-pinene mixing ratios.

Even though there were clear differences between the absolute and relative abundances of some monoterpene species during day and night, there were no clear changes in the ~~in the~~ vertical gradients (e.g. for α-pinene night time averages were 0.15±0.05 ppb for 12 m and 0.11±0.06 ppb at 24 m). For the day, the apparent difference in the abundance of α-pinene was due to a single outlier data point covering 30 minutes at noon on 19 October 2015 at 24 m, when the α-pinene mixing ratio doubled. This increase could not be explained, although it could be related to a strong change in wind speed an hour before the measurement, when the wind was blowing from the North. In general, our observations indicate that the abundance of monoterpene species does not vary much over the heights selected (12 and 24 m) within the canopy. This is consistent with the results by Kesselmeier et al. (2000), where the monoterpene composition at the rain forest floor was comparable to the above-canopy composition at their site.

3.3. Reactivity

The variability of the oxidants (OH, O_3 and NO_3) present in the Amazon air is important when considering the impact that monoterpenes can have o~~i~~n the oxidative regime in the Amazon region and Brazil in general. Hydroxyl radicals are produced mainly during the day via ozone photolysis. ~~and O^1D reaction with water.~~ Low levels of OH can be also generated by the reaction of ozone with doubly bonded species (e.g. monoterpenes and sesquiterpenes) even at night. In this assessment, we considered the monoterpene contributions to OH reactivity by day only. In contrast, NO_3 is photolytically destroyed during the day, but can become significant at night, so we assessed the impact of monoterpenes on NO_3 reactivity at night. Even though in the Amazon rainforest ozone levels are low (~10-20 ppb) compared to other areas of the world (e.g., Williams et al., 2016), it is nevertheless present, and some monoterpenes are extremely reactive towards ozone. Table 2 gives an overview of the lifetime and reactivity (which is defined as reaction rate constant (oxidant i.e. OH)*[monoterpene species]) to 1 ppb of all the investigated monoterpene species for these three oxidants. For calculating the lifetime of the different monoterpenes as presented in Table 2, typical oxidant concentrations for the Amazon rainforest conditions were used. For OH a mean value of $7\text{x}10^5$ molecules cm^{-3} was used as representative of the site (Spivakovsky et al., 2000). For ozone reactivity calculations, 12 ppb was used, as this mixing ratio was observed during the measurement period. NO_3 mixing ratios were taken from the MLC-CHEM model simulations that predicted mixing ratios of ~0.4 ppt.

~~Despite,~~While ~~the most abundant species were~~ α-pinene, limonene and myrcene were the most abundant species, ~~. However, with respect to their reactivities towards the different oxidants,~~ their relative contribution to total monoterpene reactivity ~~dramatically changed~~was not proportional to their abundances. The most abundant monoterpene, α-pinene was not the dominant~~ting~~ sink for the oxidants. ~~For instance~~In particular, α-terpinene dominated ozone reactivity associated with monoterpene abundance both during the day and night, as well as the nocturnal nitrate reactivity, despite the low mixing ratios measured for this compound (Table 2).

The monoterpene ozone reactivity was~~is~~ comparable between day (1.37x10^{-6} s^{-1}) and night (1.12x10^{-6} s^{-1}). α-T~~t~~erpinene dominated the monoterpene-ozone chemistry, followed by myrcene and limonene. Despite the relatively high abundance of α-pinene (46±25%;~~,~~ average mixing ratio and standard deviation during the day was 0.34±0.04 ppb at 12 m), its contribution to ozone reactivity with respect to other monoterpene species was only 11±7 % and 3±1 % at 24m, during the day and night, respectively~~, at 24 m,~~ and 2±1 % for both day and night at 12 m (Figure 4). As previously noted, the differences in ozone reactivity between heights were negligible for the night and slightly higher at 24 m during the day. As ozone mixing ratios are quite similar for both heights during day and night (11.4 ppb at 12 m and 10.4 ppb at 24 m during night, and 16.1 ppb at 12 m and 15.6 at 24 m during the day), the higher abundance of α-pinene during the day, and the lower α-terpinene mixing ratios at 24 m during the day mainly explain these changes in monoterpene-ozone reactivity. It is important to note that these results are derived from a relative abundance analysis, and unmeasured monoterpene species could change the proportions, although given the close similitude between PTR-MS and GC-FID measurements shown in Figure 1 this is unlikely. On the other hand, very reactive species which could dominate reactivity, may be present in very low concentrations, ~~and~~ which our measurements capabilities would not allow ~~for its monitoring~~being detected.

The monoterpene reactivity towards the NO$_3$ radical during the night ~~in this study~~ was also dominated by α-terpinene (40±36% and 42±27 %, ~~respectively~~ for 24 and 12 m, respectively), although contributions of limonene (30±13% and 25±14%, ~~respectively~~ for 24 and 12 m, respectively), α-pinene (11±6 and 11±4%, ~~respectively~~ for 24 and 12 m, respectively), and myrcene (13±11 and 16±12%, ~~respectively~~ for 24 and 12 m, respectively) were also significant. No significant differences between the reactivites~~y~~ at different heights were observed, suggesting a rather homogeneous chemical regime regarding monoterpene chemical destruction within the canopy (from 12 to 24 m). However, note that this finding reflects the use of a single simulated NO_3 mixing ratio due to the absence of direct measurements in the Amazon rainforest, which prevents us from drawing any further conclusion. ~~The~~ Our OH reactivity estimates demonstrate~~d~~ the important role of myrcene with its higher reactivity towards OH due to its acyclic nature, especially at 12 m, where myrcene was more abundant. The total OH reactivity for the sum of monoterpenes was calculated to be 2.4 and 3.4 s^{-1} for 24 and 12 m, respectively.

