

Review of

BVOC and speciated monoterpene concentrations and fluxes at a Scandinavian boreal forest

by Ross Charles Petersen et al.; MS No.: egusphere-2024-3410.

General comments

Despite the relatively large importance of boreal forests in the global biosphere and their interaction with the atmosphere e.g. by emissions of BVOC still only few data sets provide direct BVOC flux measurements. This work contributes with a long time series of BVOC flux measurements and speciation of individual monoterpenes. It is a valuable contribution to our understanding of BVOC fluxes in boreal forests in summer and well within the scope of the journal. Therefore, I recommend publication in ACP after major revisions as indicated below.

Specific comments

The abstract should give the concentrations and fluxes of the most relevant BVOC observed including their uncertainties during day and night.

Define in the introduction the difference between fluxes, emissions, and potentially different emission 'surfaces'.

The results section contains several short parts without sufficient discussion or links to the other sections. Consider restructuring this to achieve a better scientific storyline. You could revise the discussion of the uncertainties e.g. by combining them in the method section so that the reader can understand the significance of the following results better. Section 3.2. contains information on the gradient method which could find place either in the method section or the appendix.

Consider adding a comparison to an emission model like MEGAN2.1 (Günter et al., 2012). This could be useful to rationalize your observations and to potentially improve the model.

Consider adding a comparison of the terpenoids with other BVOC or their sum. This would be useful for a better general understanding but also of potential shifts in emissions of different BVOC depending on changing environmental parameters. In this context also the speciation of the SQT would be a useful information you could add. A comprehensive discussion on how the different environmental factors impact the different BVOC is somewhat missing.

For a comprehensive discussion of the BVOC chemistry in the forest a comparison of your observations with a model like the chemical transport model SOSAA (Zhou et al., 2017 <https://doi.org/10.5194/acp-17-14309-2017>, 2017) could be useful.

The discussion and implementation section should be focused on the main novel results with respect to the actual state of the art.

Abstract

L21 10 Hz is not high frequency; please reformulate.

L28 Quantify the major MT fluxes and relate them to the total BVOC flux and typical values in comparable forest.

L29 Specify the summer shifts in D3-carene emissions in the abstract.

1 Introduction

L35 Please use OH, and NO₃ radicals throughout the manuscript.

L43 Use peroxyacyl nitrates as general term since peroxyacetyl nitrate is a specific compound.

L46 Use BVOC and AVOC for biogenic and anthropogenic VOC and not anthropogenic BVOC (check the text further on).

L46 Try to be quantitative in your statements according to the references. Globally up to 90% of the VOC are BVOC.

L63 The sentence is unclear, please reformulate: "Isoprene is mainly involved in influencing production and lifetime of tropospheric ozone (Atkinson and Arey, 2003) and can be rather ineffective at increasing SOA yields in the troposphere with respect to MT."

L73 Specify typical chemotypes that have been identified in previous work for the Scots pine and Norway spruce.

L92 Mention also other potentially important environmental parameters (e.g. RH, soil moisture, ...) and discuss how they can impact BVOC emissions.

L98ff Be more specific on the criteria needed for good eddy covariance measurements.

L103-104 give a reference

L105 consider using "relatively fast" instead of "high frequency". Explain that you need to measure faster than the typical atmospheric fluctuations (e.g. 5 Hz or faster).

L105-107 The sentence is too long. Point out to what extent the method can be used to determine BVOC fluxes on ecosystem scales instead of one specific tower with a limited footprint. See e.g. Pfannerstill et al., *Environ. Sci. Technol.* 2023, 57, 41, 15533–15545.

L115 Add a citation for the MEGAN model.

2 Methods

Explain how the environmental parameters like radiation, RH or soil moisture were measured.

Figure 1: Please show the extent of trees around the tower in summer 2020 as this is hard to see on figure 3.

L168 & L173 avoid giving estimates like "ca. 4.7 s" but give the value and an uncertainty e.g.: (4.7±?) s.

L183 Explain the differences in sensitivities and e.g. relative sensitivities for isoprene, monoterpenes, and sesquiterpenes of your calibrations vs. Jensen et al., 2023.

L189 Can you say how large the typical mass drift was within 6 minutes?

L213 Did you compare the innFLUX results with a different software? E.g. one of those participating in the recent comparison by Lan et al., *AMT*, 17, 2649, 2024, <https://amt.copernicus.org/articles/17/2649/2024/>.

L219 Rather "Adsorption sampling and TD-GC-MS analysis", or?

L288 Discuss the systematic uncertainty of the gradient based flux determination employing a two point profile measurement. This should add to the uncertainty of the concentration measurement.

L289 Adsorption sampling, or?

L291 Explain all abbreviations when used first e.g. ATD-GC-MS.

L320 Is this method really resulting in landscape-scale emission information. Please be precise in the wording in the following and what you can really learn from the analysis of tower measurement on the landscape-scale.

L331 Explain how you determined the canopy temperature.

L314 Rinne et al. (2012) pointed to the large uncertainties of this methodology. How do you justify using it in a two point “gradient” analysis?

L319 Explain why you used this approach instead of comparing e.g. with the MEGAN model?

3 Results

L341 Give the environmental conditions like precipitation or soil water content in a quantitative manner.

L345 Give indicators for the variability.

L345-349 Give a description of the additional measurement methods (e.g. ozone) in the method section.

Figure 2: I guess the upper panel shows mixing ratios of isoprene, monoterpenes and sesquiterpenes but not of ions, or? The pie charts are hard to read. You may better plot them larger and separately. Another panel with wind speed and direction as well as precipitation would be useful. The environmental conditions for the June measurement days are not given.

