1 **Design and characterization of a semi-open dynamic chamber for measuring biogenic volatile**

2 **organic compounds (BVOCs) emissions from plants**

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14   **Abstract.**

15   With the accumulation of data about biogenic volatile organic compounds (BVOCs) emissions from

16   plants based on branch-scale enclosure measurements worldwide, it is vital to assure that

17   measurements are conducted using well-characterized dynamic chambers with good transfer

18   efficiencies and less disturbance on natural growing microenvironments. In this study, a self-made

19   cylindrical semi-open dynamic chamber with Teflon-coated inner surface was characterized both in

20   the lab with standard BVOC mixtures and in the field with typical broad-leaf and coniferous trees.

21   The lab simulation with a constant flow of standard mixtures and online monitoring of BVOCs by

22   proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS) revealed that lower real-

23   time mixing ratios and shorter equilibrium times than theoretically predicted due to wall loss in the

24   chamber, and larger flow rates (shorter residence times) can reduce the adsorptive loss and improve

25   the transfer efficiencies. However, even flow rates were raised to secure residence times less than 1

26   min, transfer efficiencies were still below 70 % for heavier BVOCs like α-pinene and β-

27   caryophyllene. Relative humidity (RH) impacted the adsorptive loss of BVOCs less significantly

28   when compared to flow rates, with compound specific patterns related to the influence of RH on

29   their adsorption behavior. When the chamber was applied in the field to a branch of a *mangifera*

30   *indica* tree, the enclosure-ambient temperature differences decreased from 4.5±0.3 to 1.0±0.2 °C

31   and the RH differences decreased from 9.8±0.5% to 1.2±0.1 % as flow rates increased from 3 L min$^-$

32   ^{1} (residence time ~4.5 min) to 15 L min^{-1} (residence time ~0.9 min). At a medium flow rate of 9 L

33   min^{-1} (residence time ~1.5 min), field tests with the dynamic chamber for *Mangifera indica* and

34   *Pinus massoniana* branches revealed enclosure temperature increase within +2 °C and CO_2

35   depletion within -50 ppm when compared to their ambient counterparts. The results suggested that

36   substantially higher air circulating rates would benefit reducing equilibrium time, adsorptive loss

37   and the ambient-enclosure temperature/RH differences. However, even under higher air circulating

38   rates and with inert Teflon-coated inner surfaces, the transfer efficiencies for monoterpene and

39   sesquiterpene species are not so satisfactory, implying that emission factors for these species might

40   be underestimated if they are obtained by dynamic chambers without certified transfer efficiencies,

41   and that further efforts are needed for field measurements to improve accuracies and narrow the

42   uncertainties of the emission factors.

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47 **Highlights**

48 • A dynamic chamber for measuring branch-scale BVOC emissions is characterized.

49 • Higher circulating air flow rate increases transfer efficiency and decreases equilibrium time.

50 • Higher circulating air flow rates reduce enclosure-ambient environmental differences.

51 • Transfer efficiencies of monoterpene and sesquiterpene species are below 70%.

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1 Introduction

Plants can emit a wide range of low molecular volatile organic compounds (VOCs), including isoprene, monoterpenes (MTs), sesquiterpenes (SQTs), oxygenated VOCs (OVOCs, e.g. methanol, acetone) and other reactive VOCs (Guenther et al., 2012). These compounds can be signal molecules for communication within plants, between plants, and between plants and insects (Laothawornkitkul et al., 2009; Šimpraga et al., 2016; Douma et al., 2019), and they are useful tools for plants to protect against biotic (e.g. herbivory) and abiotic (e.g. ozone, drought, heat) stresses (Loreto and Schnitzler, 2010; Holopainen et al., 2017). When emitting into atmosphere, these biogenic volatile organic compounds (BVOCs) can contribute substantially to the formation of ozone and secondary organic aerosol (SOA), and influence the budget of oxidants including hydroxyl radicals (Atkinson and Arey, 2003; de Souza et al., 2018; Di Carlo et al., 2004), and thereby directly and/or indirectly impact air quality and climate on regional and even global scale (Peñuelas et al., 2009; Kleist et al., 2012; Gu et al., 2017; Scott et al., 2017). Due to vital roles played by BVOCs in atmospheric chemistry, their emission inventory has become an indispensable part of air quality and climate models. Global annual emissions of BVOCs are estimated over 1 Pg (10^{15} g) (Guenther et al., 1995), yet these estimations may have large uncertainties (Simpson et al., 1999; Guenther et al., 2006; Zhang et al., 2020) and inaccurate emission factors are among the most important contributors to the uncertainties either regionally or globally (Wang et al., 2011; Guenther et al., 2012; Situ et al., 2014). Therefore, well-designed field works are essential and urgently needed to narrow the uncertainty (Niinemets et al., 2011).

Emissions of BVOCs from plants can be measured on leaf-, branch-, and canopy-scale. Although flux measurements above canopies by relaxed eddy accumulation or eddy covariance can obtain ecosystem-scale emission fluxes (Spirig et al., 2005; Rinne et al., 2007; Bai et al., 2017), enclosures on leaf and branch scales are the most convenient and widely-used approaches to measure BVOCs emission from plants (Chen et al., 2019; Huang et al., 2020). These enclosures can be static and dynamic. Static enclosure isolates leaves or branches from the ambient completely, and environmental parameters (e.g. temperature, relative humidity (RH), CO_2 concentration) in the enclosure may deviate far from the ambient. Temperature in the enclosure is likely to increase due to greenhouse effects, humidity increases because of leaf transpiration and CO_2 concentration depletes as a result of photosynthetic consumption by leaves (Kesselmeier et al., 1996; Aydin et al.,

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2014). These will change the physiological state of plants and cause abnormal emissions (Ortega and Helmig, 2008). For this reason, static or semi-static enclosures are considered to be screening tools to verify emitters and non-emitters (Niinemets et al., 2011; Li et al., 2019). Unlike static enclosure, dynamic enclosure introduces circulating air and can reduce the differences in environmental parameters between the enclosure and the ambient to a great extent. Therefore, dynamic enclosure is more reliable and preferred for measuring emissions of BVOCs from plants (Ortega and Helmig, 2008; Pape et al., 2009; Kolari et al., 2012). However, large differences still exist for dynamic enclosure if air exchange is slow. For example, temperature deviation of more than 10 °C between enclosure and the ambient was observed when using dynamic enclosure for field studies (Aydin et al., 2014). This way the measured emission reflects that under a temperature-disturbed environment and therefore might not well represent the real situations. In addition to deviations of environmental parameters in enclosures, adsorption of terpenes can occur on most parts of the enclosure system, including chamber walls, gasket surfaces, and system tubing (Niinemets et al., 2011). The materials used to construct enclosures, like neoprene and low-density polyethylene polymers, are thought to have potentially significant adsorption of VOCs (Niinemets et al., 2011 for a review), resulting in underestimation of emission rates.

An ideal dynamic enclosure for measuring emissions of BVOCs from plants should be one without changing the physiological state of the enclosed plant parts, and without introducing pollutions or causing systematic losses. Ortega et al. (2008) used ice water bath and copper tube to drop the temperature and humidity of the circulating air, thereby reducing the deviations of enclosure environmental parameters from the ambient. Aydin et al. (2014) also used circulating cooling water to reduce the temperature of the circulating air, but the temperature inside the enclosure is still much higher than that of the ambient. Kolari et al. (2012) evaluated the performances of dynamic chamber in uncontrolled field environment, the results indicate that the systematic losses of VOCs are higher in wet environment or under high RH. Lüpke et al. (2017) tested the chamber wall effects of an environmentally controlled dynamic chamber using Δ^2-Carene in the laboratory. Their results demonstrated that there were no chamber wall effects for Δ^2-Carene but there did exist background contaminations for some other compounds. To date, although there are a variety of dynamic chambers, including sophisticated enclosures designed for laboratory measurements (Copolovici and Niinemets, 2010; Lüpke et al., 2017; Mozaffar et al., 2017) and simple and user-friendly

113   enclosures for field measurements (Matsunaga et al., 2011; Helmig et al., 2013; Wiß et al., 2017),

114   the performances and wall effects of most dynamic enclosures, particularly those used in the field,

115   are not systematically characterized, and this would lead to difficulties in comparing results from

116   various field measurements. Therefore, in order to pool together the measurement results worldwide

117   to generate a quality dataset that can be shared by the scientific community, it is imperative to get

118   the dynamic enclosures systematically characterized before they are used in the field to measure

119   emissions of BVOCs.