As demonstrated in this data set, chemically speciated measurements are very important for understanding how monoterpenes affect Amazon air chemistry dependent on time of day and season, as each monoterpene species has a different reactivity. Therefore, a lower abundance of a certain monoterpene species could not necessarily~~only~~ be related to a lower vegetation emission, but also to a higher reactivity with atmospheric oxidants. Despite the small amount of α-terpinene present in the atmosphere, it can profoundly affect reactivity due to its fast reaction rate (its lifetime, according to the oxidant mixing ratios stated above, can be 103, 2 and 11 minutes to OH, O_3 and NO_3, respectively, ~~(~~Neeb et al., 1997). In terms of total OH reactivity accounted for by the monoterpenes, the values of this study are very low compared to the total OH reactivity measurements by Nölscher et al. (2016), with a mean of total OH reactivity for the dry season of 32 s^{-1}, mostly dominated by isoprene chemistry. This suggests that the monoterpenes contributed only a small fraction to the total OH reactivity at the ATTO site during the investigated time period. This study demonstrates that the abundance does not relate to the importance in chemical reactivity, and species that are usually not considered by atmospheric chemistry models due to their modest mixing ratios might actually play a dominant role in the monoterpene atmospheric chemistry. Therefore, it is questionable to generalize the representation of terpene chemistry in models (Hallquist et al., 2009) using one or two monoterpene species only.

The gas-phase oxidation of the monoterpenes in the Amazon has numerous impacts on the environment, including the production of a multitude of new compounds that are generally longer lived than the primary emissions, increasing the lifetimes and particle production potential of certain compounds by suppressing oxidant availability. Moreover, production of OH due to the ozonolysis of monoterpenes is known to occur (Paulson et al., 1999). The production strength varies depending on the position of the double bonds, if there is more than one (Herrmann et al., 2010). Furthermore, the products of the reaction can be manifold. For instance, when α-pinene is oxidized by OH, especially at low nitrogen oxides mixing ratios, pinonaldehyde is formed in high yields (Eddingsaas et al., 2012). Chemical processing of α-pinene can also result in a further production of different monoterpenes such as the reaction of α-pinene with nitrate during the night, which can lead to the formation of ρ-cymene (Gratien et al., 2011).

The implications of the measured monoterpene abundances for SOA formation at the ATTO site are difficult to quantify, ~~. This is caused by~~because the SOA formation yield ~~being~~is dependent on many factors. For example, it depends on the pre-existing organic aerosol mass~~,~~ into which these products can be absorbed (Griffin et al., 1999), and thus the SOA yield can vary~~. This is the reason why in~~ between regions with similar monoterpene mixing ratios and different aerosol mass loadings~~, the SOA yield can vary~~. It also varies strongly between different oxidants and terpene species. For instance, α-pinene forms negligible aerosol mass under NO_3 oxidation (Fry et al., 2014), whereas there is production of organic aerosols when the oxidation of α-pinene involves O_3 (Ehn et al., 2014) and OH (Eddingsaas et al., 2012). Monoterpenes containing endocyclic double bonds (e.g. α-pinene, 3-Carene) or open chains (e.g. myrcene) tend to form less aerosols mass from ozonolysis than monoterpenes with exocyclic double bonds (e.g. β-pinene, sabinene, Hatakeyama et al., 1989; Hoffmann et al., 1997). Following the equation established by Bonn et al. (2014, Eq. 5 in text), we were able to estimate the potential aerosol particle number formation rate initiated by monoterpene species only (1x10^{-5} to 5x10^{-5} cm^{-3} s^{-1} at 24 m) assuming steady state conditions for radicals. Those were found to be approximately two orders of magnitudes 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 (1x10^{-3} and 4.5x10^{-3} cm^{-3} s^{-1} 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). Furthermore, the level of ~~present~~ NO present (nitric oxide) also affects ~~severely~~ the potential aerosol growth (Wildt et al., 2014) and yield (Sarrafzadeh et al., 2016) at low BVOC/NO_x ratios). As the theory assumes contributions of larger organic peroxy radicals (RO_2), which are destroyed by reactions, e.g. with NO, increasing NO_x at constant BVOC mixing ratio will decrease the BVOC/NO_x ratio and lead to a decline in SOA yield. Our calculations showed this effect, with a change of NO from 0.2 ~~ppbv~~ppb to 1 ~~ppbv~~ppb 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_x exchange in aerosol formation and growth studies.

