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Emissions of isoprenoids from dominant tree species in subtropical China

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Emission factors (E_s) are among the major sources of uncertainty in regional or global emission estimates of biogenic volatile organic compounds (BVOCs). Tropical vegetation contributes approximately 70% of global BVOC emissions, yet *in situ* measurements of BVOC emissions from tropical tree species, especially naturally grown mature trees, are quite limited. In this study, BVOC emissions from twenty mature trees (15 evergreen broad-leaved and 5 evergreen needle-leaved) were measured using dynamic chambers, and the emitted BVOCs were collected using sorbent tubes and speciated with a thermal desorption-gas chromatography/mass spectrometry system (TD-GC/MS). Twenty BVOC compounds including, isoprene, 14 monoterpene (MT) species and 9 sesquiterpene (SQT) species were quantified to calculate their E_s . The results showed that *Eucalyptus urophylla* had the largest E_s of isoprene ($26.47 \pm 3.70 \mu\text{g g}^{-1} \text{h}^{-1}$) among all the measured trees, followed by *Ficus hispida* ($20.74 \pm 1.78 \mu\text{g g}^{-1} \text{h}^{-1}$), *Syzygium hainanense* ($20.49 \pm 1.36 \mu\text{g g}^{-1} \text{h}^{-1}$), *Casuarina equisetifolia* ($18.70 \pm 2.91 \mu\text{g g}^{-1} \text{h}^{-1}$), and *Mangifera indica* ($11.71 \pm 7.04 \mu\text{g g}^{-1} \text{h}^{-1}$). α -Pinene, β -pinene, and limonene were the most abundant MTs, of which the largest E_s were observed for *Magnolia denudata* ($8.33 \pm 2.05 \mu\text{g g}^{-1} \text{h}^{-1}$), *Castanopsis hystrix* ($5.29 \pm 3.24 \mu\text{g g}^{-1} \text{h}^{-1}$), and *Magnolia denudata* ($3.11 \pm 1.07 \mu\text{g g}^{-1} \text{h}^{-1}$), respectively. The E_s of SQTs for the measured trees were lower than $0.50 \mu\text{g g}^{-1} \text{h}^{-1}$ except for *Magnolia denudata* ($1.10 \pm 0.41 \mu\text{g g}^{-1} \text{h}^{-1}$). β -Caryophyllene was the most common SQT, with *Magnolia denudata* having the highest E_s of $0.09 \pm 0.03 \mu\text{g g}^{-1} \text{h}^{-1}$. The localized E_s for dominant tree species could be used to update BVOC emission factors for typical vegetation types and help improve BVOC emission estimates in typical subtropical regions and narrow their uncertainties.

KEYWORDS

biogenic volatile organic compounds (BVOCs), isoprene, monoterpenes, sesquiterpenes, dynamic chamber, emission factors, subtropical

Highlights

- BVOC emissions from subtropical tree species were measured *in situ* by a dynamic chamber.
- Fifteen evergreen broad-leaved and five needle-leaved mature trees were measured.
- Emission factors of speciated monoterpenes and sesquiterpenes were obtained.

1 Introduction

Terrestrial vegetation emits large amounts of biogenic volatile organic compounds (BVOCs), which play important roles in the biosphere and atmosphere (Loreto and Schnitzler, 2010). For plants, these compounds are infochemicals in communication with other organisms and can also provide protection against biotic and abiotic stresses (Niinemets, 2010a,b; Šimpraga et al., 2016). They can be oxidized by oxidants to form ozone and secondary organic aerosols (Di Carlo et al., 2004; Xu et al., 2015; Edwards et al., 2017; Hamilton et al., 2021; He et al., 2021; Zhang et al., 2022), and thus have profound impacts on regional air quality and climate change (Peñuelas and Staudt, 2010; Scott et al., 2017).

