Reply to comments by Reviewer #1

General comments:

The manuscript gives a good example on an evaluation of a semi open dynamic BVOC chamber. While technical in my opinion nothing significant new was introduced, the throughout characterization (e.g. transport efficiency) and behavior of different BVOC types in such chamber systems is quite helpful for further developments and corrects of such chamber setups. Currently the manuscript lacks at some parts detailed information and two major issues regarding measurement of the flow rate and background concentration C_0 arises. Length and language wise the manuscript is good. Also it would be nice if the author would show some estimated emission rates from the field test.

Abstract: Concise with enough information

Highlights: Make sense.

1 Introduction: The introduction shows the general issues and importance of testing /characterizing BVOC chamber systems in order to generate correct emission inventory data or to perform BVOC related plant experiments. Length of the introduction is sufficient. Most actual literature is covered.

2.1 The description of the chamber system lacks some details and some questions is arising regarding the measured flow of the chamber, since it is not clear if both analyzers and the automatic sampler add up to the total flow. Also I am missing a leaf temperature sensor, since air and leaf / branch temperature can slightly differ from the ambient air temperature due to heat up from the incoming radiation. Did you consider to add such as sensor or why is it not installed? Also a real photograph of the chamber should be included into the manuscript (e.g. as Fig 1 B or to the supplement) to see the construction.

Reply: An accurate flow rate is vital for calculating the emission rate. Sampling flow rates of both analyzers and samplers are constant as controlled by mass flow controllers, and these flow rates are added up to the total flow. In the revised manuscript, we added these sentences to make clear:

"Airflow for online analyzers was shunted from the main airflow through hole "3". Flow rates of online analyzers (F_2, 200 ml min^{-1} for PTR-ToF-MS and F_3, 500 ml min^{-1} for Li-7000) and automatic sampler (F_4, 200 ml min^{-1}) are controlled by built-in MFCs, and total flow rate of circulating air is the sum of these flows ($F = F_1 + F_2 + F_3 + F_4$) that is used to calculate emission rates. In addition, the accurate flow rate ($F_1 + F_2 + F_3$) through hole "3" is also measured by a soap-membrane flowmeter (Gilian Gilibrator-2, Sensidyne, USA) before and after each measurement in the field." (Lines 156-161 in the latest manuscript).

We fully agree that the leaf temperature may slightly differ from the air temperature in the chamber, as also pointed out in previous studies (Kuhn et al., 2002; Ortega et al., 2008). This temperature deviation may be not so significant as observed by Bamberger et al. (2017). However, due to the great influence of temperature on BVOCs emissions, we did add two thermocouples to monitor the leaf temperature, four thermocouples to monitor the inside air temperature, as well as two T/RH sensors (one installed inside the chamber and another installed outside the chamber) to monitor the enclosure-ambient differences in temperature and RH. We have also added sentences to indicated this in the revised manuscript:

"Four thermocouples (HTK305000, OMEGA, USA) are used to monitor air temperature inside the chamber and another two thermocouples (ST-50, RKC, Japan) are used to monitor leaf temperature. And temperature and humidity data are recorded by a data logger (HR7000, Zhejiang Jiangheng Instrument equipment Co. Ltd, China)." (Lines 163-167).

As suggested we have added real photos of the chamber in Fig. 1 (see below).