120   This paper describes a semi-open dynamic chamber for measuring BVOCs emissions from plants.

121   The purpose of this work is to present a protocol demonstrating how the performance of a dynamic

122   chamber can be characterized and optimized for measuring branch-scale emissions of BVOCs. To

123   obtain more accurate BVOC emission rates from plants grown in the field, some most important

124   aspects, including enclosure-ambient differences in environmental parameters (light, temperature

125   and RH), equilibrium time and wall effects, are assessed and discussed in this study.

126   **2 Descriptions of the semi-open dynamic chamber system**

127   **2.1 Design of the semi-open dynamic chamber system**

128   The semi-open dynamic chamber is a cylindrical structure (Fig. 1) made of polymethyl methacrylate,

129   and its inner surface is coated with fluorinated ethylene propylene (FEP) Teflon film (FEP 100, Type

130   200A; DuPont, USA). It has a volume of 13.7 L with a diameter of 250 mm and a height of 280 mm.

131   Ambient air is drawn into the enclosure with a pump at a constant flow through the front panel

132   whose inner-chamber surface is coated with FEP Teflon film (air inlet). A customized PTFE Teflon

133   fan (Shenzhen Shuangmu Plastic Material Co. Ltd, China) that driven by an electric motor

134   (BLDC4260, Shenzhen Mingyang Motor Co. Ltd, China) is secured in the middle of inner side of

135   the inlet panel to establish homogeneous chamber conditions; and small holes (5 mm I.D.) are drilled

136   at the edge and ambient air entering from the small holes can flush the inner wall of the chamber

137   and thus reduce the possible occurrence of water condensation on the inner wall. The outlet is

138   covered by polymethyl methacrylate panel which is also coated with FEP Teflon film at the inner-

139   chamber side and joined to the main chamber body by screw. Four holes (Fig. 1) are drilled on the

140   panel: the hole (10 mm I.D.) in the middle is used to seal the branch around the trunk side; the hole

141   "1" (10 mm I.D.) is used to connect temperature and RH sensor (HC2A-S, Rotronic, Switzerland);

the hole "2" (10 mm I.D.) is used to connect to adsorption cartridges for sampling BVOCs for offline analysis; and "3" (10 mm I.D.) is used to connect to the air pump and online analyzers. In order to avoid artificial disturbance to branches when installing the chamber, the polymethyl methacrylate board is cut into two pieces (Fig. 1), which are spliced together after branches are enclosed in the chamber. The gaps between the hole and the trunk are sealed by FEP Teflon tapes. All the tube lines (1/8" inch O.D.) used in the system are PTFE-made while the Swagelok tube fittings are PFA-made. An air pump (MPU2134-N920-2.08, KNF, Germany) equipped with a mass flow controller (Alicat Scientific, Inc., Tucson, AZ, USA) is used to maintain a constant flow rate (F_1) of the main airflow. Concentrations of CO_2 and H_2O inside and outside the chamber are monitored by infrared gas analyzer (Li-7000; Li-Cor Inc., Lincoln, USA). A proton transfer reaction-time of flight-mass spectrometer (PTR-ToF-MS; Ionicon Analytik GmbH, Innsbruck, Austria), which has time resolution less than one second, is used to monitor the real-time mixing ratios of BVOCs inside the chamber. More detail descriptions about the determination of BVOCs by the PTR-ToF-MS can be found elsewhere (Wang et al., 2014; Huang et al., 2016; Zhang et al., 2020). 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 their built-in MFCs, and total flow rate ($F = F_1 + F_2 + F_3 + F_4$) of circulating air is the sum of these flows and is used to calculate emission rates. In addition, the accurate flow rate ($F_1 + F_2 + F_3$) through hole "3" is measured by a soap-membrane flowmeter (Gilian Gilibrator-2, Sensidyne, USA) before and after each measurement in the field. Temperature and relative humidity (RH) are measured by sensors (HC2A-S, Rotronic, Switzerland), one is installed inside of the chamber and the other is installed outside. 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). A light sensor (Li-1500; Li-Cor Inc., Lincoln, USA) is installed on the top of the chamber to monitor the photosynthetically active radiation (PAR). 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.

2.2 Collection of offline BVOCs samples and lab analysis

Apart from online measurement by PTR-ToF-MS, offline BVOC samples are also collected since PTR-ToF-MS cannot differentiate isomers of MTs and SQTs. The air is drawn through an ozone scrubber followed by solid adsorbent cartridges (Tenax TA/Carbograph 5TD, Marks International Ltd, UK) using an automatic sampler (JEC921, Jectec Science and Technology Co., Ltd, Beijing, China) at a flow rate of 200 mL min^{-1} for 10 minutes (Fig. 1). Samples of ambient air near the inlet are collected concurrently in the same way with another automatic sampler to determine the background concentration (C_0) (Fig. 1). The collected samples are stored in a portable refrigerator at 4 °C in the field and at -20 °C after brought back to the lab. In the lab, these samples are analyzed by an automatic thermal desorption system (TD-100, Markes International Ltd, UK) coupled to a model 7890 gas chromatography (GC) with a mode 5975 mass selective detector (MSD) (Agilent Technologies, Inc., California, USA). The adsorbent cartridges are thermally desorbed by the TD-100 at 280 °C for 10 minutes and then the desorbed analytes are transferred by pure helium into a cryogenic trap (U-T11PGC-2S, Markes International Ltd, UK) at -10 °C. Then the trap is rapidly heated to transfer the analytes to the GC/MSD system with a capillary column (Agilent, HP-5MS, 30 m × 0.25 mm × 0.25 μm). The GC oven temperature is programmed to be initially at 35 °C (held for 3 minutes), then increase to 100 °C at 5 °C min^{-1} and hold for 3 minutes, to 150 °C at 10 °C min^{-1} and hold for 3 minutes, and then to 280 °C with a final hold time of 2.5 minutes. The MSD is operated in selected ion monitoring (SIM) mode, and the ionization method is electron impacting. The calibration standards were prepared by dissolving the pure liquid standards (Table S1) into n-hexane solution (Kajos et al., 2013; Fang et al., 2021) and diluted to six concentration levels. 1 μL of each standard solution with specific concentration was injected into an adsorbent cartridge and swept with pure helium at 100 mL min^{-1} for two minutes to scavenge n-hexane, and then run the same way as real samples by the TD-GC/MSD system. The chromatogram of standards was showed in Fig S1. Six-point calibration curves (Fig S2; S3) were used to quantify the compounds of interest. Method detection limits (MDLs) were determined by seven parallel analysis of the lowest concentration of calibration standards. The MDLs varied from 5 to 17 ng m^{-3} for MTs and from 1 to 8 ng m^{-3} for SQTs. The MDL for isoprene was 56 ng m^{-3} (Table S1).

2.3 Ozone scavenging

Ozone (O$_3$) may impact emissions of BVOCs from plants (Feng et al., 2019). While many dynamic

enclosures use purified air as circulating air (Chen et al., 2020; Jing et al., 2020), the semi-open

dynamic chamber, using ambient air as circulating air in order to reflect BVOCs emission from

plants in real atmosphere, need to take the effect of ozone into consideration. On the other hand, the

highly reactive BVOCs in atmosphere can be oxidized by oxidants like ozone, especially for MTs

and SQTs (Atkinson and Arey, 2003). For our semi-open dynamic chamber with volume of 13.7 L,

when the flow rate is set to be 9-12 L min^{-1}, the residence time of circulating air will be within 1.5

minutes, far below the lifetimes of some important BVOCs in the atmosphere, which are varying

from tens of minutes to tens of hours when reacting with ozone (Atkinson and Arey, 2003).

Therefore, losses of BVOCs due to reaction with ozone in the chamber can be ignored according to

some previous studies (Kolari et al., 2012; Bourtsoukidis et al., 2012; Helin et al., 2020). However,

for the sorbent cartridges used to take BVOCs samples for offline analysis (Chen et al., 2019; Aydin

et al., 2014), ozone will be adsorbed together with BVOCs, resulting in losses of BVOCs due to

reaction with ozone in the cartridges during the deliver and storage of the cartridges before lab

analysis (Pollmann et al., 2005; Ortega and Helmig, 2008).