The global BVOC emissions from vegetation are estimated to be $\sim 1,000$ Tg yr⁻¹, of which approximately 70% is contributed by isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs) (Guenther et al., 1995, 2012). There are large uncertainties in BVOC emission estimates, and in some specific regions, such as China, a factor of 3–5 may occur among different estimations (Klinger et al., 2002; Arneth et al., 2008; Guenther et al., 2012; Wang et al., 2017; Li et al., 2020). A measurement-model comparison study in China showed that there were geographical differences in the consistency between predicted and measured isoprene mixing ratios (Zhang et al., 2020). Previous studies have demonstrated that the emission factor (E_s) is one of the most important factors that induces large gaps among different studies (Guenther et al., 2006, 2012; Tsui et al., 2009; Leung et al., 2010; Zheng et al., 2010; Wang et al., 2011, 2016, 2017; Situ et al., 2014; Li et al., 2020). For decades, a large number of field and laboratory measurements have been carried out worldwide to obtain E_s of BVOCs, yet most measurements were conducted for temperate or boreal plants (Evans et al., 1982; Tarvainen et al., 2005; Helmig et al., 2006, 2007, 2013; Ortega et al., 2008; Guenther, 2013; Aydin et al., 2014; Mu et al., 2022). On a global scale, tropical trees account for about 18% of the forest area (Jardine et al., 2020), but they contribute approximately 70% of the total emissions of BVOCs and 80% of the emissions of isoprene and MTs (Guenther et al., 2012). Apart from higher emission rates of BVOCs relative to temperate and boreal regions,

tropical regions have richer vegetation diversity with more uneven spatial distribution, and emissions of BVOCs in the tropics may have stronger spatial differences (Batista et al., 2019). However, to date, measurements of BVOC emissions from tropical trees are quite limited, and most of them were conducted in South America (the Amazon region), South Africa and India (Mu et al., 2022). In addition, due to limitations in measurement methods or experimental facilities, most field measurements for tropical trees only reported emissions of isoprene (Keller and Lerdau, 1999; Lerdau and Throop, 1999; Geron et al., 2002; Singh and Varshney, 2006; Singh et al., 2007, 2008), total MTs (Singh et al., 2011, 2014) and total SQTs, and lacked emissions of individual MT and SQT compounds (Guenther et al., 1996; Klinger et al., 1998, 2002; Otter et al., 2002; Harley et al., 2003, 2004; Varshney and Singh, 2003; Padhy and Varshney, 2005a,b; Jardine et al., 2020; Taylor et al., 2021). Due to their different reactivities in atmospheric oxidation processes (Atkinson and Arey, 2003; Di Carlo et al., 2004; Edwards et al., 2017), it is necessary to further characterize the emissions of MT or SQT monomers from tropical plants.

In the tropical/subtropical Asia, field measurements of BVOC emissions from trees were mostly conducted more than a decade ago based on static enclosure or leaf cuvettes (Yang et al., 2001; Klinger et al., 2002; Zhao et al., 2004; Huang et al., 2011), and laboratory measurements were conducted on seedlings (Tsui et al., 2009; Leung et al., 2010). The reported emission rates for isoprene and total MTs varied by up to several orders of magnitude. The reliability of static enclosure measurements is questionable in comparison with dynamic enclosure measurements (Niinemets et al., 2011; Li et al., 2019; Zeng et al., 2022). The laboratory control measurements for seedlings (Tsui et al., 2009; Leung et al., 2010), however, may not well-represent real-world emissions from mature trees under natural growing environments (Niinemets et al., 2011; Emmerson et al., 2016). In addition, default proportions of MTs and SQTs were widely adopted in the Model of Emissions of Gases and Aerosols from Nature (MEGAN) to estimate emissions of individual MTs/SQTs (Leung et al., 2010; Wang et al., 2011; Li and Xie, 2014; Situ et al., 2014; Li et al., 2020; Ma et al., 2021). Therefore, field measurements of BVOCs emissions in tropical/subtropical regions are far from satisfying the accurate, timely and detailed emission estimations of BVOCs.

In this study, we conducted field measurements of BVOC emissions in Guangdong Province, which is located in a tropical/subtropical area in south China with a forest coverage of 53.5% and relatively high BVOCs emissions (Li et al., 2020; Ma et al., 2021). However, there are large uncertainties in both the amounts and the compositions of BVOC emissions (Klinger et al., 2002; Li et al., 2020; Ma et al., 2021). Unlike previous studies in this region that mostly involved static enclosures with seedlings in the laboratory to measure emissions of isoprene

and total MTs, the present study aims: (1) to obtain real-world emission factors of isoprenoids for dominant tropical/sub-tropical tree species under natural growing environments by applying a dynamic chamber that was systematically evaluated (Zeng et al., 2022); (2) to quantify the emission rates of individual MTs and SQTs along with isoprene; and (3) to provide the localized emission factors that can be used to update BVOC emission estimates in the region.