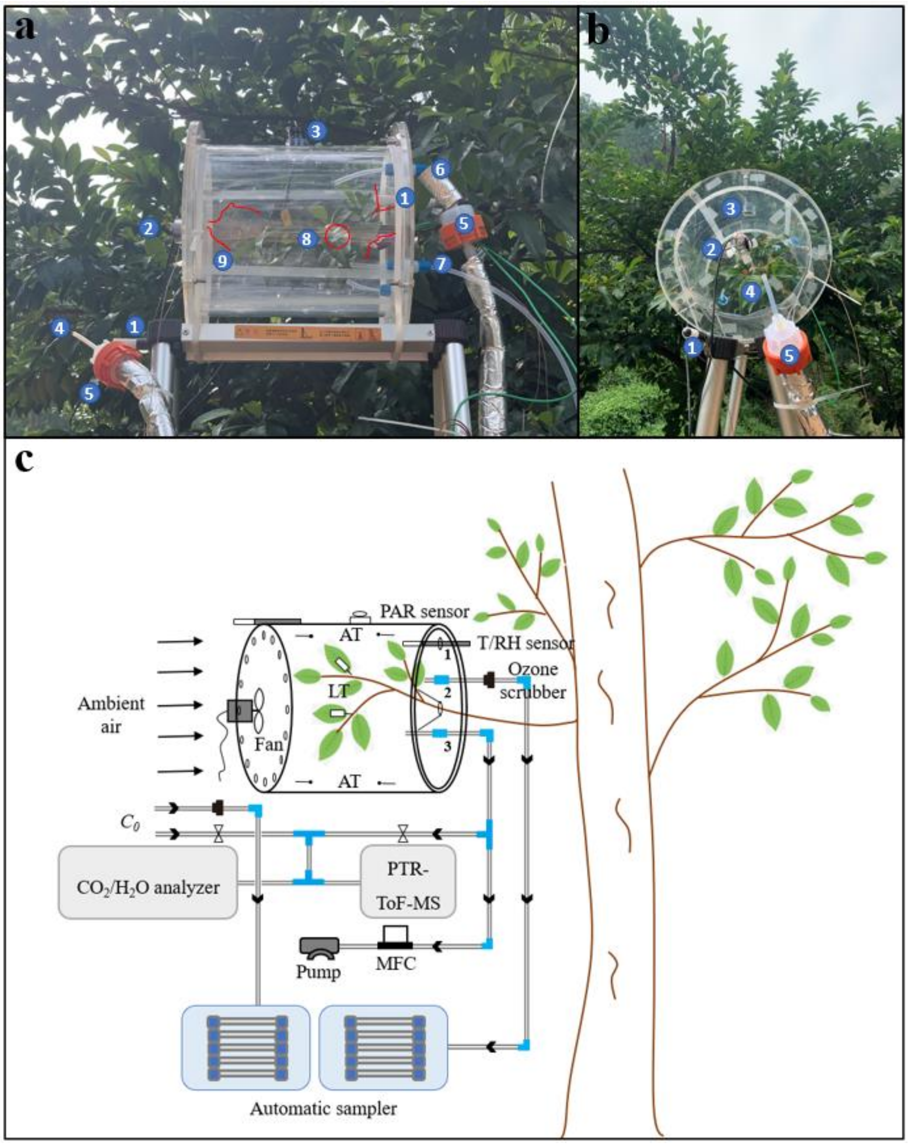

Figure 1. Photographs and schematic diagram of the semi-open dynamic chamber system for field measurements of BVOCs from plant leaves. (a) and (b) are real photographs of the chamber in the field: (1) T/RH sensors, (2) Teflon fan and electric motor, (3) PAR sensor, (4) Teflon sample tube for ambient air (C_0), (5) Ozone scrubber, (6) Teflon sample tube for chamber air (C_{in}), (7) Teflon

tube for main airflow, (8) Thermocouples (red circle) for leaf temperature, (9) Thermocouples (red lines) for chamber air temperature. (c) is the schematic diagram of the chamber, and MFC refers to mass flow controller. LT and AT refer to leaf temperature and air temperature, respectively.

2.2. Logical and sound description Some details are missing.

Reply: We have added more details about the collection and analysis of BVOCs samples in the revised manuscript (Lines 176-178; Lines 190-197). Chromatogram of standards and calibration curves were also added in the supplement (Fig S1-S3.).

2.3. Okay

2.4 Nice and interesting test. It is not clear if the holes of the inlet were closed. Please describe the sample setup a bit better.

Reply: The inlet holes were closed while we conducted tests in the laboratory. We have added more descriptions about the sample setup in the revised manuscript.

The description in the original manuscript “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.” has been changed in the revised manuscript as:

“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 again measured by PTR-ToF-MS. Transfer efficiency (%) of each compound was then calculated as the ratio of C_2/C_1. Concentrations of acetonitrile, acrylonitrile, acrolein, acetone, isoprene, methylacrolein, α-pinene and β-caryophyllene were determined by PTR-ToF-MS with *m/z* 42.019, 45.015, 57.073, 59.052, 69.060, 71.040, 137.072 and 204.986, respectively.” (Lines 252-261)

2.5 Overall ok. Some info’s are missing. How is the inlet concentration C_0 measured or did you use a second empty chamber for this? How long are the tubing in these field tests, since the chamber were in 20m and 12m height? Does length of the tubes play a role in terms of compound loss / adsorption and in case of the automatic sample add a dead unflushed volume?