3.4. Seasonality

By examining GC-FID data collected in previous campaigns, an intra- and inter-annual comparison can be made. ~~These earlier samples were collected using a GSA SG10-2 personal pump sampler. Adsorbent tubes were filled at 167 cm^3 min^{-1} (STP) air flow for 20 min.~~ Total monoterpene averages for each season were calculated from 1100h to 1600h ~~LT~~ at 24 m. Based on these data, we distinguished the monoterpene mixing ratios representative for the dry season, the wet season and the wet-to-dry transition. The dry season conditions were represented by measurements collected in November 2012, September 2013, August 2014, and the measurements from this study in October 2015. The wet season measurements were collected in March 2013 and the wet-to-dry transition measurements were collected in June 2013. For the dry season conditions, the total monoterpene mixing ratios were substantially higher (1.02 ppb) compared to the observed monoterpene mixing ratios in the wet season (0.14 ppb) and the wet-to-dry transition season (0.18 ppb) (Figure 5). This coincides with the occurrence of the highest radiation levels and temperatures as well as the lowest precipitation during these dry season measurement campaigns. During the wet season, the total monoterpene mixing ratios were~~are~~ lowest, while during the transition season in June, they were~~are~~ slightly higher.

For each season, an average monoterpene chemodiversity distribution is shown in Fig. 5. During the dry seasons, the chemodiversity seems relatively similar (39.4±4% for α-pinene, 20.3±3% for limonene), whereas it slightly changes during the wet season, and dramatically changes during the wet-to-dry transition. The reason for this difference in June could be related to changes in the phenology, as demonstrated at a Central Amazonian site (Alves et al., 2016; Lopes et al., 2016). Furthermore, during the dry season of 2015 a very strong El -Niño event ~~was taking~~took place, leading to extremely dry conditions observed region-wide (Jardine et al., 2017).

It has been shown previously that the amounts and speciation of monoterpenes vary strongly according to plant species and leaf developmental stage. For instance, Bracho-Nunez et al. (2011) found young leaves of the some Mediterranean plant species to emit more α-pinene and mature leaves to emit *e*-ocimene, *z*-ocimene and myrcene, but not α-pinene. Some species have been found to be higher emitters of α-pinene (i.e. *Hevea spruceana*), whereas others are higher emitters of myrcene (i.e. *Quercus coccifera*, Bracho-Nunez et al., 2013). The leaf developmental stage is also important, as reported for flushing young leaves emitting monoterpenes, in contrast to the isoprene emission of mature leaves of the same plant species (Kuhn et al., 2004). Such a behaviour could explain the lower mixing ratios and different chemodiversity found in June. During this time of the year, leaf flushing takes place in the Central Amazon region (Alves et al., 2016; Lopes et al., 2016). Under these conditions, lower α-pinene mixing ratios were found as compared to the dry season, when young leaves reach mature levels. Therefore, the seasonality in Amazon forest monoterpene emissions might depend more on the changes in aggregated canopy phenology than on the seasonality of climate drivers (Wu et al., 2016). Our study shows that chemodiversity remains relatively constant during at least the dry seasons, but changed between different seasons. Therefore, the implications to the atmosphere are different for each monoterpene species. Kesselmeier et al. (2002) also showed this type of behaviour in their study, where they did not find a strong difference in total mixing ratios, but different chemodiversity between seasons, likely expressing differences in seasonal plant developments and atmospheric reactivities, which should be accounted for in model implementations at the ATTO site.

3.5. Modelling analysis

To further support our analysis of the observed magnitude as well as temporal variability in the monoterpene mixing ratios inside the forest canopy, we used MLC-CHEM to: 1) explore how well the model represents the measured mixing ratios and 2) to assess the role of the different in-canopy processes in explaining the diel cycle of the observed monoterpene mixing ratios at the ATTO site.

From Fig. 6, which shows a comparison of the simulated (12.5 and 22.5 m) and observed (12 and 24 m) speciated monoterpene mixing ratios from 17 to 20 October 2015, it can be inferred that the simulated speciated monoterpene mixing ratios are of comparable magnitude to the measured observations. This comparison regarding the magnitude of observed and simulated mixing ratios ~~is~~serves mainly ~~of relevance~~ to ~~appreciate~~assess the validity of the required selection of basal emission fluxes for the different monoterpene compounds. A more relevant result seems to be the overall quite good agreement between the simulated and observed temporal variability in monoterpene mixing ratios. Note that we also conducted a simulation in which we applied temperature and light dependent monoterpene emission flux. However, those simulations did not follow the observed magnitudes and temporal variability as well as the model simulations considering monoterpene emissions that only depend on temperature.

The generally quite good agreement between the simulated and observed monoterpene mixing ratios, except of an overestimation of simulated α-pinene mixing ratios for ~~the~~ 17th ~~of~~ October, expresses the overall result of temporally varying emissions, in-canopy chemistry, turbulent mixing and deposition. The latter also involves a potentially important role of deposition to wet leaf surfaces (the inferred wet surface uptake resistances for the monoterpenes are ~300 s m^{-1}, similar to values reported by Zhou et al., (2017), MLC-CHEM uses relative humidity as a proxy for the fraction of the leaf surface being wet, ~~(~~Lammel, 1999; Sun et al., 2016). This results in substantially smaller estimates of canopy wetness on 17 October ~~2015~~ compared to the following days, which partly explains the simulated high α-pinene mixing ratios. The simulated α-pinene mixing ratios for 18-20th ~~-of~~ October, with inferred wet surface fractions up to 1 during the night and ~0.5 during daytime, are in much better agreement with the observations. Regarding the comparison of the simulated observed mixing ratios for some of the other monoterpenes, the simulated ß-pinene, limonene, and myrcene mixing ratios, especially at 12.5 m seem to capture the observed temporal variability quite well. Note that this result for limonene reflects the use of a high leaf basal emission factor (0.9 $\mu g\ C\ g^{-1}\ hr^{-1}$) required to simulate mixing ratios reaching up to 0.4 ppb. These MLC-CHEM simulations were also used to infer how much of the actual emission flux escapes the canopy, expressed by the calculated atmosphere-biosphere limonene flux divided by the canopy emission flux of limonene. This ratio reaches a maximum value of 0.5 around noontime, implying that these model simulations indicate that at the middle of the day, about 50% of the emitted limonene is removed inside the canopy by in-canopy oxidation -and deposition. During night time, this ratio reaches a minimum < 0.1 indicating simulation of very efficient in-canopy removal.