2 Materials and methods

2.1 Field measurements

The field measurements were carried out in a sub-tropical region, Guangdong Province (Figure 1A). Twenty species of mature trees, including 15 evergreen broad-leaved trees and 5 needle-leaved trees, were measured (Table 1 and Supplementary Table 1). These trees are 8–25 m in height and 4–60 years old, and they are among the dominant tree species in Guangdong Province (Figure 1B). As a tree species widely distributed in the tropical/subtropical regions of the world (He et al., 2000), *Eucalyptus* accounts for 24.11% of the forest area in Guangdong (Figure 1B). Other dominant broad-leaved trees in Guangdong include *Schima superba* (1.98%), *Acacia spp.* (1.36%), and *Casuarina equisetifolia* (0.06%). Pines are widely distributed in boreal, temperate and subtropical areas. The dominant pines in Guangdong are *Pinus massoniana* (5.08%) and *Pinus elliottii* (3.28%); while the most abundant needle-leaved species is *Cunninghamia lanceolata* (10.41%) in Guangdong. According to the Ninth National Forest Inventory,¹ the dominant tree species measured in this study are also widely distributed in other tropical/subtropical areas of southern China, such as Guangxi, Hainan, Yunnan, Jiangxi, and Fujian. In addition, we also measured some common tree species used in urban greening, such as *Ficus spp.*, *Mangifera indica*, *Syzygium sp.*, *Caryota maxima* and *Magnolia denudata*.

Branch-level BVOC emissions were measured by a cylindrical semi-open dynamic chamber, which is made of polymethyl methacrylate with an inner surface coated with fluorinated ethylene propylene (FEP) Teflon film (FEP 100, Type 200A, DuPont, Witton, USA). Detailed information about the design and characterization of this dynamic chamber was described in our previous study (Zeng et al., 2022). Briefly, the chamber has a volume of 13.7 L with a diameter of 250 mm and a height of 280 mm, the flow of circulating air is maintained at a rate of 9 L min⁻¹ by a mass flow controller (Alicat Scientific, Inc., Tucson, AZ, USA) connected to an air pump (MPU2134-N920-2.08, KNE, Freiburg, Germany). Air in the chamber is

mixed by a Teflon fan (Shenzhen Shuangmu Plastic Material Co. Ltd., Shenzhen, China) to establish homogeneous chamber conditions. In the field, measurements were conducted from 9:00 a.m. to 17:00 p.m. (local time), sunlit healthy branches of 1–4 individuals for each tree species at a height of 3–5 m were enclosed in the chamber. Then, the chamber was initially flushed with ambient air for 1–2 h to avoid erratic emissions caused by artificial disturbance on the physiological state of the enclosed leaves and to ensure that the emissions in the chamber were stable (Niinemets et al., 2011). Subsequently, the chamber air flowed through an ozone scrubber (Na₂S₂O₃, Helmig et al., 2007; Zeng et al., 2022), followed by an automatic sampler (JEC921, Jectec Science and Technology, Co., Ltd., Beijing, China) equipped with adsorbent cartridges with a constant flow rate of 200 mL min⁻¹, and the emitted BVOCs were retained in commercial adsorbent cartridges bedded with Tenax TA (35/60 mesh, 150 mg) and Carbograph 5TD (35/60 mesh, 150 mg) (C2-AAXX-5149, Markes International Ltd., Bridgend, UK) for 10 min. Ambient air near the inlet was collected concurrently in the same way with another automatic sampler to determine the background concentration. The sampled adsorbent cartridges were detached from the automatic sampler, sealed with copper caps, and then stored in a portable refrigerator at 4°C in the field and at -20°C after being taken to the laboratory. Temperature and relative humidity in the chamber were measured by sensors (HC2A-S, Rotronic, Bathersdorf, Switzerland). A light sensor (Li-1500; Li-Cor Inc., Lincoln, USA) was installed on the top of the chamber to monitor the photosynthetically active radiation (PAR). The sampled branches were cut and taken to the laboratory where they were oven-dried at 60°C to constant weights.

