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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13

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 absorptive 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 ℃

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.

43

44 **Key words:** Biogenic volatile organic compounds (BVOCs); Semi-open dynamic chamber;

45 Transfer efficiency; Wall loss; Emission rates; Ambient-enclosure differences.

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47 **Highlights**

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

49 • Higher 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%.

52

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). 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) 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, humidity, 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., 2014). These will change the physiological state of plants and cause abnormal emissions (Ortega and Helmig, 2008).

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83   For this reason, static or semi-static enclosures are considered to be screening tools to verify emitters

84   and non-emitters (Niinemets et al., 2011; Li et al., 2019). Unlike static enclosure, dynamic enclosure

85   introduces circulating air and can reduce the differences in environmental parameters between the

86   enclosure and the ambient to a great extent. Therefore, dynamic enclosure is more reliable and

87   preferred for measuring emissions of BVOCs from plants (Ortega and Helmig, 2008; Pape et al.,

88   2009; Kolari et al., 2012). However, large differences still exist for dynamic enclosure if air

89   exchange is slow. For example, temperature deviation of more than 10 ℃ between enclosure and

90   the ambient was observed when using dynamic enclosure for field studies (Aydin et al., 2014). This

91   way the measured emission reflects that under a temperature-disturbed environment and therefore

92   might not well represent the real situations. In addition to deviations of environmental parameters

93   in enclosures, adsorption of terpenes can occur on most parts of the enclosure system, including

94   chamber walls, gasket surfaces, and system tubing (Niinemets et al., 2011). The materials used to

95   construct enclosures, like neoprene and low-density polyethylene polymers, are thought to have

96   potentially significant adsorption of VOCs (Niinemets et al., 2011 for a review), resulting in

97   underestimation of emission rates.

98   An ideal dynamic enclosure for measuring emissions of BVOCs from plants should be one without

99   changing the physiological state of the enclosed plant parts, and without introducing pollutions or

100   causing systematic losses. Ortega et al. (2008) used ice water bath and copper tube to drop the

101   temperature and humidity of the circulating air, thereby reducing the deviations of enclosure

102   environmental parameters from the ambient. Aydin et al. (2014) also used circulating cooling water

103   to reduce the temperature of the circulating air, but the temperature inside the enclosure is still much

104   higher than that of the ambient. Kolari et al. (2012) evaluated the performances of dynamic chamber

105   in uncontrolled field environment, the results indicate that the systematic losses of VOCs are higher

106   in wet environment or under high relative humidity. Lüpke et al. (2017) tested the chamber wall

107   effects of an environmentally controlled dynamic chamber using Δ^2-Carene in the laboratory. Their

108   results demonstrated that there were no chamber wall effects for Δ^2-Carene but there did exist

109   background contaminations for some other compounds. To date, although there are a variety of

110   dynamic chambers, including sophisticated enclosures designed for laboratory measurements

111   (Copolovici and Niinemets, 2010; Lüpke et al., 2017; Mozaffar et al., 2017) and simple and user-

112   friendly enclosures for field measurements(Matsunaga et al., 2011; Helmig et al., 2013; Wiss et al.,

113   2017), the performances and wall effects of most dynamic enclosures, particularly those used in the

114   field, are not systematically characterized, and this would lead to difficulties in comparing results

115   from various field measurements. Therefore, in order to pool together the measurement results

116   worldwide to generate a quality dataset that can be shared by the scientific community, it is

117   imperative to get the dynamic enclosures systematically characterized before they are used in the

118   field to measure emissions of BVOCs.

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

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

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

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

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

124   and relative humidity), equilibrium time and wall effects, are assessed and discussed in this study.

125   **2 Descriptions of the semi-open dynamic chamber system**

126   **2.1 Design of the semi-open dynamic chamber system**

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

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

129   200A; DuPont, USA). It has a volume of 13.7 L with a diameter of 250 mm and a height of 280 mm.

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

131   inlet). An electric Teflon fan is secured in the middle of inner side of the inlet panel to establish

132   homogeneous chamber conditions; and small holes (5 mm I.D.) are drilled at the edge and ambient

133   air entering from the small holes can flush the inner wall of the chamber and thus reduce the possible

134   occurrence of water condensation on the inner wall. The outlet is covered by polymethyl

135   methacrylate panel which is also coated with Teflon film at the inner-chamber side and joined to the

136   main chamber body by screw. Four holes (Fig. 1) are drilled on the panel: the hole (10 mm I.D.) in

137   the middle is used to seal the branch around the trunk side; the hole "1" (10 mm I.D.) is used to

138   connect temperature and relative humidity sensor (HP32, Rotronic, Switzerland); the hole "2" (10

139   mm I.D.) is used to connect to adsorption cartridges for sampling BOVC for offline analysis; and

140   "3" (10 mm I.D.) is used to connect to the air pump. In order to avoid artificial disturbance to

141   branches when installing the chamber, the polymethyl methacrylate board is cut into two pieces (Fig.