These modelling results should be interpreted with ~~care~~caution, also given that some of the simulated processes cannot be evaluated due to missing observations of canopy wetness as well as the uptake efficiency of monoterpenes by wet surfaces. It should be considered that the simulated removal of monoterpenes by wet canopy surfaces could also compensate for a misrepresentation of other canopy processes, e.g., reduced emissions from wet canopy surfaces or an underestimation of the oxidation efficiency. Further analysis of the model simulated process tendencies (Ganzeveld et al., 2008) indicates only small changes in the simulated source of the monoterpenes over the 4-day period. Regarding the sink of, for example, α-pinene, chemical destruction of α-pinene oxidation by O_3, OH and NO_3 appears to be a relative small term, with the overall sink being dominated by deposition to wet surfaces showing quite large temporal variability. Consequently, the ~~presented~~ quite reasonable agreement between simulated and observed temporal variability in monoterpene~~s~~ mixing ratios indicates that deposition to wet surfaces may play an important role in monoterpene atmosphere-biosphere exchange. –This should be further corroborated, calling for experiments to determine the actual efficiency (and mechanisms) of uptake of monoterpenes by wet canopy surfaces.

4. Conclusions

This study presents an analysis of the measured monoterpene chemodiversity at the Amazon tropical forest measurement site, ATTO. The results showed a distinctly different chemical speciation between day and night, whereas there were little vertical differences in speciation within the canopy (12 and 24 m). Furthermore, inter- and intra-annual results demonstrate similar chemodiversity during the dry seasons analysed, but ~~this~~ a change of chemodiversity ~~changed~~ with season, similar to the seasonal measurements performed by Kesselmeier et al. (2002). Furthermore, reactivity calculations demonstrated that higher abundance of a monoterpene species~~n MT~~ does not automatically imply higher reactivity, as the most abundant compounds may not be the most atmospheric chemically relevant compounds, or the relative contribution of different monoterpenes may change with time. 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 sinks of these ~~monoterpenes~~compounds.

5. Data Availability

Even though the data are still not available in any public repository, the data are available upon request from the main author.

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Table 1: Average ~~M~~mixing ratio with standard deviation ~~s~~ in ppb at 24 and 12 m of the measured monoterpene species from~~or~~ 17 to 20 October 2015 as determined by the GC-FID analysis. The daytime period was ~~considered~~ chosen from 0900h to 1700h and the night time period from 2000h to 0500h (Local time). BLD stands for below detection limit.

Compound	Day 12 m	Night 12 m	Day 24 m	Night 24 m
α-Pinene	0.33 ± 0.04	0.15±0.05	0.38±0.21	0.11±0.06
Limonene	0.18±0.09	0.18±0.10	0.19±0.12	0.14±0.07
Myrcene	0.16±0.14	0.12±0.09	0.09±0.04	0.07±0.06
P-Cymene	0.07±0.03	0.04±0.01	0.08±0.04	0.04±0.02
β-Pinene	0.08±0.03	0.06±0.03	0.05±0.03	0.04±0.02
Camphene	0.03±0.03	0.02±0.01	0.03±0.02	0.01±0.01
α-Terpinene	0.03±0.02	0.03±0.02	0.01±0.02	0.02±0.02
γ-Terpinene	0.02±0.01	0.01±0.01	0.01±0.01	0.01±0.01
3-Carene	0.001±0.003	0.003±0.008	0.003±0.011	0 or BLD
α-Phellandrene	0 or BLD	0 or BLD	0 or BLD	0 or BLD
Sabinene	0 or BLD	0 or BLD	0 or BLD	0 or BLD
MT Sum – GC-FID	0.91±0.10	0.62±0.19	0.82±0.34	0.45±0.13
MT Sum – PTR-MS	0.96±0.27	0.54±0.17	0.77±0.22	0.56±0.16

Table 2: Lifetime of the different monoterpene species related to OH, O_3 and NO_3 for the OH daytime conditions at 24 m and at 12 m. In addition, the normalized reactivity to 1 ppb of the different monoterpene species is calculated.