Potassium iodide (KI) and sodium thiosulfate ($Na_2S_2O_3$) are widely used for ozone removal during

sampling BVOCs with adsorbent tubes (Helmig et al., 2006; Helmig et al., 2007; Aydin et al., 2014;

Yaman et al., 2015; Chen et al., 2020). In this study, four types of ozone scrubbers including KI

filter, $Na_2S_2O_3$ filter, KI tube and $Na_2S_2O_3$ tube were prepared. The KI/$Na_2S_2O_3$ filters were prepared

by cutting quartz fibre filter (23.4×17.6 cm^2; Whatman) into circles, getting them soaked in saturated

KI or $Na_2S_2O_3$ solution and then dried at 50 °C. The KI/$Na_2S_2O_3$ tube filters were prepared with

copper tubes (1/4" inch in I.D. × 50 cm length) by injecting 5 mL saturated KI/$Na_2S_2O_3$ solution

and then swept to dry with nitrogen. As showed in Fig. S4, air flow with ozone concentration of

about 100 ppb, which is the daytime peak level that can occur in our study area (the Pearl River

Delta region), was generated by an ozone generator and passed through the ozone scrubbers. Ozone

analyzer (EC9810, Ecotech, Australia) was used to monitor ozone concentration before and after

passing through the scrubbers. All of the ozone scrubbers have ~100 % ozone removal efficiency

(Table S2), which means that all of them can effectively scavenge ozone. Besides, to test if any

losses of BVOCs happened in the scrubbers, a mixture of BVOCs (~ 20 ppb in nitrogen) was passing

through the ozone scrubbers at the same flow rate of 200 mL min^{-1} as normal field sampling, and

the concentrations of BVOCs were monitored before and after passing through the scrubber using

231 the PTR-ToF-MS (Fig. S5). The results revealed that the recoveries of BVOCs on average were

232 10.05 %, 100.89 %, 100.63 % and 66.70 % for KI filter, $Na_2S_2O_3$ filter, KI tube and $Na_2S_2O_3$ tube,

233 respectively (Table S2). Therefore, both $Na_2S_2O_3$ filter and KI tube can be used to scavenge ozone

234 with good recoveries. Here $Na_2S_2O_3$ filters were used to scavenge ozone as in previous studies

235 (Helmig et al.,2006; 2007).

2.4 Optimization of flow rates

237 The air flow rate is the most important parameter that influence the equilibrium time, the transfer

238 efficiency, the enclosure-ambient differences in temperature and RH, and the steady state

239 concentration of BVOCs as well. Firstly, we tested equilibrium time and transfer efficiency using

240 standard mixtures in the laboratory under 25 °C. The standard mixtures contained representative

241 species emitted from plants, including acetonitrile, acrylonitrile, acrolein, acetone, isoprene,

242 methylacrolein, α-pinene and β-caryophyllene (Table S3); they were prepared in pure nitrogen with

243 mixing ratios of 300-600 ppbv and compressed into a stainless steel canister with a pressure of 40-

244 50 bar in the same way by Rhoderick and Lin (2013) and Mermet et al. (2019). As shown in Fig. 2,

245 this standard gas mixture was released into the chamber at a constant flow rate to simulate the

246 emission of VOCs from enclosed plant branches with a constant emission factor. While the

247 equilibrium time was tested at flow rates of 3, 6, 9, 12 and 15 L min⁻¹ (dry air, RH=0 %) in the lab,

248 the transfer efficiency was further tested in the lab with flow rates of 3, 6, 9, 12 and 15 L min⁻¹ and

249 under RH of 20 %, 40 %, 60 %, 80 % and 100 %, respectively. The RH of circulating air was

250 adjusted by mixing dry air (RH=0 %) with humidified air (RH=100 %). All the flow rates were

251 controlled by mass flow controllers (MFCs) (Alicat Scientific, Inc., Tucson, AZ, USA) and

252 calibrated by a soap-membrane flowmeter (Gilian Gilibrator-2, Sensidyne, USA). Mixing ratios of

253 each compound in the standard mixture stored in the stainless steel canister were initially measured

254 by PTR-ToF-MS. The standard mixture was mixed with pure dry air and the mixing ratio of each

255 compound (C_1) in this mixed air was measured by PTR-ToF-MS. This mixed air was switched into

256 the camber at a constant flow to simulate BVOCs emissions from enclosed plant branches, and the

257 steady state mixing ratios of each compound (C_2) in the chamber was again measured by PTR-ToF-

258 MS. Transfer efficiency (%) of each compound was then calculated as the ratio of C_2/C_1. Mixing

259 ratios of acetonitrile, acrylonitrile, acrolein, acetone, isoprene, methylacrolein, α-pinene and β-

260 caryophyllene were determined by PTR-ToF-MS with *m/z* 42.019, 45.015, 57.073, 59.052, 69.060,

261   71.040, 137.072 and 204.986, respectively.

262   **2.5 Field tests**

263   The influence of flow rate on enclosure-ambient differences in temperature and RH was carried out

264   in the campus of Guangzhou Institute of Geochemistry (GIG) with branches of *Mangifera indica* (a

265   broad-leaved isoprene emitter) under sunny and cloudless days with small winds. Totally about 7.0

266   g dry mass of leaves were enclosed in the chamber. The ambient air temperature was 31-33 °C and

267   PAR was 1000-1200 μmol m^{-2} s^{-1}. The enclosure and ambient temperature/RH were measured by

268   calibrated sensors (HC2A-S, Rotronic, Switzerland) under circulating air flow rates of 3, 6, 9, 12

269   and 15 L min^{-1}.

270   Field tests were also carried out during 9:00-17:30 local time (UTC+8) on October 8th, 2019 in the

271   Guangdong Tree Garden (23.20° N, 113.38° E) of the Guangdong Academy of Forestry in

272   Guangzhou, south China. The coniferous pine trees are typical monoterpene emitters (Aydin et al.,

273   2014). *Pinus massoniana*, which is a widely distributed pine tree species in south China (Gu et al.,

274   2019; Wang et al., 2019) was selected for our field tests. Healthy nature-grown branches of *Pinus*

275   *massoniana* (~20-year-old and ~12 m high) were enclosed in the dynamic chamber (Fig. 1), and

276   environmental parameters inside and outside of the chamber were compared only under a medium

277   circulating air flow rate of 9 L min^{-1}.

278   **3 Results and discussion**

279   3.1 Equilibrium time

280   Theoretically concentrations of BVOC species that emitted by plant leaves inside a dynamic

281   chamber can be described as below (Niinemets et al., 2011):

282      $$V \frac{dC}{dt} = E - F (C - C_0) \qquad (1)$$

283   where V (L) is the volume of the chamber, E (μg min^{-1}) is the emission rates of BVOCs; C_0 (μg L^{-1}

284   ^{1}) are background concentrations of the BVOC species in air entering into the chamber, which

285   were determined by PTR-ToF-MS in the lab tests, and in field tests were determined both online by

286   PTR-ToF-MS and offline by sampling ambient air near the inlet with adsorbent cartridges followed

287   by TD-GC/MSD analysis back to the lab); C (μg L^{-1}) is the concentrations of the BVOCs species in

288   air exiting the chamber; and F (L min^{-1}) is air flow rate through the chamber. The above equation

289   can be expressed explicitly for changing $C(t)$ with time t as below:

$$C(t) = C_0 + \frac{E}{F} \times (1 - e^{-\frac{F}{V} \cdot t}) \qquad (2)$$

Based on the above Eq. (2), with prolonged time t, $C(t)$ will approach a steady state concentration C_s:

$$C_s = C_0 + \frac{E}{F} \qquad (3)$$

and then E can be calculated as

$$E = F \times (C_s - C_0) \qquad (4)$$

With leaf dry mass (m, g), the emission factors (EF, µg g^{-1} min^{-1}) of enclosed leaves can be expressed as

$$EF = F \times (C_s - C_0)/m \qquad (5)$$

As showed in Eq. (2), the F/V value, which is the reciprocal of residence time (V/F), determines how fast a steady state will reach. At a given E, a lower F will result in a longer time to reach steady state but a higher steady state concentration that benefits instrumental measurements, and vice versa. In the field measurements, we prefer a shorter equilibrium time to track the variation of emission rates with changing environment parameters (like PAR) if E/F is well above the method detection limits. In fact, as showed in Fig. S6, theoretically steady state concentrations inside the enclosure would decrease with the increasing flow rates. However, even at flow rates as high as 50 L min^{-1} (residence time <15 seconds), if leaves with 5.0 g dry mass are enclosed, a BVOC species with an extremely low emission rate of 0.01 µg g^{-1} h^{-1} would have predicted steady state concentration of ~10 µg m^{-3}, which is still well above the method detection limits (Table S1) of SQTs that typically have much lower emission rates when compared to isoprene and MTs. Therefore, the influence of circulating air flow rates on the detection of BVOCs is not an important issue to limit the performance of the dynamic enclosure method and thus will be not discussed hereafter.

