This study examines the transfer efficiency of different BVOC in a self-made cylindrical semi-open dynamic chamber designed to conduct BVOC measurements from a branch enclosure. The results show how the higher airflow through the cuvette system reduces the equilibration time, adsorptive loss of volatiles, as well as the differences between the ambient and enclosure temperature and relative humidity. Furthermore, the authors found that the transfer efficiency was low for some BVOC (i.e. α-pinene and β-caryophyllene) even at the condition with low residence time. The authors conclude that performing the BVOC measurements on a well-characterized cuvette system is paramount to determine correct emission factors.

Overall, I appreciate the technical characterization of the cuvette system, and I fully agree that it is important to test a new cuvette system before starting BVOC measurements. However, it is known that heavier volatile such as the C10-C15 analyzed in this study, a significant loss of volatiles occur due to adsorbance to surfaces and tube system (e.g., Bourtsoukidis et al. 2012, Niinemets et al. 2011). A way to consider that loss is to perform the calibration by passing a certified BVOC standard mixture throughout the whole system (e.g. Ghirardo et al. 2011, 2020). Because the instrument's sensitivities are based on measurements performed at steady-state conditions and are calculated using the inlet air standard concentrations, the potential loss of volatiles (due to any chamber effects, including adsorption, gas-phase reactions etc.) won't affect the correct determination of the emission factors. Since BVOC standards are available (and some companies offer a broad customized mixture) and in any case are required for the calibration of PTRMS or GCMS instruments, it remains unclear why the chamber-based BVOC measurement technique could not be based on such a commonly used calibration procedure. Therefore, I do not see how this paper makes a substantial contribution to the field.

Reply: Thanks for your comments. In fact we had noticed the amazingly good practice of whole system calibration by Ghirardo et al. (2011, 2020), we have modified our discussion and cited these references in our references. We did not follow the method by Ghirardo et al. (2011) for reasons including: 1) the main purpose of this study is to evaluate the performance of a dynamic chamber considering deviations from real emission rates and real environmental parameters; that is, how to minimize the adsorptive loss by surfaces and disturbance to the naturally growing conditions. For this purpose it would be better not to consider the whole system as a "black box" and conduct the whole system calibration. As a matter of fact, our study reveal that both adsorptive loss on walls and disturbance to the naturally growing conditions could be largely reduced simply by choosing a proper flow rate. So we think our results do bear some useful implications and thereby make a little bit contribution to the field. 2) We had read carefully the work by Ghirardo et al. (2011) and tried to find what kind of the calibration curves the authors had obtained. We did try this approach in our study. We thought we should wait for a steady state even performing the calibration by passing the standard mixtures through the whole gas exchange system. Theoretically, adsorption is complex process although there are already models to describe the adsorptive behaviors. In fact, in our practice of whole system calibration, it seemed that we could not get satisfactory linear or exponential fitting calibration curves, and therefore might be substantial errors due to the calibration. Moreover, during field tests, surface areas inside the

chamber including chamber wall surface areas and surface areas of enclosed leaves, so surface areas would change case by case and thus calibration is needed case by case. This is one of reasons why we did not practice this whole system calibration in our study. 3) although we used PTR-ToF-MS in our study, its usage was limited to lab tests and tracking the trends in the field if it could be brought to the measurement site. PTR-ToF-MS has three fatal shortcomings in monitoring BVOCs: a) It can not differentiate monoterpene and sesquiterpene isomers and can only give collective signals for monoterpenes and sesquiterpenes. This is more and more unbearable as monoterpenes or sesquiterpenes may vary greatly in their atmospheric behaviors. b) PTR-ToF-MS can not be so portable as the offline samplers and for field tests it is hard to bring them to places that vehicle can reach, otherwise you may need very long tubes to introduce air from the chamber to the PTR-ToF-MS, and this indeed would induce other concerns like dead volume, time delay or more adsorptive loss and memory effect. Therefore in our field tests, we rely on the sampling with sorbent cartridges in the field followed TD-GC-MS in the lab to get emission rates for speciated BVOCs. This way it is difficult to conduct the whole system calibration.