Monoterpenes investigated	Formula	Lifetime (minutes)			Normalized r~~R~~eactivity to 1 ppb s^{-1}		
		OH	O_3	NO_3	OH	O_3	NO_3
α-Pinene	$C_{10}H_{16}$	449	615	250	1.42	2.3E-06	0.17
Camphene	$C_{10}H_{16}$	447	57422	2461	1.43	2.4E-08	0.02
Sabinene	$C_{10}H_{16}$	400	623	155	1.60	2.2E-06	0.27
β-Pinene	$C_{10}H_{16}$	320	3445	618	2.00	4.0E-07	0.07
Myrcene	$C_{10}H_{16}$	71	110	141	8.98	1.3E-05	0.30
α-Phellandrene	$C_{10}H_{16}$	132	17	21	4.84	8.1E-05	1.96

Δ3-Carene	$C_{10}H_{16}$	271	1397	170	2.37	9.9E-07	0.24
α-Terpinene	$C_{10}H_{16}$	103	2	11	6.24	5.6E-04	3.76
ρ-Cymene	$C_{10}H_{14}$	1577	>90000	>90000	0.41	1.3E-09	2.7E-05
Limonene	$C_{10}H_{16}$	145	246	127	4.41	5.6E-06	0.33
γ-Terpinene	$C_{10}H_{16}$	140	369	53	4.57	3.8E-06	0.78
Isoprene	C_5H_8	238	4069	238	2.69	3.4E-07	0.02

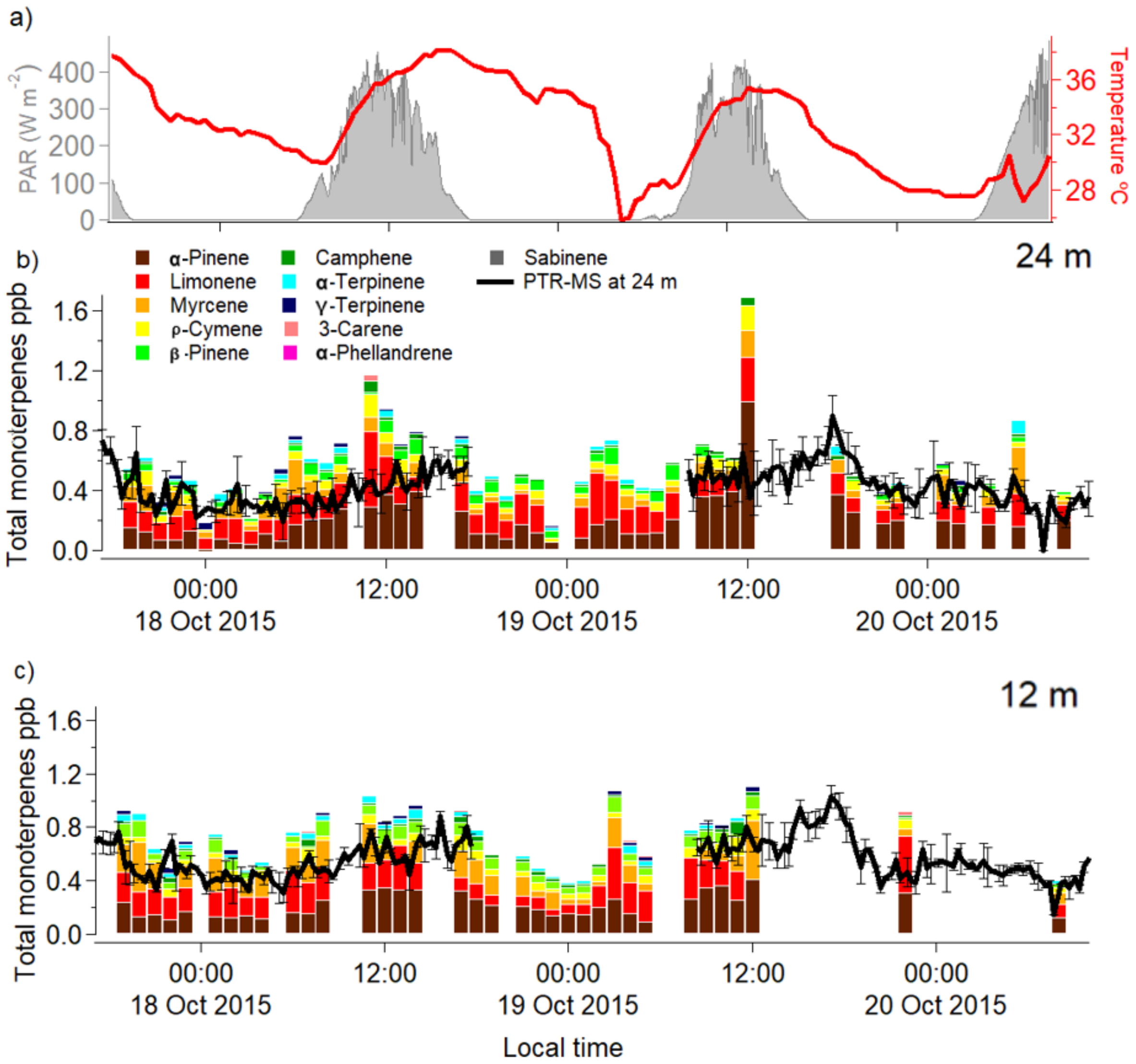

Figure 1: Graph showing the speciated monoterpene mixing ratios measured hourly from 17 to 20 October 2015 for ~~b)~~ 24 m (b) and ~~c)~~ 12 m (c). The colours on the stacked bar plot indicate the different monoterpene species as they are denoted in the legend. The black line represents the PTR-MS total monoterpene mixing ratio, with a gap of data on the 19 October 2015. Temperature at 80 m is shown ~~in~~ as the red thick line and photosynthetically active radiation at 39 m is shown ~~in~~ by the shaded areas ~~in~~ (a).