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142 1), which are spliced together after branches are enclosed in the chamber. The gaps between the hole

143 and the trunk are sealed by Teflon taps. All the tubing lines in the system are Teflon made. The air

144 pump is equipped with a flowmeter and a mass flow controller is used to maintain a constant flow

145 rate. Concentrations of CO_2 and H_2O inside and outside the chamber are monitored by infrared gas

146 analyzer (Li-7000; Li-Cor Inc., Lincoln, USA). A proton transfer reaction-time of flight-mass

147 spectrometer (PTR-ToF-MS; Ionicon Analytik GmbH, Innsbruck, Austria), which has time

148 resolution up to one second, is used to monitor the real-time concentrations of BVOCs inside the

149 chamber. More detail descriptions about the determination of BVOCs by the PTR-ToF-MS can be

150 found elsewhere (Wang et al., 2014; Huang et al., 2016; Zhang et al., 2020). Temperature and

151 relative humidity (RH) are measured by sensors, one is installed inside of the chamber and the other

152 is installed outside. A light sensor (Li-1500; Li-Cor Inc., Lincoln, USA) is installed on the top of

153 the chamber to monitor the photosynthetically active radiation (PAR).

154 **2.2 Collection of offline BVOCs samples and lab analysis**

155 Apart from online measurement by PTR-ToF-MS, offline BVOC samples are also collected since

156 PTR-ToF-MS cannot differentiate isomers of MTs and SQTs. The air is drawn through an ozone

157 scrubber followed by solid adsorbent cartridges (Tenax TA/Carbograph 5TD, Marks International

158 Ltd, UK) using an automatic sampler (JEC921, Jectec Science and Technology, Co., Ltd, Beijing,

159 China) at a flow rate of 200 mL min^{-1} for 10 minutes (Fig. 1). Ambient air samples are collected

160 concurrently in the same way. The collected samples are stored in a portable refrigerator at 4 ℃ in

161 the field and at -20 ℃ after brought back to the lab. In the lab, these samples are analyzed by an

162 automatic thermal desorption system (TD-100, Markes International Ltd, UK) coupled to a model

163 7890 gas chromatography (GC) with a mode 5975 mass selective detector (MSD) (Agilent

164 Technologies, Inc., California, USA). The adsorbent cartridges are thermally desorbed by the TD-

165 100 at 280 ℃ for 10 minutes and then the desorbed analytes are transferred by pure helium into a

166 cryogenic trap at -10 ℃. Then the trap is rapidly heated to transfer the analytes to the GC/MSD

167 system with a capillary column (Agilent, HP-5MS, 30 m × 0.25 mm × 0.25 μm). The GC oven

168 temperature is programmed to be initially at 35 ℃ (held for 3 minutes), then increase to 100 ℃ at

169 5 ℃ min^{-1} and hold for 3 minutes, to 150 ℃ at 10 ℃ min^{-1} and hold for 3 minutes, and then to

170 280 ℃ with a final hold time of 2.5 minutes. The MSD is operated in selected ion monitoring (SIM)

171 mode, and the ionization method is electron impacting. The calibration standards were prepared by

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172 dissolving the pure liquid standards (Table S1) into n-hexane solution (Kajos et al., 2013; Fang et

173 al., 2021). 1 µL of each standard solution was injected into an adsorbent cartridge and swept with

174 pure helium at 100 mL min^{-1} for two minutes to scavenge n-hexane, and then run the same way as

175 real samples by the TD-GC/MSD system. The method detection limits (MDLs) varied from 5 to 17

176 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).

177 **2.3 Ozone scavenging**

178 Ozone (O_3) may impact emissions of BVOCs from plants (Feng et al., 2019). While many dynamic

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

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

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

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

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

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

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

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

187 Therefore, losses of BVOCs due to reaction with ozone in the chamber can be ignored (Kolari et al.,

188 2012). However, for the sorbent cartridges used to take BVOCs samples for off-line analysis (Chen

189 et al., 2019; Aydin et al., 2014), ozone will be adsorbed together with BVOCs, resulting in losses of

190 BVOCs due to reaction with ozone in the cartridges during the deliver and storage of the cartridges

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

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

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

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

195 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

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

197 KI or $Na_2S_2O_3$ solution and then dried in 50 ℃. The KI/$Na_2S_2O_3$ tube filters were prepared with

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

199 and then swept to dry with nitrogen. As showed in Fig. S1, air flow with ozone concentration of

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

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

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

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

204   which means that all of them can effectively scavenge ozone. Besides, to test if any losses of BVOCs

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

206   ozone scrubbers at the same flow rate of 200 mL min⁻¹ as normal field sampling, and the

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

208   PTR-ToF-MS (Fig. S2). The results revealed that the recoveries of BVOCs on average were 10.05 %,

209   100.89 %, 100.63 % and 66.70 % for KI filter, $Na_2S_2O_3$ filter, KI tube and $Na_2S_2O_3$ tube, respectively.