2.2 Laboratory analysis

In the laboratory, cartridge samples were analyzed by an automatic thermal desorption system (TD-100, Markes International Ltd., Bridgend, UK) coupled to a mode 7,890 gas chromatography (GC) with a model 5,975 mass selective detector (MSD) (Agilent Technologies, Inc., CA, USA). The adsorbent cartridges were thermally desorbed by the TD-100 at 280°C for 10 min and then the desorbed analytes were transferred by pure helium into a cryogenic trap (U-T11PGC-2S, Markes International Ltd., Bridgend, UK) at -10°C. Then the trap was rapidly heated to transfer the analytes to the GC/MSD system with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, CA, USA). The GC oven temperature was programmed to be initially at 35°C (held for 3 min), then increased to 100°C at 5°C min⁻¹ and held for 3 min, to 150°C at 10°C min⁻¹ and held for 3 min, and then to 280°C with a final hold time of 2.5 min. The MSD was operated under the mode of selected ion monitoring (SIM) with ionization of electron impacting

¹ <http://www.forestdata.cn>

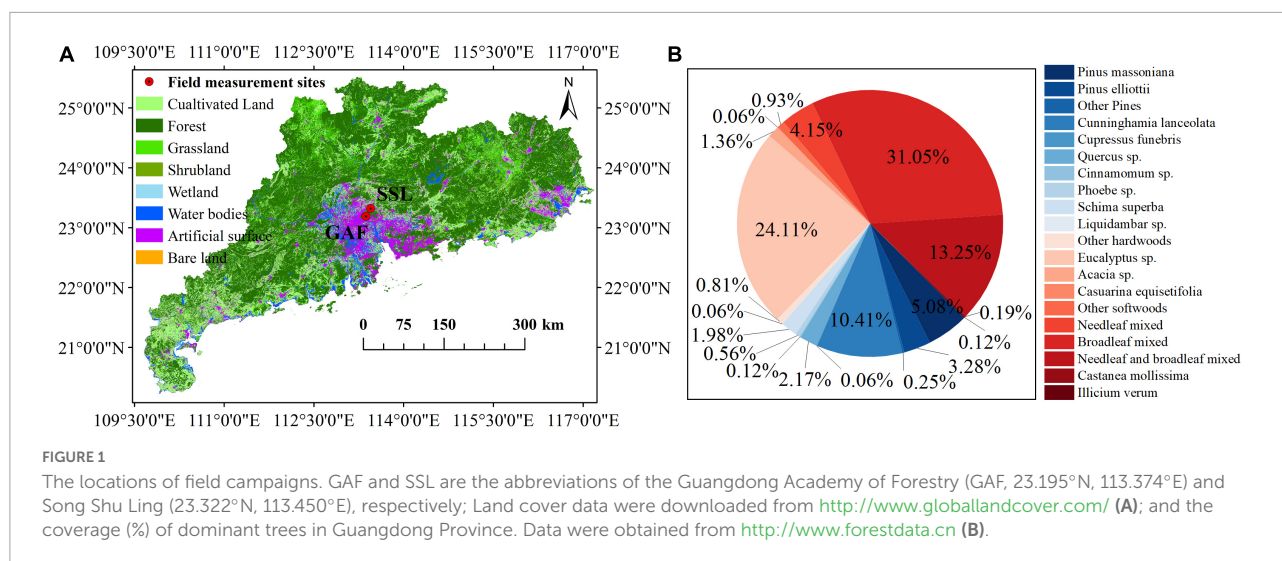


TABLE 1 Emission factors and percentages of isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs) for the 20 measured trees.