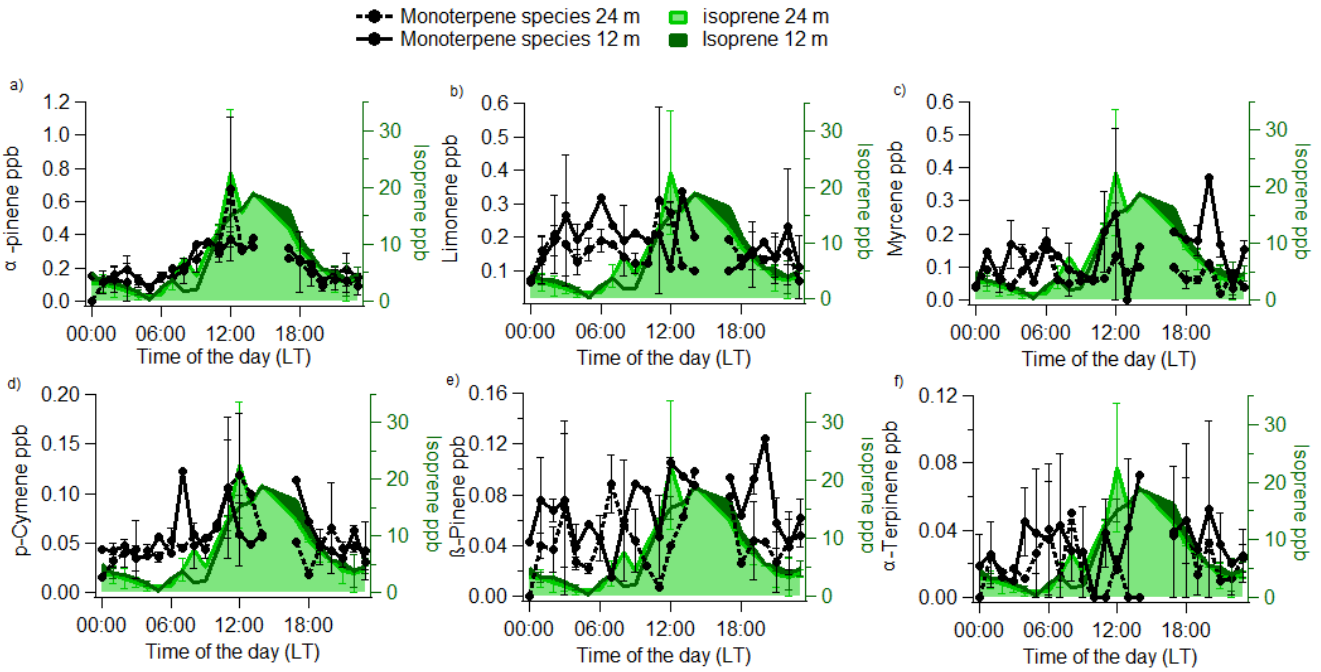

Figure 2: Average diel cycles for α-pinene (a), limonene (b), myrcene (c), ρ-cymene (d), β-pinene (e) and α-terpinene (f) mixing ratios for 24 m (dashed line) and 12 m (thick line). In the back, average diel cycle of isoprene mixing ratios as measured by the GC-FID are shown for 24 m (light green) and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