210   Therefore, both $Na_2S_2O_3$ filter and KI tube can be used to scavenge ozone with good recoveries.

211   Here $Na_2S_2O_3$ filters were used to scavenge ozone as in previous studies (Helmig et al.,2006; 2007).

2.4 Optimization of flow rates

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

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

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

216   standard mixtures in the laboratory under 25 ℃. The standard mixtures contained representative

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

218   methylacrolein, α-pinene and β-caryophyllene (Table S2); they were prepared in pure nitrogen with

219   concentrations of 300-600 ppbv and compressed into a stainless steel canister with a pressure of 40-

220   50 mbar in the same way by Rhoderick and Lin (2013) and Mermet et al. (2019). As shown in Fig.

221   2, this standard gas mixture was released into the chamber at a constant flow rate to simulate the

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

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

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

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

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

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

228   calibrated by a soap-membrane flowmeter (Gilian Gilibrator-2, Sensidyne, USA). The real-time

229   concentrations of the standard mixtures in the chamber were measured by PTR-ToF-MS, and the

230   concentrations of these VOCs stored in the stainless steel canister were also measured by PTR-ToF-

231   MS before introduced into the chamber. Acetonitrile, acrylonitrile, acrolein, acetone, isoprene,

232   methylacrolein, α-pinene and β-caryophyllene were detected with *m/z* 42.019, 45.015, 57.073,

233   59.052, 69.060, 71.040, 137.072 and 204.986, respectively. Transfer efficiency for each compound

234   is expressed as the ratio (%) of outgoing air concentration and incoming air concentration at steady

235   state.

236   **2.5 Field tests**

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

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

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

240   g dry mass of leaves were enclosed in the chamber. The air temperature was 31-33 ℃ and PAR was

241   1000-1200 μmol m^{-2} s^{-1}. The enclosure and ambient temperature/relative humidity were measured

242   by calibrated sensors (HP32, Rotronic, Switzerland) under circulating air flow rates of 3, 6, 9, 12

243   and 15 L min^{-1}.

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

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

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

247   2014). *Pinus massoniana*, which is a widely distributed tree species in south China (Gu et al., 2019;

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

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

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

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

252   **3 Results and discussion**

253   Theoretically concentrations of BVOC species emitted by plant leaves inside a dynamic chamber

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

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

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

257   background concentrations of the BVOC species in air entering into the chamber and C (μg L^{-1}) is

258   the concentrations of the BVOCs species in air exiting the chamber, and F (L min^{-1}) is air flow rate

259   through the chamber. The above equation can be expressed explicitly for changing $C(t)$ with time t

260   as below:

261
$$C(t) = C_0 + \frac{E}{F} \cdot (1 - e^{-\frac{F}{V} \cdot t}) \qquad (2)$$

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

263   C_s:

264
$$C_s = C_0 + \frac{E}{F} \qquad (3)$$

265   and then E can be calculated as

266
$$E = F \times (C_s - C_0) \qquad (4)$$

267   As showed in Eq. (2), the F/V value, which is the reciprocal of residence time (V/F), determines

268   how fast a steady state will reach. At a given E, a lower F will result in a longer time to reach steady

269   state but a higher steady state concentration that benefits instrumental measurements, and vice versa.

270   In the field measurements, we prefer a shorter equilibrium time to track the variation of emission

271   rates with changing environment parameters (like PAR) if E/F is well above the method detection

272   limits. In fact, as showed in Fig. S3, theoretically steady state concentrations inside the enclosure

273   would decrease with the increasing flow rates. However, even at flow rates as high as 50 L min^{-1}

274   (residence time <15 seconds), if leaves with 5.0 g dry mass are enclosed, a BVOC species with an

275   extremely low emission rate of 0.01 μg g^{-1} h^{-1} would have predicted steady state concentration of

276   ~10 μg m^{-3}, which is still well above the method detection limits (Table S1) of SQTs that typically

277   have much lower emission rates when compared to isoprene and MTs. Therefore, the influence of

278   circulating air flow rates on the detection of BVOCs is not an important issue to limit the

279   performance of the dynamic enclosure method and thus will be not discussed hereafter.

280   **3.1 Equilibrium time**

281   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

282   residence time), $e^{-(F/V \times t)} < 0.01$, and in this case it can be concluded with confidence that after 5 cycles

283   of residence time the equilibrium or the steady state is reached.