Equilibrium time is vital for evaluating the performance of a dynamic chamber. Base on Eq. (2), if $t=3 \times V/F$ (3 cycles of residence time), $e^{-(F/V \times t)} \approx 0.05$; and if $t =5 \times V/F$ (5 cycles of residence time), $e^{-(F/V \times t)} < 0.01$, and in this case it can be concluded with confidence that after 5 cycles of residence time the equilibrium or the steady state is reached. With the high time resolution online monitoring by PTR-ToF-MS, equilibrium time could be determined more directly in our lab tests.

Figure 3 shows real-time concentrations of VOCs in the chamber at a flow rate of 9 L min^{-1} when using a standard mixture to imitate the BVOC emission in the lab (Fig. 2). The mixing ratios of

VOCs in the chamber increased with time and became stable after ~3-6 minutes or ~2-4 cycles of residence time (Fig. 3). The representative VOC species differs in their times reaching steady state, varying from ~3 minutes for α-pinene to ~6 minutes for acetone and acrylonitrile. The equilibrium time are all within the 5 cycles of residence time (7.5 min).

The real-time mixing ratios of VOCs in the chamber changed in a pattern that was in fairly good agreement with that theoretically predicted by above Eq. (2); however, they were all close and consistently lower than the theoretically predicted values (Fig. 3). The gaps between the measured and predicted values seemed to be larger for heavier BVOC compounds (e.g. α-pinene and β-caryophyllene) than lighter species (e.g. isoprene). Also as showed in Fig. 3, after the stop of injecting the standard mixture, the mixing ratios inside the chamber dropped to their initial background values in a way that was fitted well with theoretical prediction.

The lower than predicted steady-state concentrations were largely due to losses of VOCs in the chamber, which would result in a lower C_s in Eq. (3) and thereby a lower "real" E by Eq. (4). Therefore, apart from equilibrium time, the loss or transfer efficiency must be further considered for an accurate emission measurement by a dynamic chamber.

3.2 Transfer efficiency

Adsorption losses of BVOCs can be a significant fraction in enclosure systems (Helmig et al., 2004). Although Tedlar or Teflon films, which are chemically inert with low surface uptake rates for BVOCs, were used for most dynamic enclosures to diminish the adsorption in the enclosure (Ortega and Helmig, 2008; Gomez et al., 2019; Chen et al., 2020), adsorptive losses cannot be completely eliminated. Kolari et al. (2012) observed 6-29 % compounds losses in a chamber made of transparent acrylic plastic with Teflon-coated inner surfaces. Hohaus et al. (2016) observed average losses of 15 % in their enclosure consisting of FEP film. In this study, to assess the adsorptive losses and transfer efficiencies, tests were conducted under different flow rates and RH in the lab with the standard mixture (Fig. 2).

3.2.1 Influence of flow rate on transfer efficiency

Figure 4 shows transfer efficiencies under air circulating rates (dry air) of 3, 6, 9, 12 and 15 L min^{-1}. Transfer efficiencies of all species increased when flow rates increased from 3 to 15 L min^{-1}, such as from 41.9±2.6 % to 85.4±4.6 % for acetonitrile, 56.5±5.5 % to 90.8±8.7 % for acrylonitrile, 24.7±3.0 % to 65.4±2.8 % for acrolein, 42.5±3.5 % to 110.9±2.9 % for acetone, 48.4±4.6 % to

349   106.9±8.3 % for isoprene, 40.6±5.2 % to 92.8±5.8 % for methylacrolein, 26.6±3.2 % to 69.7±3.7 %

350   for α-pinene, and 22.8±3.4 % to 65.9±3.8 % for β-caryophyllene.

351   Transfer efficiencies were apparently unsatisfactory at lower flow rates. For example, at a flow rate

352   of 3 L min^{-1}, for the most important BVOC species like isoprene and α-pinene, their transfer

353   efficiencies on average were as low as 48.4 % and 26.6 %, respectively (Fig. 4). This confirms that

354   larger losses might occur if a static chamber is used to measure emission rates. Even at a flow rate

355   of 15 L min^{-1} (residence time < 1 min), transfer efficiencies were still below 70 % for acrolein, α-

356   pinene, and β-caryophyllene (Fig. 4) although fairly good transfer efficiencies (85 %-111 %) were

357   observed for other species. This result implies that measured emission rates from branches in

358   enclosures might be seriously flawed in case transfer efficiencies are not well characterized and

359   optimized.

360   For a given volume chamber, a higher flow rate is associated with a lower residence time (V/F).

361   More adsorptive losses would occur at longer residence time since VOCs have more time to adsorb

362   onto chamber inner surfaces (Kolari et al., 2012). Therefore, the VOCs loss ratios increased with

363   residence times (Fig. 5) and decreased with flow rates (Fig. S7), and a larger flow rate would be

364   preferred if the losses are to be reduced to acceptable levels.

365   Adsorptive losses may vary with VOC species. The loss is generally related to vapor pressure, which

366   is modified by molecular weight and boiling point (Ortega and Helmig, 2008). As a result, heavier

367   VOCs like α-pinene and β-caryophyllene with lower vapor pressure are easier to be adsorbed. Kolari

368   et al. (2012) observed that heavier VOCs (m/z > 100) such as hexanal and MTs showed stronger

369   adsorption in their dynamic chamber. Schaub et al. (2010) also found stronger adsorption for SQTs

370   in a branch chamber where weaker adsorption occurred at higher temperature. Our results also

371   demonstrated that running conditions like flow rates are needed to be carefully modulated especially

372   for heavier BVOCs like MTs and SQTs.

373   **3.2.2 Influence of RH on Transfer efficiency**

374   The influence of RH on transfer efficiencies or adsorptive loss of BVOC in a chamber is not so

375   consistent in previous studies. While Kolari et al. (2012) observed notable adsorptive loss for

376   isoprene and methyl vinyl ketone at wet environment and no significant differences between wet

377   and dry environment for hexanal and α-pinene, Hohaus et al. (2016) observed transfer efficiencies

378   independent on RH (ranging 25-100 %) for VOCs with different vapor pressure and polarity through

379   the "PLant chamber Unit for Simulation (PLUS)". In this study, transfer efficiency under different

380   RH (0 %, 20 %, 40 %, 60 %, 80 %, 100 %) and flow rates (3, 6, 9, 12, 15 L min^{-1}) were further

381   investigated with the standard VOCs mixture (Fig. 2).

382   As showed in Fig. 6, unlike flow rates, RH seemed to have less influence on transfer efficiencies,

383   as reflected by the relative standard deviation (RSD) of transfer efficiencies at different RH. The

384   RSD of transfer efficiencies under different RH varied from 2.6 % for acetone at 15 L min^{-1} to 14.8 %

385   for sesquiterpene at 3 L min^{-1}. There is no consistent decreasing or increasing trend for transfer

386   efficiencies with the increase of RH. Instead, the influence of RH on transfer efficiencies showed

387   compound specific patterns. For acetonitrile and methylacrolein, the highest transfer efficiency

388   occurred at low RH=0 % (dry air); for α-pinene and β-caryophyllene, the highest transfer efficiency

389   occurred under higher RH (100 %); for acrylonitrile, acetone and isoprene, higher transfer efficiency

390   occurred at medium humidity levels (~40 %); and for acrolein, transfer efficiencies were close to

391   each other under different RH, agreeing to the results by Hohaus et al. (2016). Theoretically, the

392   influence of RH on adsorptive loss depends on the competition of adsorption sites by water

393   molecules on the surfaces and the modification of energy spectrum of the adsorption sites by

394   condensed water on the surfaces. Therefore, for water-insoluble or hydrophobic BVOCs like

395   isoprene, MTs and SQTs, higher RH may help suppress their uptake on surfaces, while for water

396   soluble or hydrophilic OVOCs, lower RH would be preferred for higher transfer efficiencies.