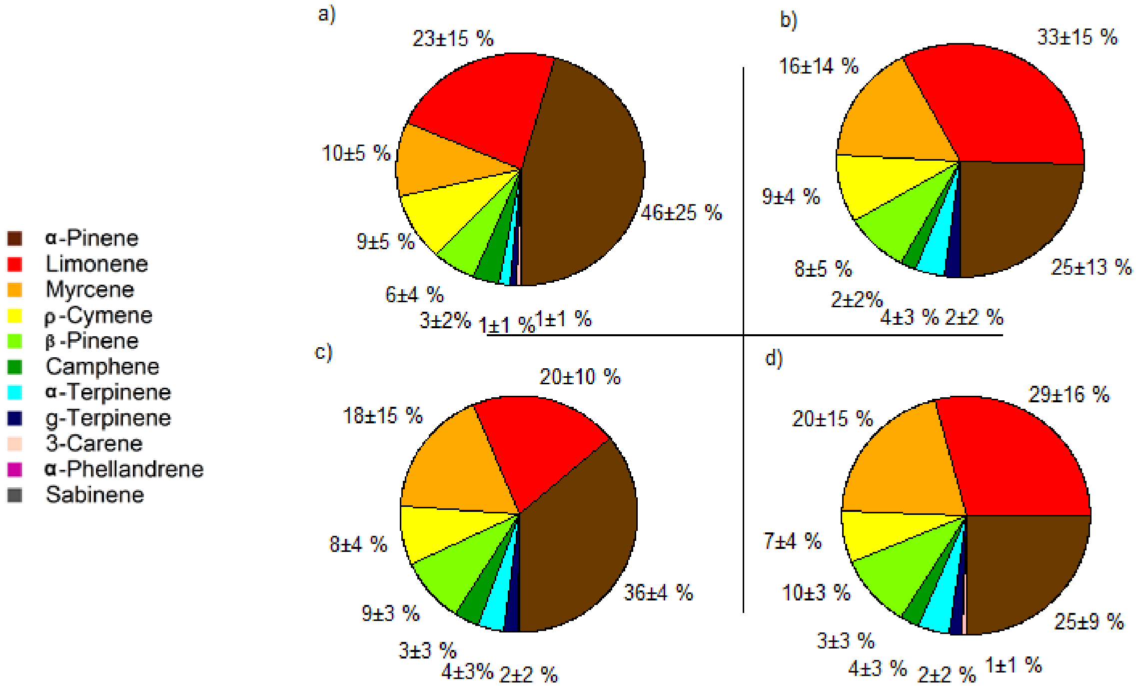

Figure 3: Pie charts representing the day (a and c) and night (b and d) average~~t~~ monoterpene species abundances from 17 to 20 October 2015, ~~in~~with the average percentages and standard deviations at 24 (a and b) and 24 (c and d) m. ~~D~~The day period was from 0900h to 1700h and the night period was from 2000h to 0500h.

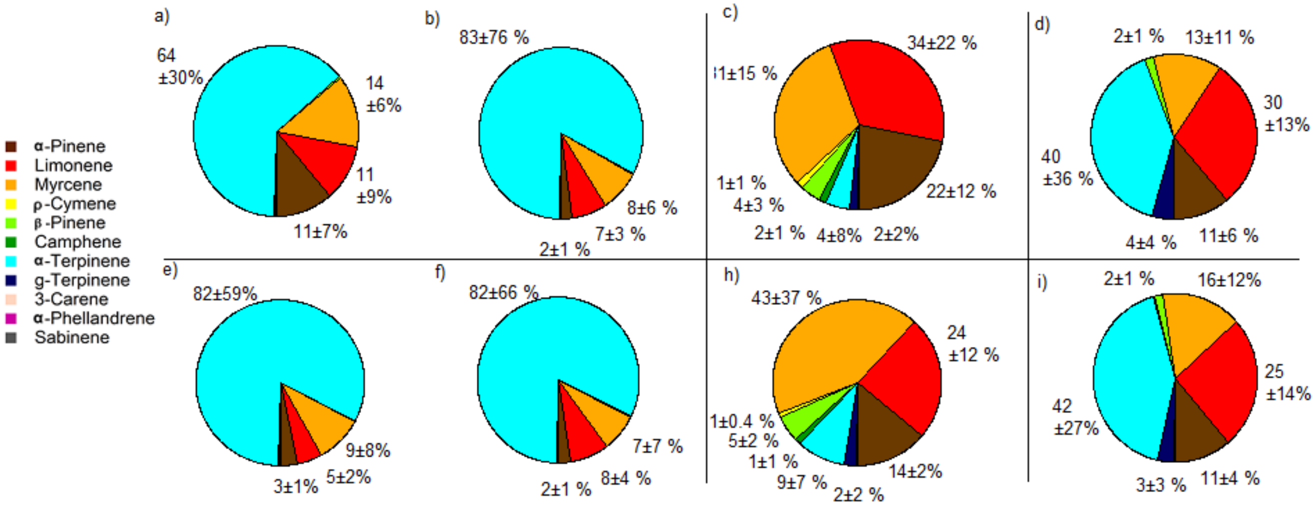

Figure 4: Pie charts representing day (a and e) and night (b and f) ozone reactivity, OH reactivity (only for day, c and h) and NO$_3$ reactivities from 17 to 20 October 2015, with the average percentages and

standard deviations (only for night, d and i), for 12 m on the bottom and 24 m on the top. The day period was from 0900h to 1700h and the night period was from 2000h to 0500h.