Reply: The concentration C_0 of incoming ambient air was determined by sampling ambient air near the inlet with adsorbent cartridges for offline TD-GC/MSD analysis. In field tests, the chamber was generally installed at heights of ~2-3 m, and the portable sampler can be installed just near the chamber for sampling with adsorbent cartridges and the length of 1/8" Teflon tube is within 1.5 m with a dead volume within ~ 5 mL, which is far smaller than the sampling volume of 2 L. Moreover, air sampling was conducted after a steady or pseudo-steady state is reached, and the sampling volume is calculated based on sampling time and flow rate controlled by MFC, so the tubes would not influence the sampling volume. In terms of compound loss/adsorption, for a 2m×1/8" Teflon tube, its inner surface area is less than 2% of the Teflon-coated surface area of the chamber, so loss/adsorption due to the tube is negligible. However, the influence might be larger for online analysis with PTR-ToF-MS, since PTR-ToF-MS cannot be placed near the test tree in most field campaigns and thus a much longer tube (~20 m) is needed. This case the adsorption loss on the tube wall is of concern. As air is drawn continuously by the PTR-ToF-MS, the adsorption may be greater initially but would be largely diminished later on after a dynamic equilibrium is reached. We only use PTR-ToF-MS to monitor the real time changes, and not use it to obtain compound specific emission rates since it cannot differentiate monoterpene isomers or sesquiterpene isomers, and it cannot give a compound specific accurate concentrations as the sorbent tube sampling followed by offline TD-GC/MSD analysis. We did take great cautions on the influence of tubing in our field tests, and as discussed above we think it is not a problem in our technical approach.

3. Should this section not be 3.1 with a header? How is C_0 measured? This was not stated in section 2 and is crucial for all calculations. Also this part might be also fitting more into the method section.

Reply: Thanks for your comments and suggestion. We have merged this paragraph into Sect. 3.1 and stated how the background concentrations of circulating air (C_0) were determined:

“The background concentrations in circulating air (C_0) were determined by PTR-ToF-MS in the lab tests; in field tests they are determined both offline by sampling ambient air near the inlet with adsorbent cartridges followed by TD-GC/MSD analysis back to the lab, and online by PTR-ToF-MS” (Lines 285-288)

3.1. Maybe add that these results are based on the lab test, it is a bit unclear in the beginning.

Reply: In the beginning we want to present theoretically how the concentration changes in the chamber and how long an equilibrium will reach. Then we can verify based on our results from the lab test. To make this more clear, in the revised manuscript we have added “Equilibrium time is vital for evaluating the performance of a dynamic chamber.” (Line 312) and “With the high time resolution online monitoring by PTR-ToF-MS, equilibrium time could be determined more directly in our lab tests.” (Lines 315-316).

3.2.2 Could you please implement a statistical test to verify your result are differing between the humidity ranges.

Reply: We did try the statistical tests. It would be good if we could find significant trends or significant differences. In our tests, at each RH level we have 5 TEs under 5 different flow rates. Unfortunately, for TEs of each compound we did not observed any significant difference among the RHs, and did not observed any significant linear relations between the TEs and RHs.

3.2.3 Interesting idea. Should be somehow tested in future studies in the field.

Reply: Thanks. We are planning this.

3.3 Overall nice insights on the chamber performance. I am somehow missing the report of any emission rates derived from the field tests.

Reply: In this manuscript we did not present the results of emission rates, and instead just showed chromatograms of the detected compounds. Since the focus this manuscript is the performance evaluation, we think it might be unnecessary to present the results especially for its lack of representativeness just from a single test. We are preparing another manuscript about the emission rates measured by our semi-open dynamic chamber for major tree species in subtropical/tropical China, so we did not report the emission rates in this manuscript to avoid the improper use of the unrepresentative emission rates from a single test.

3.3.1 Okay, sound reasonable and should be expected, since heat is transported out of the chamber.

4\. Conclusion Please specify future research a bit more detailed.