Species	N	Isoprene	MTs	SQTs	Isoprene	MTs	SQTs
		$E_s \pm 1\sigma$ ($\mu\text{g g}^{-1}\text{h}^{-1}$)			Percentage (%)		
Broad-leaved trees							
<i>Acacia auriculaeformis</i>	17	0.12 ± 0.04	1.60 ± 0.79	0.18 ± 0.08	6%	84%	10%
<i>Acacia confusa</i>	17	0.42 ± 0.37	0.08 ± 0.03	0.04 ± 0.02	77%	15%	8%
<i>Bambusa ventricosa</i>	4	4.00 ± 0.81	1.65 ± 1.08	0.10 ± 0.03	71%	29%	2%
<i>Bombax ceiba</i>	16	0.28 ± 0.27	0.21 ± 0.18	0.00 ± 0.00	57%	42%	1%
<i>Caryota maxima</i>	25	4.06 ± 0.77	BDL	BDL	100%	BDL	BDL
<i>Castanopsis hystrix</i>	17	1.91 ± 0.10	7.49 ± 4.13	0.04 ± 0.03	20%	79%	1%
<i>Casuarina equisetifolia</i>	20	18.70 ± 2.91	BDL	BDL	100%	BDL	BDL
<i>Eucalyptus urophylla</i>	17	26.47 ± 3.70	1.02 ± 0.65	0.05 ± 0.03	96%	4%	0%
<i>Ficus hispida</i>	20	20.74 ± 1.78	BDL	BDL	100%	BDL	BDL
<i>Ficus microcarpa</i>	4	5.44 ± 0.07	BDL	BDL	100%	BDL	BDL
<i>Magnolia denudata</i>	4	4.75 ± 0.22	17.6 ± 4.74	1.10 ± 0.41	20%	75%	5%
<i>Mangifera indica</i>	4	11.71 ± 7.04	0.69 ± 0.28	0.08 ± 0.02	93%	6%	1%
<i>Schima superba</i>	20	0.31 ± 0.15	1.44 ± 1.31	0.06 ± 0.05	17%	80%	3%
<i>Syzygium hainanense</i>	16	20.49 ± 1.36	1.47 ± 0.40	0.17 ± 0.04	92%	7%	1%
<i>Syzygium jambos</i>	17	5.60 ± 0.86	BDL	BDL	100%	BDL	BDL
Needle-leaved trees							
<i>Araucaria cunninghamii</i>	4	BDL	0.06 ± 0.02	0.01 ± 0.00	BDL	89%	11%
<i>Cryptomeria fortunei</i>	4	0.96 ± 0.85	0.54 ± 0.06	BDL	64%	36%	BDL
<i>Cunninghamia lanceolata</i>	8	0.09 ± 0.01	0.54 ± 0.15	0.01 ± 0.01	15%	83%	2%
<i>Pinus elliottii</i>	8	BDL	2.72 ± 0.77	0.09 ± 0.02	BDL	97%	3%
<i>Pinus massoniana</i>	16	0.19 ± 0.08	5.21 ± 2.26	0.01 ± 0.01	4%	96%	0%

BDL, below detection limit; N represents the number of samples; MTs and SQTs are abbreviations of monoterpenes and sesquiterpenes, respectively.

at 70 eV. Target compounds were identified by comparing their retention times with authentic standards (Supplementary Table 2 and Supplementary Figure 1); and the specific ions

for each BVOC species are shown in Supplementary Table 3. Target compounds are quantified with standard calibration curves. More detailed descriptions of the identification and

quantification were provided in our previous study (Zeng et al., 2022).

2.3 Quality assurance and quality control (QA/QC)

The cartridges were conditioned with pure helium at a flow rate of 100 mL min⁻¹ for 60 min at 330°C. To ensure that each group of cartridges had been cleaned, one of them was extracted randomly and analyzed in the same way as the field samples with TD-GC/MSD. If the target compounds were higher than the detection limits, re-cleaning of this group of cartridges was performed. During sampling, a field blank was collected by installing the cartridge onto the automatic sampler for 10 min but without air flow across it. To check if there was any breakthrough during sampling, two cleaned cartridges were connected in series to collect BVOC samples in the same way as the other field samples. The results showed that target compounds were not detected or were below the method detection limits (MDLs) in the second cartridge. Two repeated analyses of the same samples showed that the target compounds in the second analysis were less than 1% of those in the first analysis. Each day, one-point calibration was performed to ensure that the retention times of the target compounds did not deviate. The instrument detection limits (IDLs) were determined by seven parallel analyses of standards with a concentration of 0.5 µg mL⁻¹. The IDLs vary from 0.011 to 0.109 ng for MTs and from 0.002 to 0.016 ng for SQTs. The measurement precision varied from 3 to 9% for MTs and from 3 to 15% for SQTs. Based on a sampling volume of 2 L, the MDLs ranged from 5 to 17 ng m⁻³ for MTs and from 1 to 8 ng m⁻³ for SQTs. For isoprene, the MDL and measurement precision were 56 ng m⁻³ and 1%, respectively (Zeng et al., 2022).