284   Figure 3 shows real-time concentrations of VOCs in the chamber at a flow rate of 9 L min^{-1} when

285   using a standard mixture to imitate the BVOC emission in the lab (Fig. 2). The mixing ratios of

286   VOCs in the chamber increased with time and became stable after ~3-6 minutes or ~2-4 cycles of

287   residence time (Fig. 3). The representative VOC species differs in their times reaching steady state,

288   varying from ~3 minutes for α-pinene to ~6 minutes for acetone and acrylonitrile. The equilibrium

289   time are all within the 5 cycles of residence time (7.5 min).

290　The real-time mixing ratios of VOCs in the chamber changed in a pattern that was in fairly good

291　agreement with that theoretically predicted by above Eq. (2); however, they were all close and

292　consistently lower than the theoretically predicted values (Fig. 3). The gaps between the measured

293　and predicted values seemed to be larger for heavier BVOC compounds (e.g. α-pinene and β-

294　caryophyllene) than lighter species (e.g. isoprene). Also as showed in Fig. 3, after the stop of

295　injecting the standard mixture, the mixing ratios inside the chamber dropped to their initial

296　background values in a way that was fitted well with theoretical prediction.

297　The lower than predicted steady-state concentrations were largely due to losses of VOCs in the

298　chamber, which would result in a lower C_s in Eq. (3) and thereby a lower "real" E by Eq. (4).

299　Therefore, apart from equilibrium time, the loss or transfer efficiency must be further considered

300　for an accurate emission measurement by a dynamic chamber.

301　**3.2 Transfer efficiency**

302　Adsorption losses of BVOCs can be a significant fraction in enclosure systems (Helmig et al., 2004).

303　Although Tedlar or Teflon films, which are chemically inert with low surface uptake rates for

304　BVOCs, were used for most dynamic enclosures to diminish the adsorption in the enclosure (Ortega

305　and Helmig, 2008; Gomez et al., 2019; Chen et al., 2020), adsorptive losses cannot be completely

306　eliminated. Kolari et al. (2012) observed 6-29 % compounds losses in a chamber made of transparent

307　acrylic plastic with Teflon-coated inner surfaces. Hohaus et al. (2016) observed average losses of

308　15 % in their enclosure consisting of FEP film. In this study, to assess the adsorptive losses and

309　transfer efficiencies, tests were conducted under different flow rates and RH in the lab with the

310　standard mixture (Fig. 2).

311　**3.2.1 Influence of flow rate on transfer efficiency**

312　Figure 4 shows transfer efficiencies under air circulating rates (dry air) of 3, 6, 9, 12 and 15 L min⁻

313　^{1}. Transfer efficiencies of all species increased when flow rates increased from 3 to 15 L min⁻¹, such

314　as from 41.9±2.6 % to 85.4±4.6 % for acetonitrile, 56.5±5.5 % to 90.8±8.7 % for acrylonitrile,

315　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

316　106.9±8.3 % for isoprene, 40.6±5.2 % to 92.8±5.8 % for methylacrolein, 26.6±3.2 % to 69.7±3.7 %

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

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

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

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

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

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

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

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

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

326   optimized.

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

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

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

330   residence times (Fig. 5) and decreased with flow rates (Fig. S4), and a larger flow rate would be

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

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

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

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

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

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

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

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

339   for heavier BVOCs like MTs and SQTs.

340   **3.2.2 Influence of RH on Transfer efficiency**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

364   **3.2.3 Possible correction of VOCs losses in lab simulations**

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

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

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

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

369    $$V \frac{dC}{dt} = E - F \times (C - C_0) - k \times C \qquad (5)$$

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

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

372    $$E = F \times (C_s - C_0) + k \times C_s \qquad (6)$$

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

374   the steady state concentration C_s, based on above Eq. (6) we could calculate the adsorptive loss term

375    $k \times C_s$ and k as well.

376   The correction factors for different VOCs at different flow rates and RH are presented in Table S3.

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377   Consistent with the lower transfer efficiencies at lower flow rates, for a VOC species, the largest k

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

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

380   behavior on the surfaces.

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

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

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

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

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

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

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

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

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

390   such procedure would also set enough time for adsorption of emitted compounds and thereby benefit

391   lowering the adsorptive loss during tests afterwards. On the other hand, adsorption of VOCs on

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

393   2012). Some more adsorptive species, like SQTs, after getting adsorption saturated at lower

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

395   2010). Consider the temperature effect on the adsorptive loss, field enclosure measurements of

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

397   have less interferences by adsorptive loss.

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

399   be implicative to deal with the more complex adsorption behavior in field measurements. Ortega et

400   al. (2008) made adsorption loss corrections of VOCs by adding internal standard into the enclosure

401   to calculate the recovery. Therefore, for more accurate emission measurements by dynamic

402   enclosures in the field, adding surrogate compounds in the circulating air in the same way as this

403   simulation study (Fig. 2) would be a possible way to evaluate *in situ* transfer efficiencies.