397   **3.2.3 Possible correction of VOCs losses in lab simulations**

398   Due to the adsorptive losses, the measured emission rates from plant leaves would be

399   underestimated, particularly for those with unsatisfactory transfer efficiencies even under high flow

400   rates and short residence times. If the adsorptive loss rate is simplified to be linearly proportional to

401   the VOC concentration inside the chamber, Eq. (1) can be rewritten as:

402    $$V \frac{dC}{dt} = E - F \times (C - C_0) - k \times C \qquad (6)$$

403   where k is the correction factor due to adsorptive loss. When the VOC concentration in the chamber

404   reaches steady state C_s, the emission rates can be estimated as:

405    $$E = F \times (C_s - C_0) + k \times C_s \qquad (7)$$

406   In our simulation tests in the lab with the standard mixtures with the known E and F, after measuring

407   the steady state concentration C_s, based on above Eq. (7) we could calculate the adsorptive loss term

408    $\boldsymbol{k} \times \boldsymbol{C_s}$ and $\boldsymbol{k}$ as well.

409   The correction factors for different VOCs at different flow rates and RH are presented in Table S4.

410   Consistent with the lower transfer efficiencies at lower flow rates, for a VOC species, the largest $\boldsymbol{k}$

411   value occurs at 3 L min^{-1} while the smallest $\boldsymbol{k}$ value occurs at 15 L min^{-1}. Also $\boldsymbol{k}$ is less affected by

412   RH than by flow rates, and varies among the VOCs probably due to their different adsorptive

413   behavior on the surfaces.

414   It is under question, however, if this kind of simplified loss correction in lab simulations can be

415   applicable to field measurements due to complex adsorption behavior. For example, in field

416   measurements of branch-scale emissions, the surfaces may have limited adsorption capacity

417   especially for the Teflon-coated inner walls, and thus with the prolonged enclosure time of a branch

418   in the chamber, some species may become adsorption saturated on the surfaces and thus would be

419   less affected by the adsorptive loss. To avoid the influence of VOCs adsorption, it may be a plausible

420   way to measure emissions after getting adsorption saturation (Chen et al., 2019). In the field, one to

421   two hours of balance time prior to tests will be set to reduce the artificial disturbance to the

422   physiological state of the enclosed branch and to ensure that emissions in the enclosure get stabilized,

423   such a procedure would also set enough time for adsorption of emitted compounds and thereby

424   benefit lowering the adsorptive loss during tests afterwards. On the other hand, adsorption of VOCs

425   on surfaces in the enclosure will be weakened at high temperatures (Schaub et al., 2010; Kolari et

426   al., 2012). Some more adsorptive species, like SQTs, after getting adsorption saturated at lower

427   temperature, would release again from the surface when air temperature elevated (Schaub et al.,

428   2010). Consider the temperature effect on the adsorptive loss, field enclosure measurements of

429   branch-scale emissions at higher temperature intervals (e.g. near noon time) during a day would

430   have less interferences by adsorptive loss.

431   Despite of the limitation of loss correction from the lab simulation in this study, this approach might

432   be implicative to deal with the more complex adsorption behavior in field measurements. Previous

433   lab studies also eliminated loss by using VOCs standards to calibrate the whole measuring system

434   (Ghirardo et al., 2011; 2020). Ortega et al. (2008) made adsorption loss corrections of VOCs by

435   adding internal standard into the enclosure to calculate the recovery. Therefore, for more accurate

436   emission measurements by dynamic enclosures in the field, adding surrogate compounds in the

circulating air in the same way as this simulation study (Fig. 2) would be a possible way to evaluate *in situ* transfer efficiencies.

3.3 Comparison of environmental parameters inside and outside of the chamber in field measurements

When conducting field measurements of BVOCs with branch enclosures, it is vital that environmental parameters, particularly temperature, resemble the natural growing conditions and are not seriously deviated due to enclosure. As temperature will affect the emission of BVOCs from plants in an exponential way mainly due to the fact that temperature can modify the activity of biosynthetic enzymes, the vapor pressures and the cellular diffusion rates of BVOCs (Laothawornkitkul et al., 2009), and a small change in leaf temperature may induce big variation in BVOCs emissions. Here we first conducted tests about the influence of flow rates (3-15 L min^{-1}) on the differences in temperature and RH between ambient and enclosure, then we conducted tests for *Pinus massoniana* at a medium flow rate of 9 L min^{-1}.

3.3.1 Enclosure-ambient T/RH differences under different flow rates

As showed in Fig. 7, when conducting tests of BVOCs emissions (Fig. S8) with a branch of *Mangifera indica* (~7 g dry mass of leaves) under ambient air temperature of 31-33 °C and PAR of 1000-1200 μmol m^{-2} s^{-1}, the differences in both temperature and RH between enclosure and ambient air decreased sharply with the increase of flow rates. As flow rates increased from 3 L min^{-1} (residence time ~4.5 min) to 15 L min^{-1} (residence time ~0.9 min), the enclosure-ambient temperature differences (ΔT) decreased from 4.5±0.3 to 1.0±0.2 °C (Fig. 7a), the RH differences (ΔRH) decreased from 9.8±0.5 % to 1.2±0.1 % (Fig. 7b). The results confirmed that the ambient-enclosure differences in T/RH could be largely reduced if enclosure air is sufficiently circulated. It seemed that at a flow rate of 9 L min^{-1} (residence time ~1.5 min), the differences could be fairly satisfactory ($\Delta T < 2$°C; $\Delta RH < 5$ %).

3.3.2 Enclosure-ambient differences of environmental parameters during field tests of BVOC emissions from *Pinus massoniana*

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.

467 As expected, higher temperature and RH but lower PAR and CO_2 concentrations were observed

468 inside than outside the enclosure (Fig. S9). On average the temperature deviation inside the chamber

469 was +1.2±1.1 °C, and the RH deviation was +12.8±4.0 %; The CO_2 concentrations inside showed -

470 53 ppm deviation on average with the relative deviation of -(4-15) % during the day. The light

471 transmittance was 92.4±5.4 % on average.

472 Higher temperature inside the chamber could be attributed to the greenhouse effect (Ortega et al.,

473 2008). The temperature deviation inside the chamber in this study is smaller when compared to

474 those reported previously (Fig. 8). The largest relative temperature deviation of 11.4 % was much

475 lower than that of over 50 % reported in previous studies (Fig. 8a). Even under full sunlight at noon

476 a temperature deviation of 4 °C was observed in this study, lower than that of 6-7 °C observed by

477 Helmig et al. (2006), 8 °C by Ortega et al. (2008), and comparable to 3-4 °C by Kolari et al. (2012)

478 (Fig. 8b). Higher RH inside the chamber is caused by leaf transpiration and the +12.8 % deviation

479 is acceptable in field tests. Photosynthetic adsorption by leaves will lead to depletion of CO_2 in the

480 chamber. Kesselmeier et al. (1996) also observed 50 ppm lower CO_2 concentration (relative

481 deviation of -13.2 %) in their chamber due to the depletion, and they considered that it was well

482 within an acceptable range for normal physiological conditions. The light transmittance of 92.4±5.4 %

483 in this study is comparable with those reported in previous studies, such as that of 90 % by Aydin et

484 al. (2014), 92 % by Karlik et al. (2001), 95 % by Chen et al. (2020) and 97 % by Lüpke et al. (2017).

485 The comparison suggests the environmental parameters in the semi-open dynamic chamber were

486 less disturbed. Moreover, tests in this study were conducted at flow rates of 9 L min^{-1} with residence

487 time of 1.5 min, and observed steady state concentrations for major emitted BVOC species (such as

488 ~15 μg m^{-3} for α-pinene) were orders of magnitude higher above their MDLs. Therefore, as

489 discussed above, if we raised flow rates to be as high as 50 min L^{-1} with residence time of ~15

490 seconds, we could still successfully measure the emission rates for the major species, and the

491 equilibrium time, the adsorptive loss, as well as the inside-outside differences of temperature and

492 RH, would be further reduced to a larger extent.

493 **4 Conclusions**

494 In order to obtain accurate emission rates of BVOCs from plants growing under natural environment,

495 it is vital for branch-scale enclosure to reduce the adsorptive loss and minimize the disturbance to

496 the natural growing microenvironments. In this study, based on tests in the lab and in the field with

a self-made dynamic enclosure, we demonstrated that operational parameters like air circulating rates could impact heavily on the performance of dynamic enclosures, and therefore should be optimized before field applications. As revealed by the results, higher circulating rates could not only reduce the equilibrium time and facilitate higher time resolution emission measurements, but also reduce the adsorptive losses and the enclosure-ambient temperature/RH differences and thus obtain more accurate emission rates under natural conditions. Therefore, in field measurements using the dynamic enclosure method, if advanced analytical techniques like PTR-ToF-MS can assure sensitive enough detections, higher air circulating flow rates are preferred.