2.4 Calculation of emission rates and emission factors

The BVOC emission rates (E , µg g⁻¹ min⁻¹) can be calculated according to the following equation:

$$E = \frac{F(C_{out} - C_{in})}{g_{dw}} \quad (1)$$

where F (L min⁻¹) is the flow rate of circulating air, C_{in} (µg L⁻¹) and C_{out} (µg L⁻¹) are the BVOC concentrations of inlet air and outlet air, respectively; and g_{dw} is the dry mass of the leaves in the chamber. The standardized emission rates, also called basal emission rates or emission factors (E_s) in models, are calculated by Eq. (2) for isoprene (Guenther et al., 1993). The algorithm for light- and temperature-dependent compounds, such as isoprene, is expressed as:

$$E = E_s \cdot C_T \cdot C_L \quad (2)$$

where E (µg g⁻¹ h⁻¹) is the emission rate at actual leaf temperature and light, E_s (µg g⁻¹ h⁻¹) is emission rate under standard conditions (30°C and 1,000 µmol m⁻² s⁻¹), and C_T and C_L are the light and temperature dependences of isoprene emission, respectively, which can be calculated by Eqs. (3) and (4), respectively. C_T is expressed as:

$$C_T = \frac{\exp\left(\frac{C_{T1}(T-T_s)}{RT_sT}\right)}{1 + \exp\left(\frac{C_{T2}(T-T_M)}{RT_sT}\right)} \quad (3)$$

where T is the temperature inside the chamber, T_s is the leaf temperature under standard conditions (303.15 K), R is the ideal gas constant (8.314 J K⁻¹ mol⁻¹), and C_{T1} , C_{T2} , and T_M are empirical coefficients of 95,000 J mol⁻¹, 230,000 J mol⁻¹, and 314 K, respectively. C_L is expressed as:

$$C_L = \frac{\alpha C_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \quad (4)$$

where Q (µmol m⁻² s⁻¹) is the quantum flux density. Both α (0.0027) and C_{L1} (1.066) are empirical coefficients. The algorithm for temperature-dependent compounds, such as MTs and SQTs, is expressed as:

$$E = E_s \cdot \exp[\beta(T - T_s)] \quad (5)$$

where β is an empirical coefficient that reflects the exponential relationship between emission rates and temperature. In the present study, β values of 0.1 K⁻¹ and 0.17 K⁻¹ were applied to calculate the E_s of MTs and SQTs, respectively (Ortega et al., 2008; Guenther et al., 2012).

For the comparison of canopy-scale emission factors (EFs, µg m⁻² h⁻¹) in the models, the leaf E_s (µg g⁻¹ h⁻¹) were up-scaled to canopy-scale EFs according to the widely used Eq. 6 below (Guenther et al., 1995; Harley et al., 2004; Wang et al., 2016; Purser et al., 2021):

$$EFs = E_s \cdot SLM \cdot LAI \quad (6)$$

where EFs is the canopy-scale (landscape) emission factor; E_s is the standard leaf emission factor calculated in this study; SLM is the specific leaf mass (g m⁻²); and LAI is the leaf area index (m² m⁻²).

3 Results and discussion

3.1 Standardized BVOC emission rates (E_s)

Among the 20 tree species measured, 18 species are isoprene emitters, while 15 and 14 species are MT and SQT emitters, respectively (Table 1). Isoprene and MTs accounted for over 85% of BVOC emissions for all species, and SQTs accounted for less than 15% of the total emissions. All 15 broad-leaved