404   **3.3 Comparison of environmental parameters inside and outside of the chamber in field**

405   **measurements**

406   When conducting field measurements of BVOCs with branch enclosures, it is vital that

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407 environmental parameters, particularly temperature, resemble the natural growing conditions and

408 are not seriously deviated due to enclosure. As temperature will affect the emission of BVOCs from

409 plants in an exponential way mainly due to the fact that temperature can modify the activity of

410 biosynthetic enzymes, the vapor pressures and the cellular diffusion rates of BVOCs

411 (Laothawornkitkul et al., 2009), and a small change in temperature may induce big variation in

412 BVOCs emissions. Here we first conducted tests about the influence of flow rates (3-15 L min^{-1}) on

413 the differences in temperature and RH between ambient and enclosure, then we conducted tests for

414 *Pinus massoniana* at a medium flow rate of 9 L min^{-1}.

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

416 As showed in Fig. 7, when conducting tests of BVOCs emissions (Fig. S5) with a branch of

417 *Mangifera indica* (~7 g dry mass of leaves) under ambient air temperature of 31-33 ℃ and PAR of

418 1000-1200 μmol m^{-2} s^{-1}, the differences in both temperature and RH between enclosure and ambient

419 air decreased sharply with the increase of flow rates. As flow rates increased from 3 L min^{-1}

420 (residence time ~4.5 min) to 15 L min^{-1} (residence time ~0.9 min), the enclosure-ambient

421 temperature differences (ΔT) decreased from 4.5±0.3 to 1.0±0.2 ℃ (Fig. 7a), the RH differences

422 (ΔRH) decreased from 9.8±0.5 % to 1.2±0.1 % (Fig. 7b). The results confirmed that the ambient-

423 enclosure differences in T/RH could be largely reduced if enclosure air is sufficiently circulated. It

424 seemed that at a flow rate of 9 L min^{-1} (residence time ~1.5 min), the differences could be fairly

425 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*

428 As mentioned above, higher flow rates will result in lower steady state concentrations. To guarantee

429 the detection of BVOCs species (Fig. S5) with very low emission rates, we only adopted a medium

430 flow rate of 9 L min^{-1} when conducting tests during 9:00-17:30 on 8 October 2019 with healthy

431 nature-grown branches of a pine (*Pinus massoniana*) tree (~20-year-old and ~12 m high) to compare

432 the environmental parameters inside and outside the enclosure.

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

434 inside than outside the enclosure (Fig. S6). On average the temperature deviation inside the chamber

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

436 53 ppm deviation on average with the relative deviation of -(4-15) % during the day. The light

437   transmittance was 92.4±5.4 % on average.

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

439   2008). The temperature deviation inside the chamber in this study is smaller when compared to

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

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

442   a temperature deviation of 4 ℃ was observed in this study, lower than that of 6-7 ℃ observed by

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

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

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

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

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

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

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

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

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

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

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

454   ~15 μg m^{-3} for α-pinene) were orders of magnitude higher above their MDLs. Therefore, as

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

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

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

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

459   **4 Conclusions**

460   In order to obtain accurate emission rates of BVOCs from plants grown under natural environment,

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

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

463   a self-made dynamic enclosure, we demonstrated that operational parameters like air circulating

464   rates could impact heavily on the performance of dynamic enclosures, and therefore should be

465   optimized before field applications. As revealed by the results, higher circulating rates could not

466   only reduce the equilibrium time and facilitate higher time resolution emission measurements, but

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467 also reduce the adsorptive losses and the enclosure-ambient temperature/RH differences and thus

468 obtain more accurate emission rates under natural conditions. Therefore, in field measurements

469 using the dynamic enclosure method, if advanced analytical techniques like PTR-ToF-MS can

470 assure sensitive enough detections, higher air circulating flow rates are preferred.

471 It is worth noting that although the inner surfaces were coated with inert Teflon films, based on lab

472 simulation with standard mixtures, BVOC species like monoterpenes and sesquiterpenes showed

473 transfer efficiencies less than 70% even the residence times were kept as low as <1 min. This

474 suggests that emission factors of these species from dynamic enclosures might be underestimated if

475 the adsorptive losses were not seriously considered and reduced, and further efforts are needed to

476 develop a certified protocol to assure accurate emission measurements particularly for species (e.g.,

477 monoterpenes and sesquiterpenes) with lower transfer efficiencies.

478

479 **Author contributions**

480 JQZ designed and characterized the chamber with the support of HNZ, XMW, YLZ and WS. JQZ

481 and HNZ carried out the chamber assessments. JQZ, HNZ and ZFW carried out the BVOCs

482 measurements in the field. JQZ prepared the manuscript with input from all co-authors.