Reply: Thanks. We tried to avoid making exaggerated claims/statements about future research. With your kind encouragement, we have added a sentence as below:

"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." (Lines 512-518).

Specific comments:

L.130: specify the pump; is the flow controlled with a mass flow controller? If I interpret Fig 1 correctly the pump is connected to outlet 3 or? So in case you use the automatic sampler another pump is sucking the air the cartridges. Is this also mass flow controlled?

Reply: Yes, the constant flow rate was maintained by a mass flow controller (Alicat Scientific, Inc., Tucson, AZ, USA) coupled with a diaphragm vacuum pump (MPU2134-N920-2.08, KNF, Germany). The flow rate of the automatic sampler was also maintained by its built-in MFC. (Lines 158-160)

L.131: specify the fan

Reply: The fan was customized using PTFE Teflon material by Shenzhen Shuangmu plastic material Co. Ltd, China, and it was driven by an electric motor (BLDC4260, Shenzhen Mingyang Motor Co. Ltd, China) (lines 133-134)

L.138: is the sensor housing also made from an inert material?

Reply: Yes. Sensor housing is made from inert PTFE Teflon material.

L.143: what diameter do the tubes have? Are the connectors / fittings also made of Teflon.

Reply: The tubes are 1/8" inch O.D. Teflon-made ones (Lines 146-147).

L.144. please specify the flowmeter and mass flow controller. The PTRMS and CO2 / H2O analyzer is connected to outlet 3. Do both analyzers have their own pump and mass flow controllers. Does this add up to overall flow? If so, the flowmeter should be placed before the outlet to the analyzers. Other calculations of the emission would be wrong, since you have slight higher flowrate than measured.

Reply: Yes. Both online analyzers and the automatic sampler have constant sampling flow rates that are controlled by their built-in mass flow controllers, and these flow rates were added up to the total flow for emission calculation. To ensure its accuracy, the total flow rates were also calibrated by a soap-membrane flowmeter (Gilian Gilibrator-2, Sensidyne, USA) before and after each measurement.

L.150 Do the air temperature sensors have a radiation protection?

Reply: Yes. The sensors are located inside the PTFE Teflon housing.

L.159: How long is tube to the sampler. Is outlet 2 also constantly flushed by the outlet air? Otherwise you would measure a relative old dead volume of air (depending of the tube length) which does not represent the actual concentration and composition in the chamber.

Reply: Generally, the sampling tube is within 2 m for sampling with adsorption cartridges. As answered above about this concern, the dead volume would have a negligible influence on sampling volume or adsorption loss.

L.164-166. How do you deal with humidity in the cartridges? Is there some pre flush of the tube to extract humidity before it goes into the analyzer?

Reply: Yes. The cartridges were pre-flushed with high purity nitrogen for 3 min at a flow rate of 100 mL min^{-1} in the automatic TD 100.

L.166. What trap material was used?

Reply: The cryogenic trap (U-T11PGC-2S, Marks International Ltd, UK) is a glass tube filled with Graphitized Carbon. We have specified the cryogenic trap in the revised manuscript (Line184).

L.170 maybe add to the supplement what M/Z were selected.

Reply: We have added the selected m/z into Table S1 in the supplement.

L.206 Since you test this with pure nitrogen. Does humidity affect the filter performance?

Reply: Humidity may affect the more water-soluble oxygenated VOCs, but much less to the hydrophobic isoprenoids that are of top priority among BVOCs.

L.208 Is 10.05% a typo?

Reply: It is not a typo. We have re-checked it.

L.239 How did you dry the leaves? Was this done for both tree species?

Reply: The enclosed branch was harvested after each measurement and brought back to the lab to determine the dry mass of leaves after heating in an oven under 60 °C for 48 hours. We have added this in the revised manuscript as "After each measurement, branches in the enclosure are harvested and brought back to the lab to determine the dry mass of leaves after heating in an oven at 60 °C for 48 hours." (Lines 168-170).

L.240 Temperature outside or inside of the chamber?

Reply: The temperature here referred to the ambient air temperature outside of the chamber. We have clarified this in the revised manuscript (Line 266).

L.402 Is there any compound, you would suggest to use which probably does not interact with the plant?