It is worth noting that although the inner surfaces were coated with inert Teflon films, based on lab simulation with standard mixtures, BVOC species like monoterpenes and sesquiterpenes showed transfer efficiencies less than 70% even the residence times were kept as low as <1 min. This suggests that emission factors of these species from dynamic enclosures might be underestimated if the adsorptive losses were not seriously considered and reduced, and further efforts are needed to develop a certified protocol to assure accurate emission measurements particularly for species (e.g., monoterpenes and sesquiterpenes) with lower transfer efficiencies.

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.

Author contributions

JQZ designed and characterized the chamber with the support of HNZ, XMW, YLZ and WS. JQZ and HNZ carried out the chamber assessments. JQZ, HNZ and ZFW carried out the BVOCs measurements in the field. JQZ prepared the manuscript with input from all co-authors. XMW and YLZ revised the manuscript.

Data availability

527   Data are available from Zenodo (https://zenodo.org/record/5347841#.YS5YYRQzapo) or request

528   by contacting the corresponding authors (zhang_yl86@gig.ac.cn; wangxm@gig.ac.cn).

529

530   **Supplement**

531   The supplement related to this article is available online.

532

533   **Competing interests**

534   The authors declare that they have no conflict of interests.

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Figure captions

Figure 1. Schematic diagram of the semi-open dynamic chamber system for field measurements of BVOCs from plant leaves.

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

Figure 3. Changes of BVOCs concentrations in the chamber during lab simulation experiments. The black dashed lines are background concentrations. Blue solid lines represent the theoretically predicted BVOCs concentrations in the chamber. The green circles are concentrations measured by the PTR-ToF-MS. Green solid lines represent fitted BVOCs concentrations in the chamber.

Figure 4. Transfer efficiencies of BVOCs when passing through the chamber under different flow rates in the lab simulation experiments. Error bars represents standard deviations of triplicate measurements.

Figure 5. Changes of BVOCs loss ratios (mean $\pm$ 1σ, n=5) with residence times.

Figure 6. Influence of relative humidity and flow rates on transfer efficiencies of BVOCs, (a)-(h) represents acetonitrile, acrylonitrile, acrolein, acetone, isoprene, methylacrolein, α-pinene and β-caryophyllene, respectively.

Figure 7. Enclosure-ambient differences in temperature (a) and RH (b) under different flow rates. Circles with errors bars are the measured means and standard deviations. The solid lines are fitted changes.

Figure 8. Comparison of temperature deviation (°C) and relative temperature deviation (%) with that reported in previous studies: (a) temperature deviation versus ambient temperature; (b) temperature deviation (°C) under normal and full sunlight in different enclosures.
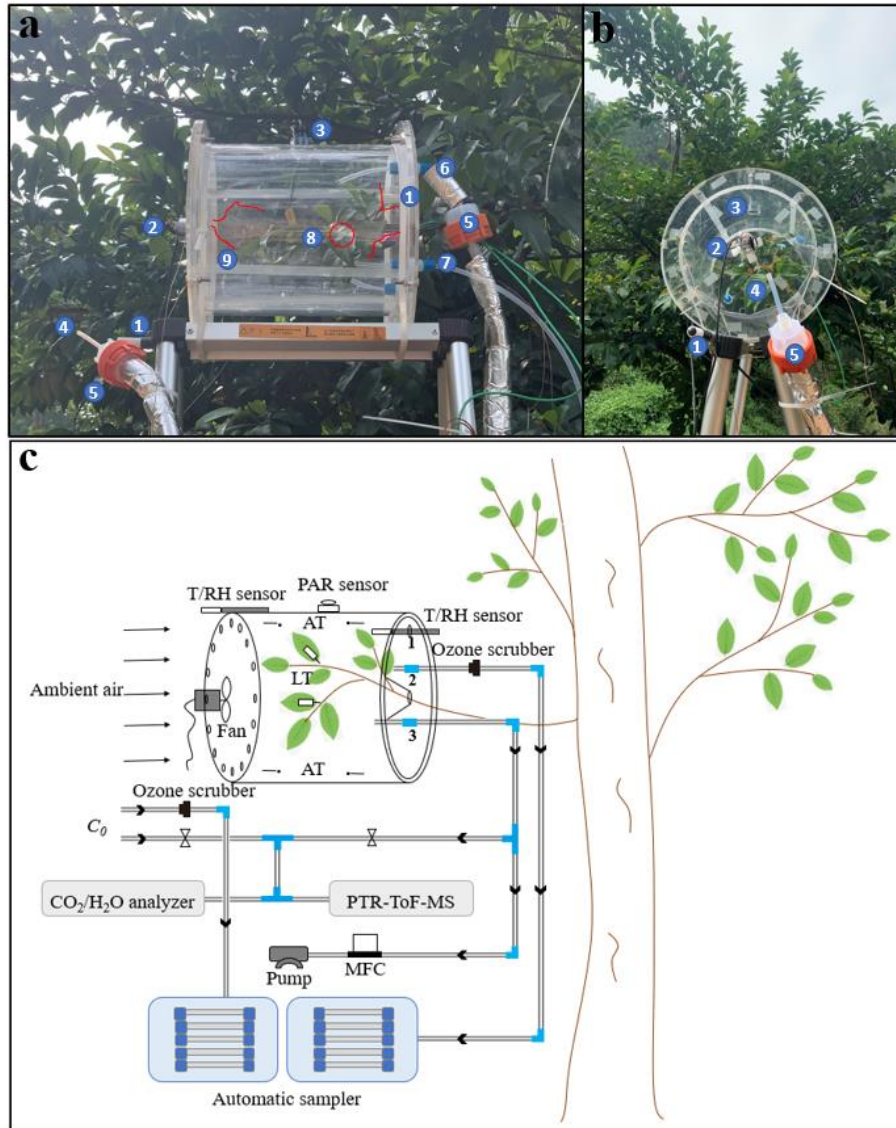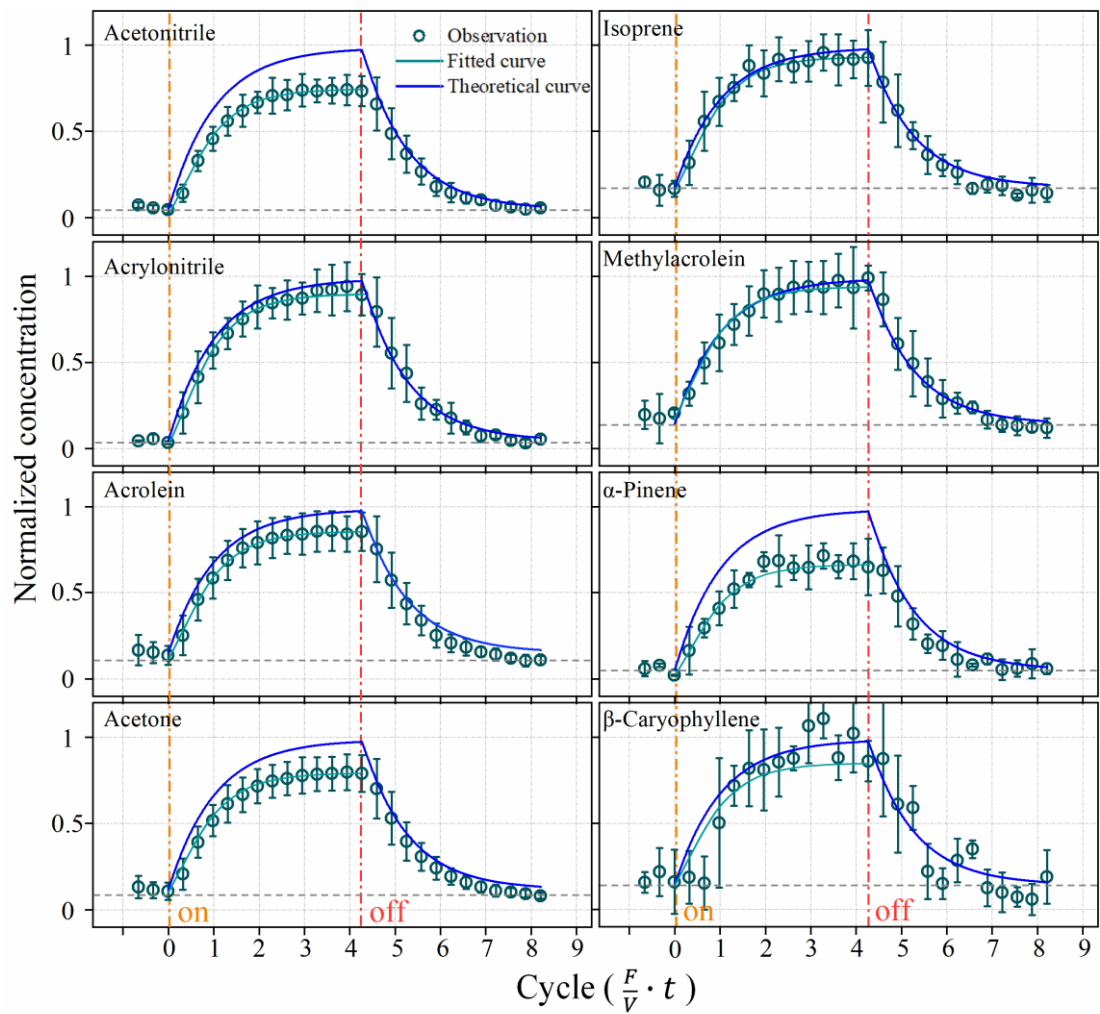
Figure 1. Photographs and schematic diagram of the semi-open dynamic chamber system for field measurements of BVOCs from plant leaves. (a) and (b) are photographs of the chamber in the field: (1) T/RH sensors, (2) Teflon fan and electric motor, (3) PAR sensor, (4) Teflon tube for sampling ambient air, (5) Ozone scrubber, (6) Teflon tube for sampling chamber air, (7) Teflon tube for main airflow, (8) Thermocouples (red circle) for leaf temperature, (9) Thermocouples (red lines) for chamber air temperature. (c) schematic diagram of the chamber system. MFC refers to mass flow controller. LT and AT refer to leaf temperature and air temperature, respectively.