483

484 **Data availability**

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

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

487

488 **Supplement**

489 The supplement related to this article is available online.

490

491 **Competing interests**

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

493

494 **Acknowledgements**

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721 **Figure captions**

722 Figure 1. Schematic diagram of the semi-open dynamic chamber system for field measurements of

723 BVOCs from plant leaves.

724 Figure 2. Schematic diagram of chamber characterization experiments in the laboratory using

725 standard BVOCs mixture to imitate emissions of BVOCs from branches.

726 Figure 3. Changes of BVOCs concentrations in the chamber during lab simulation experiments. The

727 black dashed lines are background concentrations. Blue solid lines represent the theoretically

728 predicted BVOCs concentrations in the chamber. The green circles are concentrations measured by

729 the PTR-ToF-MS. Green solid lines represent fitted BVOCs concentrations in the chamber.

730 Figure 4. Transfer efficiencies of BVOCs when passing through the chamber under different flow

731 rates in the lab simulation experiments. Error bars represents standard deviations of triplicate

732 measurements.

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

734 Figure 6. Influence of relative humidity and flow rates on transfer efficiencies of BVOCs, (a)-(h)

735 represents acetonitrile, acrylonitrile, acrolein, acetone, isoprene, methylacrolein, α-pinene and β-

736 caryophyllene, respectively.

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

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

739 changes.

740 Figure 8. Comparison of temperature deviation (℃) and relative temperature deviation (%) with

741 that reported in previous studies: (a) temperature deviation versus ambient temperature; (b)

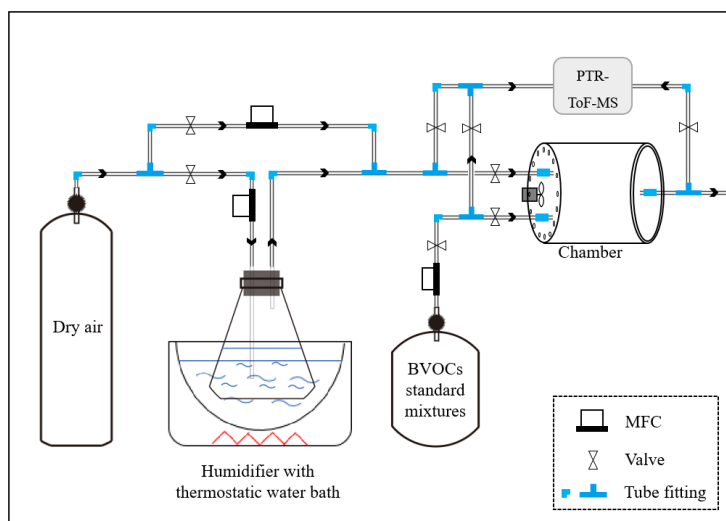742 temperature deviation (℃) under normal and full sunlight in different enclosures.