Nevertheless, we do regard the whole system calibration by Ghirardo et al. (2011) as a very wonderful approach, particularly if dynamic enclosure conditions are optimized as described in this study. The who system may be calibrated online by passing circulating air doped with deuterated monoterpenes and sesquiterpenes while conducting field tests, or releasing the deuterated monoterpenes and sesquiterpenes standard mixture into the chamber during the field tests. This way the calibration of target species as well chamber performance evaluation can be both achieved. We have added this concern in the conclusion part in the revised manuscript:

"In the future, surrogate compounds like deuterated monoterpenes and sesquiterpenes can be added in the circulating air as did in our lab simulation study, to track the chamber performance and to correct the losses. Ghirardo et al. (2011, 2020) performed calibrations by passing a mixture of VOCs in N_2 through the whole gas exchange system. Inspired by this approach, in field tests deuterated monoterpenes and sesquiterpenes can be doped into circulating air, or deuterated monoterpenes and sesquiterpenes standard mixture can be released into the chamber at a constant flow rate. This way we may both calibrate target species and evaluate chamber performance."

Other limitations:

Ozone: the system does not use ozone-free conditions, meaning that some of the VOC will disappear by reacting with O3. Given that the lifetime of b-caryophyllene (one major sesquiterpene) in the presence of 40 ppb of O3 is of ~1.5min-1 (Rinne et al. 2007) and that the measurements were performed using conditions that lead to a residence time of 0.9-4.5 min., I would expect that a significant part of the SQT will be lost mainly by O3 reaction (but also with OH and NO3). Notably, because the OH, NO3, and O3 concentrations cannot be controlled and their concentrations are fluctuating through the day/weeks, and ozone levels might reach 100ppb in your study (L200), how can the authors measure reliable emission factor of SQT under variable pollutant conditions with the proposed cuvette/chamber method?

Reply: The purpose of using ambient air in this study is to reflect BVOCs emissions under real

atmosphere conditions. The most important BVOCs species, isoprene and monoterpenes, may be less affected by O_3 in the chamber due to short residence time and longer lifetimes of these species relative to sesquiterpenes. For BVOCs like some sesquiterpenes (e.g. β-caryophyllene) reaction with oxidants like O_3 in the chamber might be of concern. Yes, as reported by Rinne et al. (2007), lifetime of β-caryophyllene is ~1.5 min^{-1} under 40 ppb of O_3. However, more recent papers revealed quite different results. For example, Helin et al. (2020) reported that the losses of several sesquiterpenes including β-caryophyllene were less than 5 % when reacting with O_3 under mixing ratio of 40 ppbv for 5 min; Bourtsoukidis et al. (2012) also reported that SQTs losses due to reaction with O_3 (3-84.5 ppbv) did not show any substantial deviations on the calculated emissions when measuring terpenoid emissions from Norway spruce (*Picea abies*) using a glass chamber with residence time of ~8.3 min. Considering these recent results, we think reaction losses of SQT in our chamber with residence time of <1.5 min will be negligible. In fact, as stated in our manuscript, the residence time of circulating air can be further shorten by increasing flow rates since the detection of BVOCs is not a problem even when flow rates increased up to 50 L min^{-1} with residence time of ~15 seconds. This way the reaction losses of SQT could be further reduced.

Temperature sensors: Are leaf temperatures being recorded to link ambient to leaf temperatures beside the inside and outside air temperatures of the cuvette?

Reply: The leaf temperature may slightly differ from the air temperature in the chamber (Kuhn et al., 2002; Ortega et al., 2008). But this temperature deviation may be not significant as observed by Bamberger et al. (2017). In this study, we had two thermocouples to monitor the leaf temperature, four thermocouples to monitor the inside air temperature, and two T/RH sensors (one inside the chamber and another outside the chamber) to determine the enclosure-ambient differences in temperature and RH.

The methods describing the enclosure experiments using standards in the laboratory are not given.

Reply: As suggested also by another reviewer in this aspect, we made some changes in the revised manuscript (L. 254-261).

We have changes the sentences: "The real-time concentrations of the standard mixtures in the chamber were measured by PTR-ToF-MS, and the concentrations of these VOCs stored in the stainless steel canister were also measured by PTR-ToF-MS before introduced into the chamber. Acetonitrile, acrylonitrile, acrolein, acetone, isoprene, methylacrolein, α-pinene and β-caryophyllene were detected with *m/z* 42.019, 45.015, 57.073, 59.052, 69.060, 71.040, 137.072 and 204.986, respectively. Transfer efficiency for each compound is expressed as the ratio (%) of outgoing air concentration and incoming air concentration at steady state." As below:

"Mixing ratios of each compound in the standard mixture stored in the stainless steel canister were initially measured by PTR-ToF-MS. The standard mixture was mixed with pure dry air and the mixing ratio of each compound (C_1) in this mixed air was measured by PTR-ToF-MS. This mixed air was switched into the camber at a constant flow to simulate BVOCs emissions from enclosed plant branches, and the steady state concentration of each compound (C_2) in the chamber was

How does humidity affect the sensitivities of the VOC? Here it would be helpful to separate chamber effects to instrumentation challenge (humidity can strongly affect the sensitivity of the PTRMS of some VOCs). Also, it is important to separate VOC according to their octanol/water coefficient and polarity, as there are clear humidity effects for e.g, oxygenated monoterpenes compared to isoprene.