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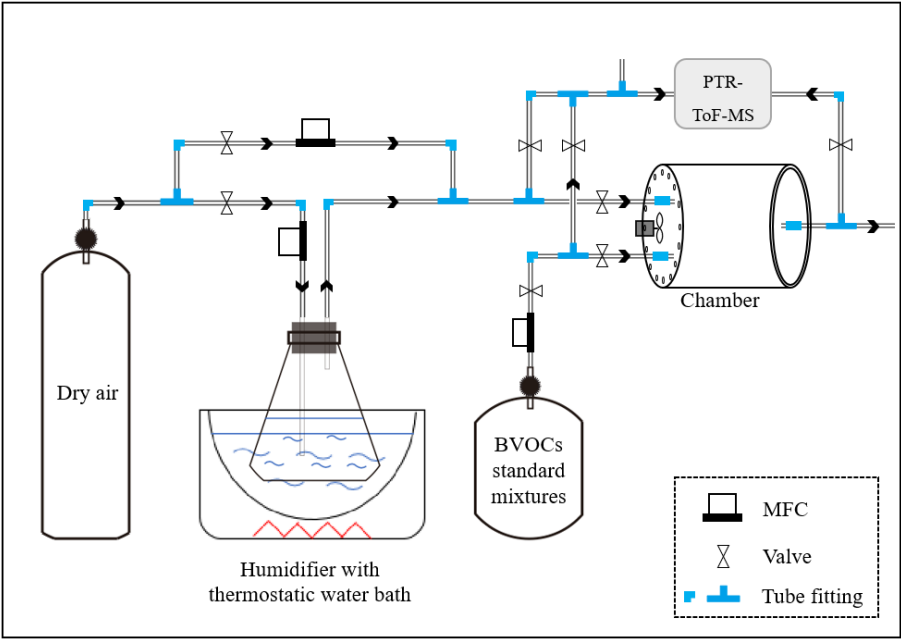
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Figure 2. Schematic diagram of chamber characterization experiments in the laboratory using standard BVOCs mixture to imitate emissions of BVOCs from branches. MFC: mass flow controller.