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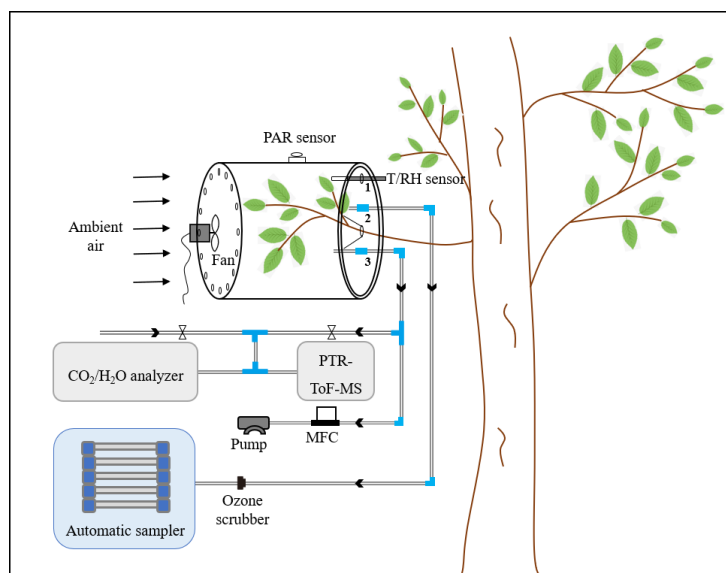
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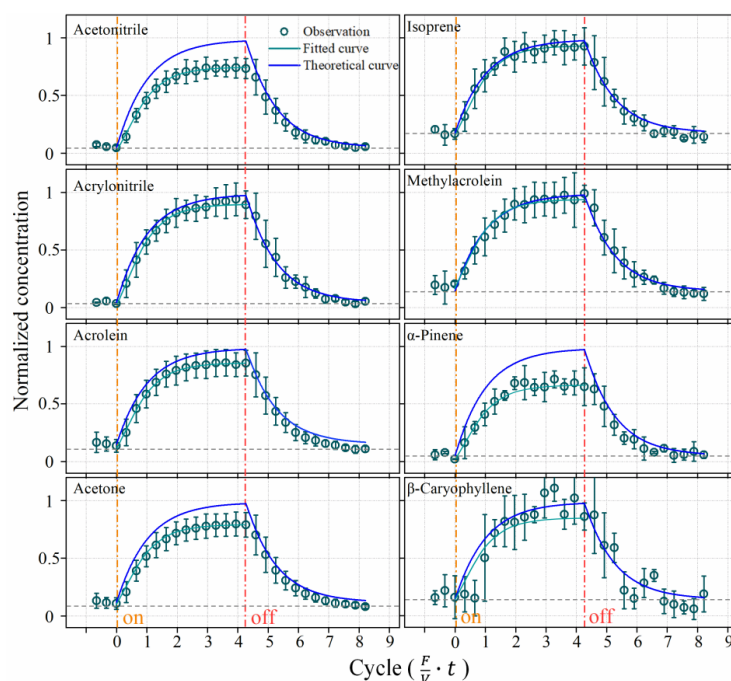
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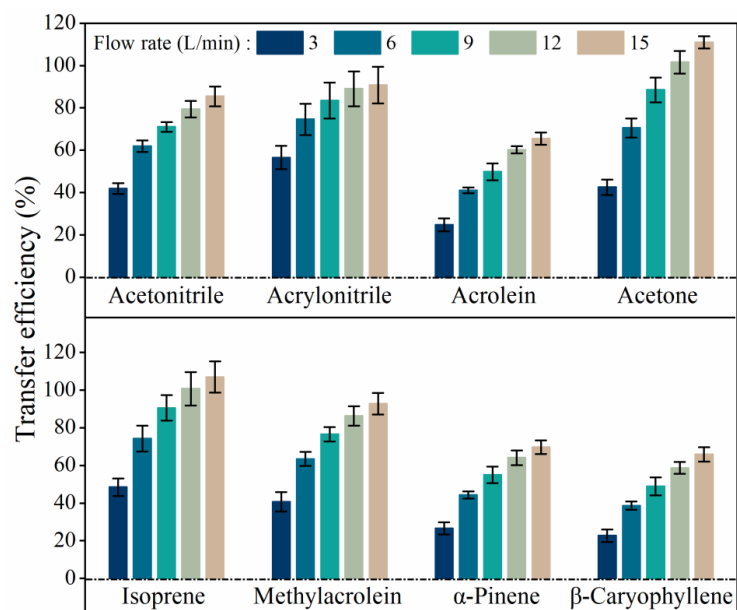
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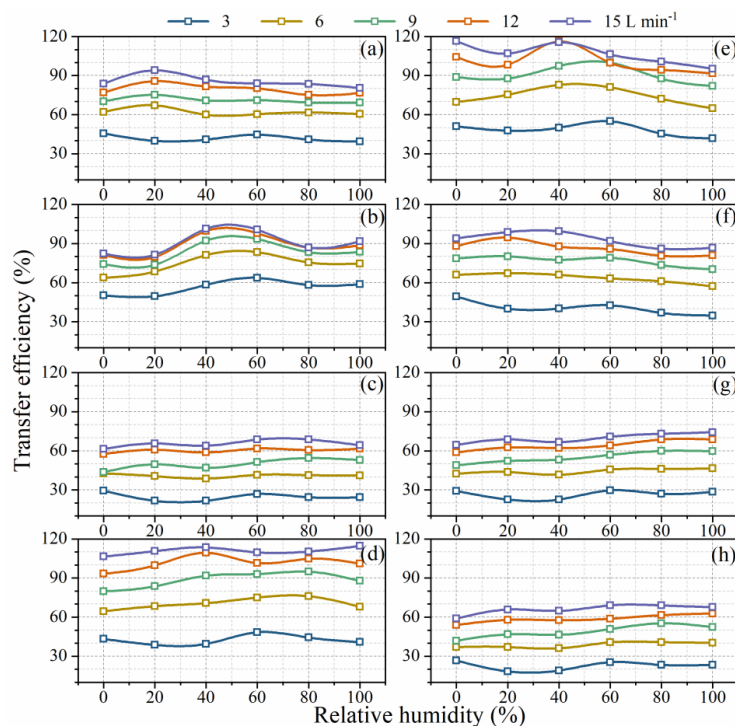
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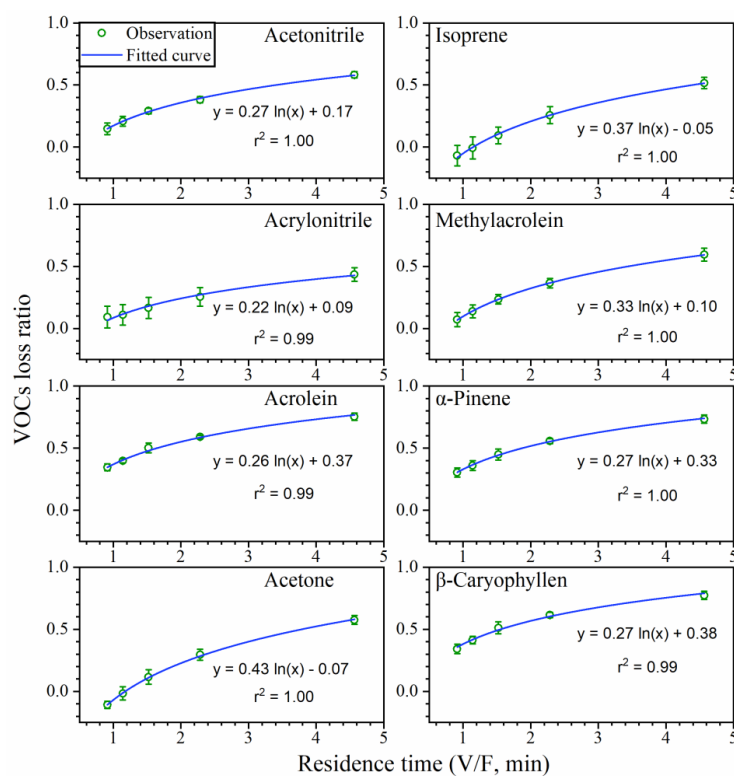
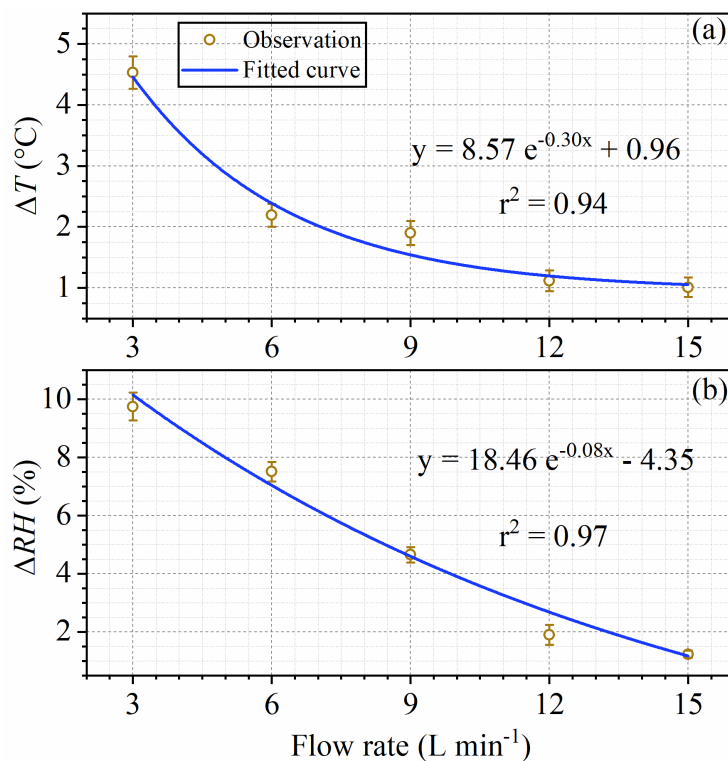Figure 5. Changes of BVOCs loss ratios (mean $\pm 1\sigma$, n=5) with residence times.