Reply: Yes. Maybe deuterated monoterpenes and sesquiterpenes that have very similar behaviors as the normal monoterpenes and sesquiterpenes can serve as ideal surrogate compounds. We have mentioned this in the revised manuscript. (Lines 512-514)

L.408 it should be tissue temperature

Reply: Yes. We have made this clear (Line 446).

L.430-432 Redundant, was already mentioned in 2.5

Reply: We have shorted the sentences as below:

"As mentioned above, higher flow rates will result in lower steady state concentrations. To guarantee the detection of BVOCs species (Fig. S8) with very low emission rates, we only adopted a medium flow rate of 9 L min^{-1} when conducting tests on a pine (*Pinus massoniana*) tree to compare the environmental parameters inside and outside the enclosure." (Lines 463-466).

L.437 How was this measured?

Reply: The light transmittance was measured by placing one PAR sensor inside the chamber and another outside the chamber. The transmittance was expressed as the ratio of PAR measured inside to that measured outside.

L.455 Such high flow rates might however affect may be transpiration rates of the leaf and thus affect the plant physiology.

Reply: This high flow rate might have less impact on the transpiration rates, because the residence time of commonly used leaf cuvette like Li-Cor 6400/6800 for transpiration rate measurements is generally shorter than 10 seconds.

L.744-L746 Please add more details to Fig. 1 Were is C_0 measured? If you use abbreviation such as MFC, please write it out in the description. A photo of the real chamber would really nice to see.

Reply:

The C_0 is measured by sampling ambient air near the inlet of the chamber (Fig. 1). Photos of the real chamber were also included in Fig. 1.