trees were found to emit isoprene, and consistent with previous studies reporting that broad-leaved trees mainly emit isoprene (Aydin et al., 2014; Yuan et al., 2020), BVOC emissions from 11 of the 15 broad-leaved trees were dominated by isoprene: *F. hispida*, *S. jambos*, *F. macrocarpa*, *C. equisetifolia*, and *C. maxima* are isoprene-only emitters; BVOC emissions from *Eucalyptus urophylla*, *M. indica*, *S. hainanense*, *A. confuse*, *Bombax ceiba*, *Bambusa ventricosa*, and *Cryptomeria fortunei* are dominated by isoprene (> 50%). In contrast, BVOC emissions from needle-leaved species such as *P. massoniana*, *P. elliotii* and *C. lanceolata* are dominated by MTs (> 80%). However, some broad-leaved species, such as *A. auriculaeformis*, *Castanopsis hystrix*, *S. superba* and *M. denudata*, emitted more MTs than isoprene. In fact, MTs have also been reported previously as major BVOCs from broad-leaved trees including *Quercus coccifera*, *Q. ilex*, *Q. aucheri* and *Ligustrum vicaryi* (Staudt and Lhoutellier, 2011; Yaman et al., 2015; Jing et al., 2020).

The E_s of isoprene for isoprene emitters ranged from 0.09 ± 0.01 (*C. lanceolata*) to $26.47 \pm 3.70 \mu\text{g g}^{-1}\text{h}^{-1}$ (*E. urophylla*) (Table 1). Other broad-leaved trees, such as *F. hispida*, *S. hainanense*, *C. equisetifolia* and *M. indica*, also showed relatively higher isoprene emissions, with E_s values of 20.74 ± 1.78 , 20.49 ± 1.36 , 18.70 ± 2.91 , and $11.71 \pm 7.04 \mu\text{g g}^{-1}\text{h}^{-1}$, respectively. Meanwhile, the E_s of MTs ranged from 0.06 ± 0.02 (*Araucaria cunninghamii*) to $17.60 \pm 4.74 \mu\text{g g}^{-1}\text{h}^{-1}$ (*M. denudata*) for MT emitters. Higher emissions of MTs were also observed from *C. hystrix* ($7.49 \pm 4.13 \mu\text{g g}^{-1}\text{h}^{-1}$), *P. massoniana* ($5.21 \pm 2.26 \mu\text{g g}^{-1}\text{h}^{-1}$), and *P. elliotii* ($2.72 \pm 0.77 \mu\text{g g}^{-1}\text{h}^{-1}$). The E_s of SQTs were less than $0.5 \mu\text{g g}^{-1}\text{h}^{-1}$ for all measured tree species except for *M. denudata* with an E_s of $1.10 \pm 0.41 \mu\text{g g}^{-1}\text{h}^{-1}$.

It is worth noting that the reported E_s of isoprene and MTs were highly variable among different studies, even for the same tree species (Table 2). For example, isoprene emissions from *C. maxima* varied from $1.88 \mu\text{g g}^{-1}\text{h}^{-1}$ (Huang et al., 2011) to as high as $250 \mu\text{g g}^{-1}\text{h}^{-1}$ (Klinger et al., 2002), and emissions of MTs from *S. superba* ranged from 0.16 to $119 \mu\text{g g}^{-1}\text{h}^{-1}$ (Yang et al., 2001; Klinger et al., 2002; Zhao et al., 2004). In this study, the E_s of isoprene for *A. auriculaeformis*, *A. confuse*, *C. maxima*, *F. hispida*, *F. microcarpa*, *S. superba*, and *P. massoniana* were comparable or within the ranges in previous studies (Bai et al., 2001; Yang et al., 2001; Klinger et al., 2002; Zhao et al., 2004; Baker et al., 2005; Tsui et al., 2009; Leung et al., 2010; Huang et al., 2011). However, the E_s of isoprene for *E. urophylla* ($26.47 \pm 3.70 \mu\text{g g}^{-1}\text{h}^{-1}$) in this study was much higher than those of $0.45 \mu\text{g g}^{-1}\text{h}^{-1}$ (Yang et al., 2001) or $1.40 \mu\text{g g}^{-1}\text{h}^{-1}$ (Zhao et al., 2004), while the E_s of isoprene for *C. maxima* ($4.06 \pm 0.77 \mu\text{g g}^{-1}\text{h}^{-1}$) in this study was much lower than the previously reported 56.1 – $250 \mu\text{g g}^{-1}\text{h}^{-1}$ (Bai et al., 2001; Klinger et al., 2002). The E_s of MTs from *P. massoniana* ($5.21 \pm 2.26 \mu\text{g g}^{-1}\text{h}^{-1}$) in this study were significantly higher than those of $0.96 \mu\text{g g}^{-1}\text{h}^{-1}$