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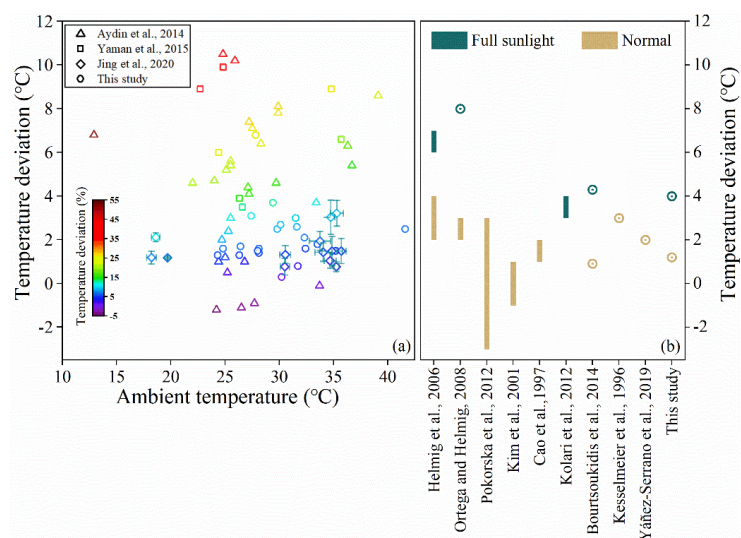
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