Figure 2a: It would be nice to have a comparison of the MT concentrations derived with the two independent methods. Consider adding the mean total MT concentrations measured by TD-GC-MS for each of the three daytime periods by symbols with uncertainties.

Figure 2b: It would be nice to have a comparison of the MT fluxes derived with the two different methods. Consider adding the mean fluxes estimated by the SLG method for each of the three daytime periods by symbols with uncertainties.

L364/365 You didn't sample gradients. Please revise the sentence.

L365 Describe the flux footprint model in the method section.

Figure 3: The caption doesn't explain the figure. Only green lines but no red or blue. What is the grayscale background showing?

L373 The VOCUS inlet was at 35 m, or?

L392-393 Please add the information on when the different conditions were prevailing and how this has influence on the results presented.

L399 Isoprene emission should be replaced by isoprene fluxes or concentrations.

L405 Be more specific which time period you mean, the summer season, a defined campaign period or just the time for which you did the EC flux measurements?

L424-425 it would be helpful for the reader to have the estimated chemical lifetimes for SQT, MT, Isoprene.

L429 Figures 5e&h show concentrations but not fluxes. Revise the wording regarding emissions.

L432 It would be useful to add the observed behaviors of other BVOC of biological relevance, e.g. acetone, acetaldehyde, hexanol, in comparison with the isoprene, MT, and SQT in figure 5.

L436 Explain what the surface is. Did you calculate the exchange rates for canopy level emissions?

L438 Define the SER vs. E in $R=F/E$. Are they the same?

L440 Please explain which reactions are included. Can you identify from the off-line GC-MS analysis the major SQT species and justify if using the relatively high rate coefficient of β -caryophyllene especially with ozone for all SQT is justified?

L447 Why don't you give an average value for nighttime F/E with uncertainties as for the other cases?

Figure 7: Improve the visibility of the different lines and axis labels.

L476 Explain why you don't use e.g. the MEGAN model here for comparison.

L508 Explain how you choose the other VOCs and why you don't treat the biogenic ones in a similar way as the terpenoids before. It may be useful in terms of understand changing plant physiology with environmental conditions.

L527 Consider adding the speciated SQT here as this another interesting group of indicators for the plant physiology.

L533: Figure A4: Please give the data with the same Y-axis to allow for better comparison. It would also help the reader if the order of the compounds would be the same as in figure 9. Please add the sum of the MT values and the values from the on-line analysis (VOCUS) for the same time periods. Make clear that these are daytime (09:30-17:00) and not daily data!

L535-537 You don't give uncertainties here. Is this change really significant?

L538 Consider summarizing the data in a table including the sum of the MT concentrations.

L545 Figure9: Consider adding the sum of the MT values and the values from the on-line analysis (VOCUS) for the same time periods (daytime). Make clear that these are daytime (09:30-17:00) and not daily data!

L553-555 Is this a comparison of the mean daytime values and what are the uncertainties given? Here the accuracies should be given.

Figure 10: Rescale to make the variation over daytime better visible. The sum values given in the text have higher values for the on-line measurements but the pots show the opposite.

Can you identify a significant daytime variation the relative abundancies of the individual MT or SQT?

L564 Figure 9 shows the off-line data. Please revise to figure 5. However, this value is hard to see there.

L564-590 The uncertainties discussed in this section should be given and discussed in the sections where the results are presented first or in a concise way in the method section.

Discussion

L594 Please give the results like '2/3rds' with uncertainties and averaging period.

L596 You did show differences in fluxes of MT e.g. in figure 9 and A4. Aren't they significant?

L601-605 To long sentence. How do your observations compare with chamber data?

L619 A chemical speciation typically doesn't influence SER, or? Please reformulate.

L620-644 The main issue of this section should be mentioned under 2.8 so that the reader understand the following results better and the details should be added to the appendix. Although you find not a big difference in using the reactivity of α -pinene for all MT for day and night this may not be the case for β -caryophyllene and all SQT for which the chemical degradation is also much more relevant. You should add a corresponding analysis to the method part (& appendix) and discuss the consequences in the discussion section.

L650ff A quantitative comparison of all major sources of uncertainty for the flux determination should be given.

Implications

L655-665 You measured only in one summer season and observed almost no changes in e.g. MT composition. Wouldn't the overall change of BVOC levels with temperature for changing seasons be anyway much more significant for chemical reactivity?

L666 Do you mean the reactivity of the MT mixture decreased?

L672ff The uncertainties given for the changes of oxidative capacity seem to be too small.

L681-687 As mentioned before you should give the speciation of the SQT and the corresponding composition based flux estimates in the results section.

L691-693 You didn't measure OH and NO₃ radicals. Please reformulate.

L695-699 To long sentence. Please revise.

Code and data availability

L701 Consider making e.g. the timelines of VOC data also available e.g. via a suitable database.

Technical corrections

L201,255,261,... Please give all equations a number starting with the first one.

L228-L230 write MnO₂

L315 Please use subscripts for all chemical formulas in the manuscript: NO₃.

L479 E₀

Figure 8: Give the fit functions in a better readable form. E.g. the regression coefficient & function in the plot. The parameters are already given in the text. Give the uncertainties for the temperature dependencies and add correct units on the temperature axis.

L483-485 β in °C⁻¹; also in the following.

L533 Add a dot after figure 9.

L547 Figure A4 not A8.

L596 Delete 'clear' in this sentence.

L628 β -myrcene instead of b-myrcene

L637 O₃, NO₃

L695 Delete one ,to'.

L1140ff Give the table captions on top of the tables.