Reply: Yes. The detection of some water-soluble compounds by PTR-MS may be slightly affected by humidity. For instance, slight variations of sensitivity (ncps ppb^{-1}) were observed for acetic (13.51-9.40 ncps ppb^{-1}) and formic acid (8.98-5.69 ncps ppb^{-1}) with relative humidity (RH) changing from 11 % to 88 % (Baasandorj et al., 2015). However, the humidity effects have been found to be not significant for hydrophobic compounds like isoprene, aromatics, monoterpenes and sesquiterpenes, and even for some water-soluble compounds like acetonitrile, acetaldehyde and acetone (Baasandorj et al., 2015; Sarkar et al., 2016; Huang et al., 2017). For example, Sarkar et al., 2016 reported that the sensitivities for acetonitrile and acetaldehyde remained very stable under RH of from 60% to 90 %. We have also confirmed in the lab that when testing incoming air with same target VOCs levels but different RH by PTR-MS, no significant humidity effect is found for detecting the target VOCs.

As for discussing the humidity effect by separating VOCs according to their octanol/water coefficient and polarity, we think it is a very good idea and did consult many experts in related fields. The octanol/water coefficient, or K_{ow}, is widely used as a primary measure of the tendency of a compound to move from the aqueous phase into lipids, and polarity is closely related to the water solubility. Some experts argued that adsorption of VOCs on surface is the interaction between air and solid surface (or water film on solid surface under much high RH), and K_{ow} might not be a good indicator, and instead there are many models to describe the adsorption dynamics, and the adsorption might be much more complex than Kow-controlled partition. They say if we interpret the adsorption in terms of K_{ow}, we would suffer more "attacks". As stated in the text, theoretically the influence of RH on adsorptive loss depends on the competition of adsorption sites by water molecules on the surfaces and the modification of energy spectrum of the adsorption sites by condensed water on the surfaces. So it is far more complex than expected. As humidity seems to have much smaller effects than parameters like flow rates and temperature, so we did not go further to have in-depth discussion about this topic.

The first paragraph of the results section does not report any results but rather some method and discussion. Therefore, this should be fixed.

Reply: Thanks. We have merged this paragraph into Sect. 3.1.

L187: I do not think so. See my comment above.

Reply: As replied above, more recent studies demonstrated that the influence of ozone on sesquiterpenes might be not so large as predicted by Rinne et al. (2007). To reflect the real emission, we used ambient air as the circulating air. Possibly there are some losses for more reactive BVOCs in the chamber due to reaction with O_3. To reduce the reaction losses of important BVOCs, the residence time of circulating air were shorten to < 1.5 min, and this residence time and the reaction losses can be further reduced by increasing flow rates in field tests.

Minor comments:

L24: why "absorption" and not "adsorption"?

Reply: Thanks for your careful check. It should be "adsorption" instead of "absorption". We have got it revised. (Line 24)

L205: which compounds have been used for testing? Did you include sesquiterpenes?

Reply: Here we just used some monoterpenes for testing. The $Na_2S_2O_3$ filter and Teflon sampling tubes would have less impact on losses of BVOCs including sesquiterpenes according to previous studies (Jones et al., 2014; Hellén et al., 2012; Helin et al., 2020; Fang et al., 2021).

L208: Fig. S2 contains the schema of the experiment. It would be helpful to see the data.

Reply: We have showed the data in the Supplement (Table S2)

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L253: "concentrations" are not "emitted by plants".

Reply: Here we refer to the BVOCs species emitted by enclosed plant leaves.

L321-326: that depends on the calibration procedure…

Reply: As we stated above, the calibration of instruments and characterization of chamber system were done separately in our approach. In this study and in most other field studies, characterizing BVOCs losses in the chamber is very important for obtaining accurate emission factors.

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