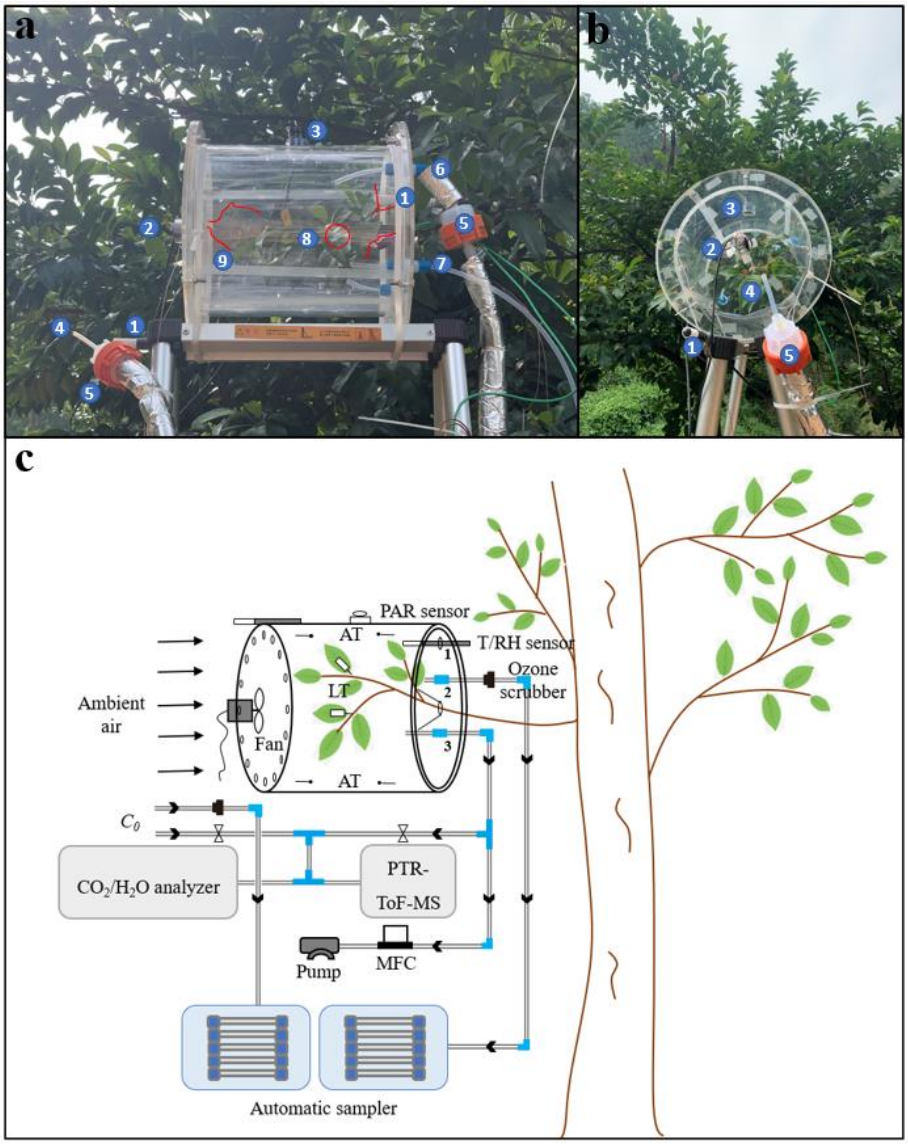

Figure 1. Photographs and schematic diagram of the semi-open dynamic chamber system for field measurements of BVOCs from plant leaves. (a) and (b) are real photographs of the chamber in the field: (1) T/RH sensors, (2) Teflon fan and electric motor, (3) PAR sensor, (4) Teflon sample tube for ambient air (C_0), (5) Ozone scrubber, (6) Teflon sample tube for chamber air (C_{in}), (7) Teflon tube for main airflow, (8) Thermocouples (red circle) for leaf temperature, (9) Thermocouples (red lines) for chamber air temperature. (c) is the schematic diagram of the chamber, and MFC refers to abbreviation of mass flow controller. LT and AT refer to leaf temperature and air temperature, respectively.

L.747-750 Fig. 2 Make the arrows a big bigger

Reply: We have changed the arrows in Fig. 2 as suggested (below).

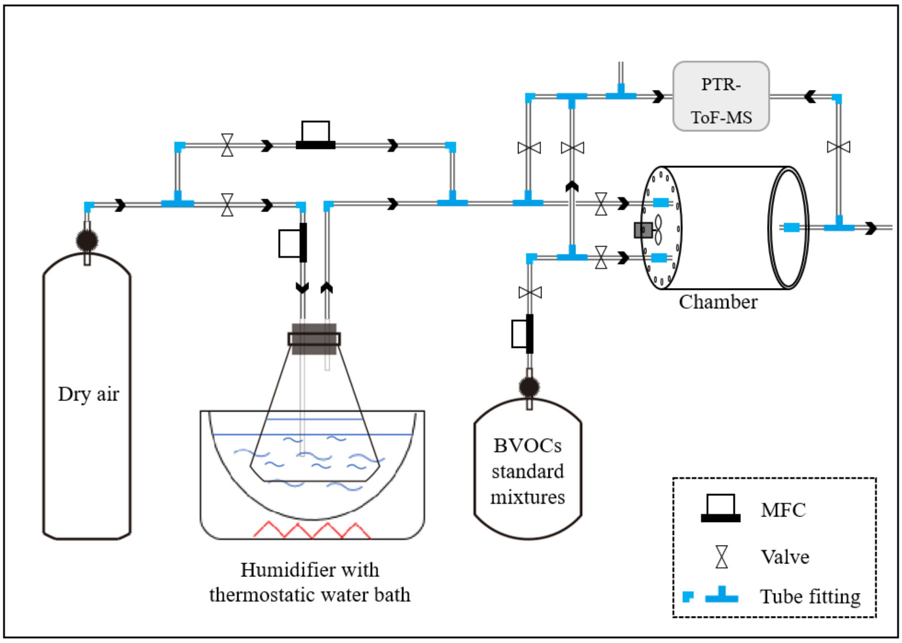

Figure 2. Schematic diagram of chamber characterization experiments in the laboratory using standard BVOCs mixture to imitate emissions of BVOCs from branches. MFC refers to mass flow controller.

Reference：

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Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part B: Applications, Chemosphere, 72, 365-380, https://doi.org/10.1016/j.chemosphere.2008.02.054, 2008.

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Ghirardo, A., Lindstein, F., Koch, K., Buegger, F., Schloter, M., Albert, A., Michelsen, A., Winkler, J. B., Schnitzler, J. P., and Rinnan, R.: Origin of volatile organic compound emissions from subarctic tundra under global warming, Glob Chang Biol, 26, 1908-1925, 10.1111/gcb.14935, 2020.