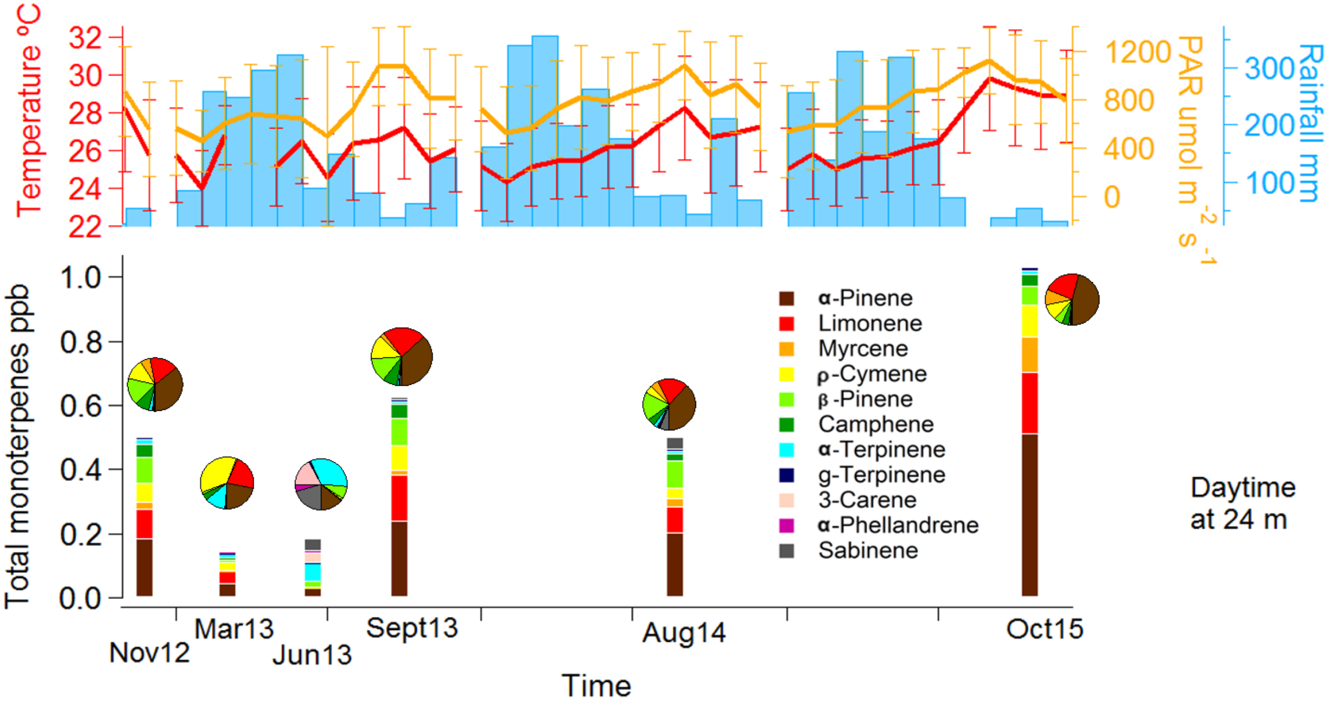

Figure 5: Monoterpene mixing ratio chemical speciation during the seasons of measurement~~s~~. In the top, the monthly average of temperature (in red) and photosynthetically active radiation (in orange) are displayed with their standard deviations for the 80 m height. Rain, also on top, is displayed as mm per month (bars). ~~In~~ At the bottom, the different monoterpene species are differentiated by colours, stacked together adding up to the sum of monoterpenes. On top of each bar, a chart pie with the chemical speciation is shown for easier visualization.

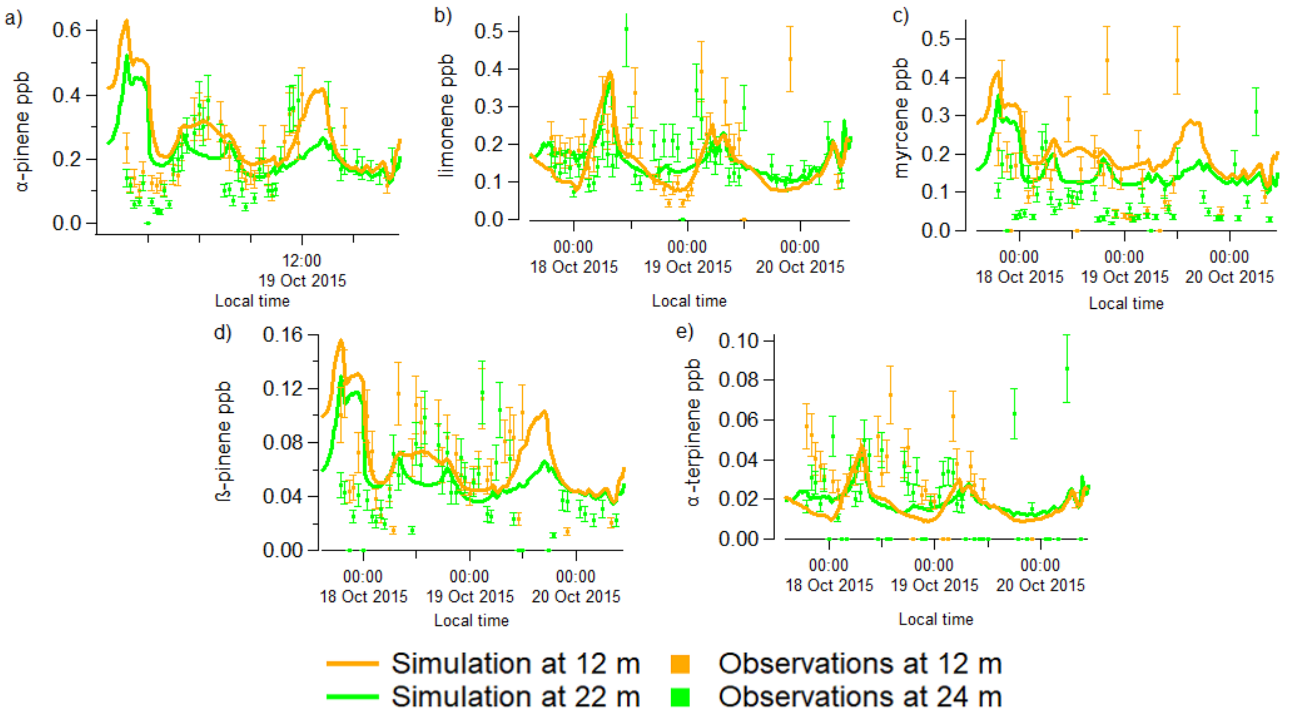

Figure 6: Comparison between- simulated results (solid lines) for 12.5 m (orange) and 22.5 m (green) from ~~the~~ MLC-CHEM, with the GC-FID speciated mixing ratios measurements (in ppb) for α-pinene (a), limonene (b), myrcene (c), β-pinene (d) and α-terpinene (e) at ATTO from 17 to 20 October 2015. The error bars represent the 20% uncertainty involved in the GC-FID measurements.