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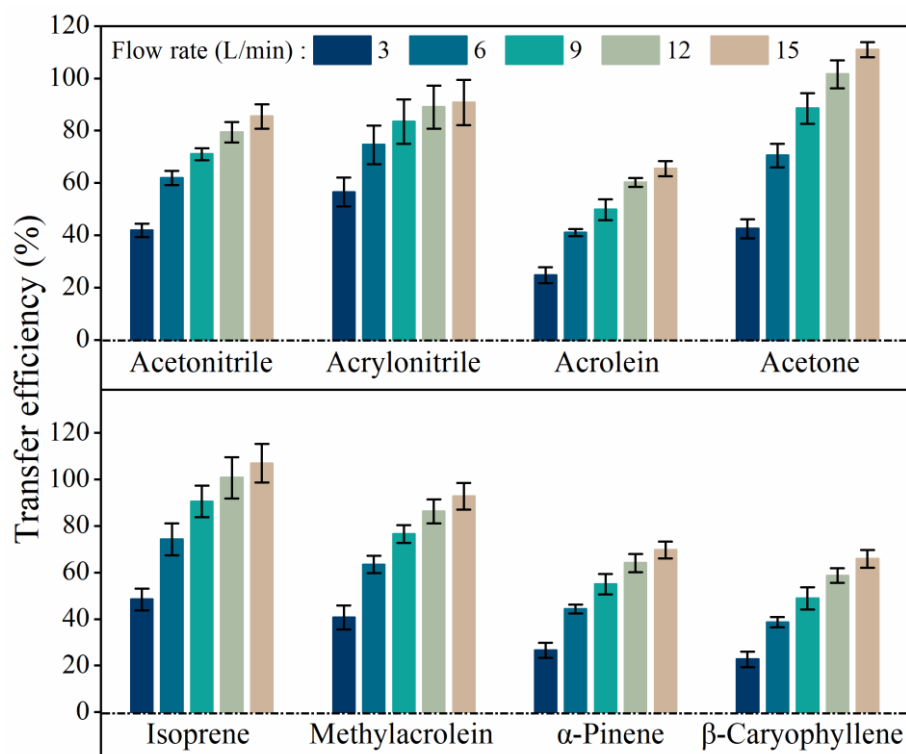
Figure 4. Transfer efficiencies of BVOCs when passing through the chamber under different flow rates in the lab simulation experiments. Error bars represents standard deviations of triplicate measurements.
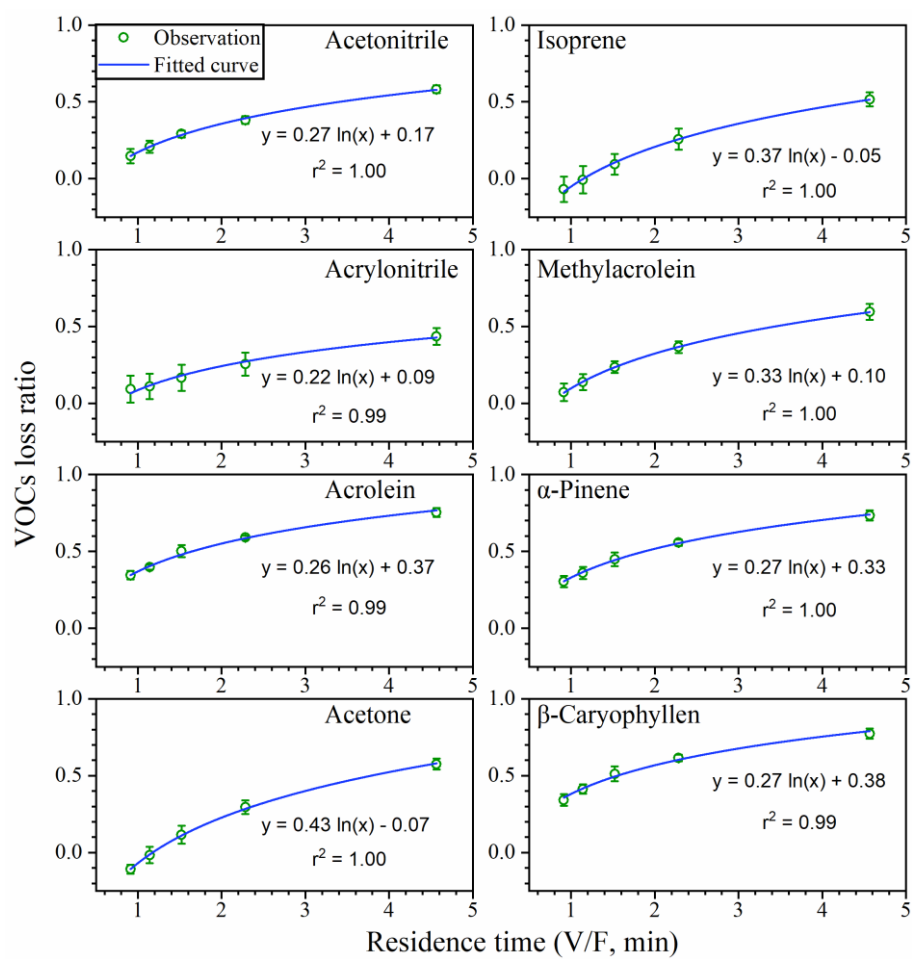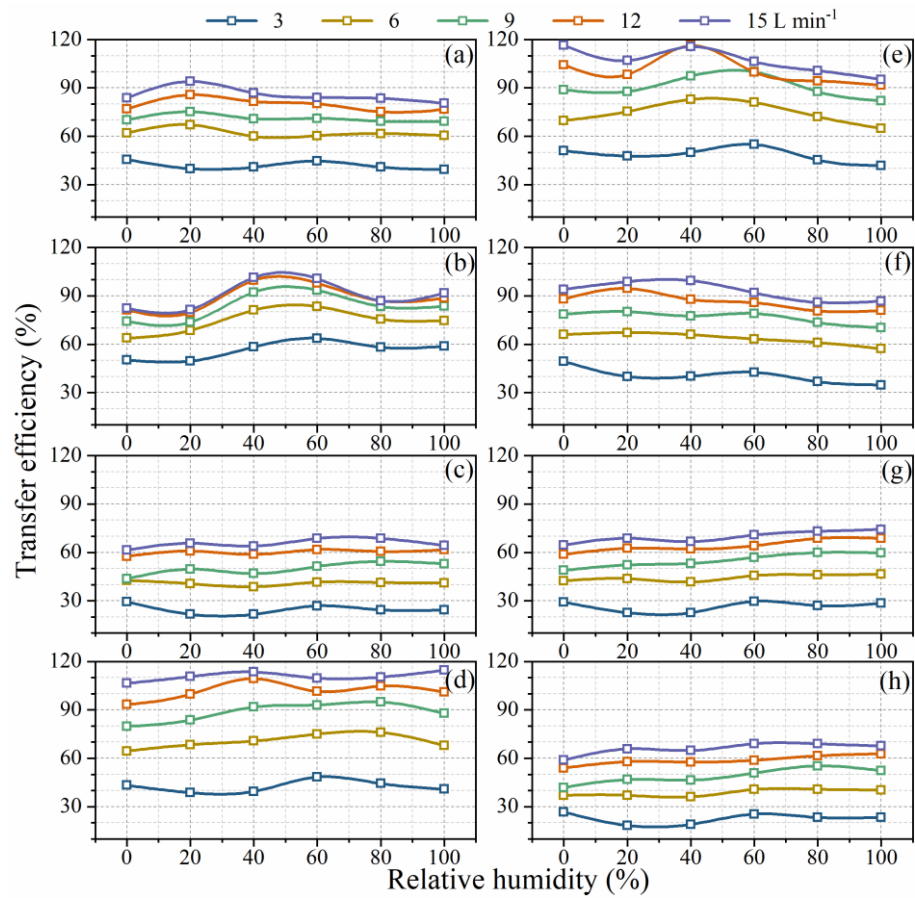
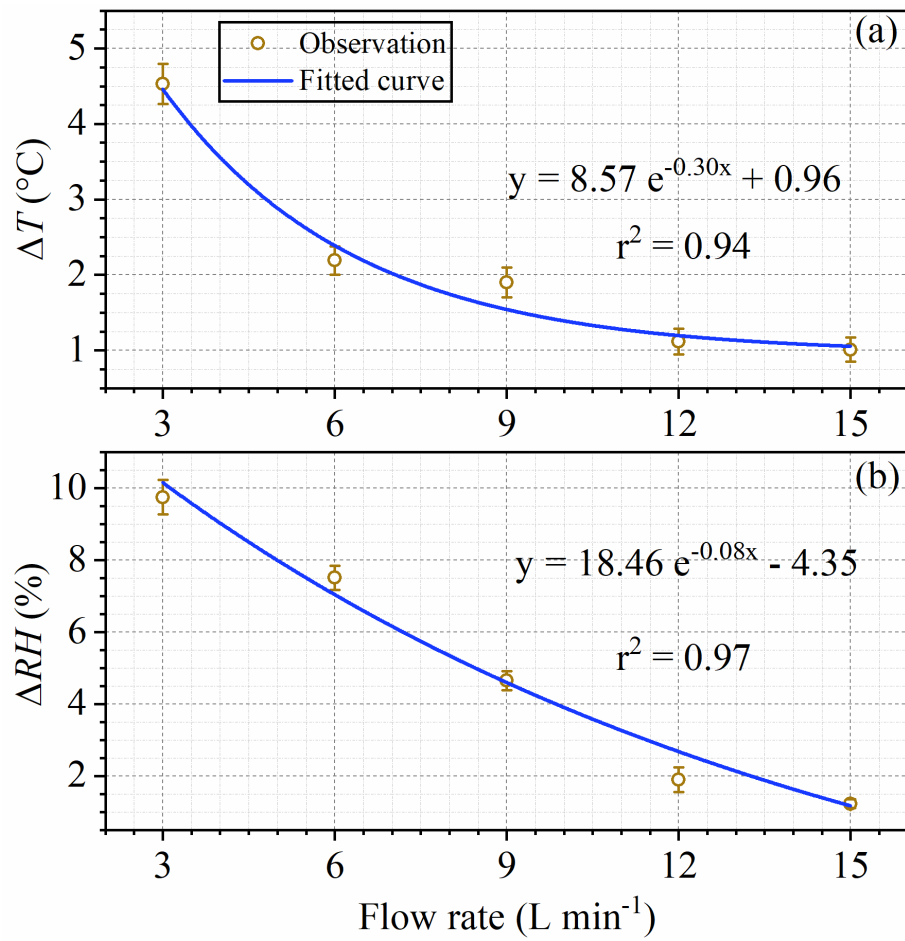Figure 5. Changes of BVOCs loss ratios (mean ± 1σ, n=5) with residence times.

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847 Figure 7. Enclosure-ambient differences in temperature (a) and RH (b) under different flow rates.

848 Circles with errors bars are the measured means and standard deviations. The solid lines are

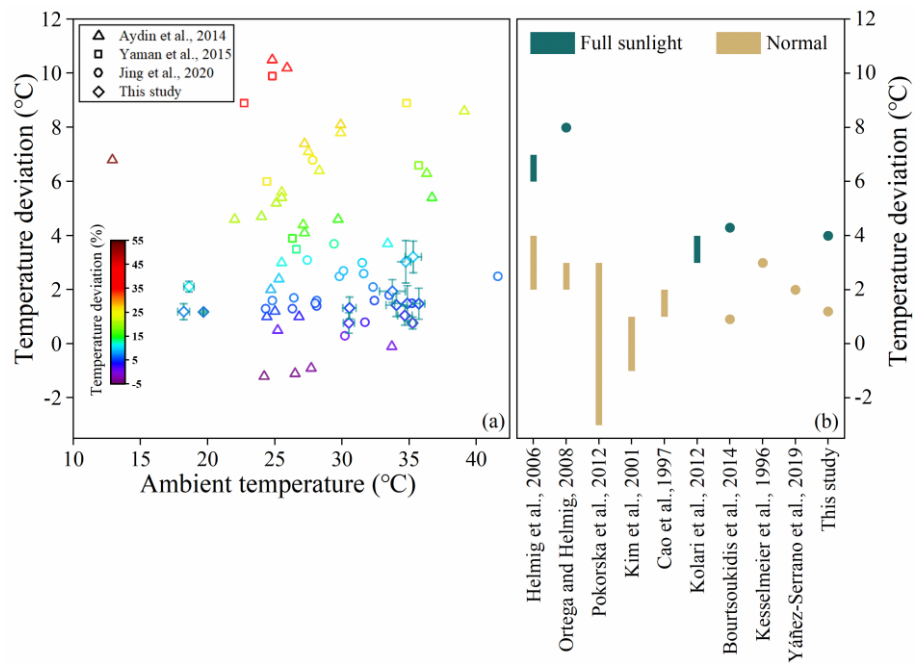849 exponential fit curves.

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