in Yang et al. (2001), $1.00 \mu\text{g g}^{-1}\text{h}^{-1}$ in Zhao et al. (2004) and $1.39 \mu\text{g g}^{-1}\text{h}^{-1}$ in Huang et al. (2011) but lower than that of $11.50 \mu\text{g g}^{-1}\text{h}^{-1}$ in Klinger et al. (2002). In this study, the E_s of the SQTs for the measured tree species (0.01 – $1.10 \mu\text{g g}^{-1}\text{h}^{-1}$) are within the ranges (0.0028 – $1.25 \mu\text{g g}^{-1}\text{h}^{-1}$) in previous studies (Ortega et al., 2008; Ormeno et al., 2010; Aydin et al., 2014). For the typical needle-leaved trees, *P. massoniana* and *P. elliotii* had SQT E_s of 0.01 ± 0.01 and $0.09 \pm 0.02 \mu\text{g g}^{-1}\text{h}^{-1}$, respectively, which on average are near those for pine trees in Turkey (0.0059 – $0.16 \mu\text{g g}^{-1}\text{h}^{-1}$; Aydin et al., 2014), but lower than those for pine trees in the USA (< 0.004 – $0.35 \mu\text{g g}^{-1}\text{h}^{-1}$; Helmig et al., 2007). The E_s of SQTs for *E. urophylla* in our study ($0.05 \pm 0.03 \mu\text{g g}^{-1}\text{h}^{-1}$) lies in the middle range of E_s for *E. globulus* (0.01 – $1.2 \mu\text{g g}^{-1}\text{h}^{-1}$) reported by Ortega et al. (2008).

The large variations in the E_s of BVOCs could be partly derived from inter- and intra-specific variations (Staudt et al., 2001; Tarvainen et al., 2005; Lim et al., 2011; Welter et al., 2012; Jing et al., 2020). Welter et al. (2012) found that the intraspecific variation in the E_s of MTs among 17 *Quercus afares* individuals (6 – $89 \mu\text{g g}^{-1}\text{h}^{-1}$) could reach over an order of magnitude. Other factors, such as genetic and geographic differences, leaf age, plant age, growth stage, physiological status of plants, seasonality, soil moisture and nutrient status, shading and microclimate, can also result in variations in emission rates (Harley et al., 1997; Loreto et al., 2009; Singh et al., 2011; Welter et al., 2012; Llusà et al., 2013). Moreover, the inconsistent measurement enclosure systems used in different studies may be an important factor that introduces substantial uncertainty for E_s (Ortega and Helmig, 2008; Niinemets et al., 2011; Li et al., 2019). Overall, the E_s of isoprene from all the measured tree species measured by dynamic chambers are higher than those from static chambers except for *A. auriculaeformis* and *F. macrocarpa* (Table 2). The E_s of isoprene for *E. urophylla* and the E_s of MTs for *P. massoniana* in this study by a dynamic enclosure were much higher than those measured by static enclosures (Yang et al., 2001; Zhao et al., 2004; Huang et al., 2011). When compared to the E_s reported previously also by the dynamic chamber method for Eucalyptus trees at different locations, our results were within the range (1.76 – $70.00 \mu\text{g g}^{-1}\text{h}^{-1}$) and very close to the mean values of those studies ($26.44 \pm 22.73 \mu\text{g g}^{-1}\text{h}^{-1}$) (Supplementary Figure 2).

The underestimated isoprene E_s by the static enclosure is probably because the static enclosure completely isolates the plant leaves from the ambient environment, causing a rapid decrease in CO_2 concentration inside the enclosure due to the photosynthetic uptake of CO_2 by the leaves, and resulting in a decrease in isoprene biosynthesis and its emission rate (Niinemets et al., 2011). In addition, accumulation of BVOCs in a static chamber would result in elevated levels of BVOCs inside the chamber and thereby hinder the diffusion of BVOCs from leaves into the chamber (Niinemets et al., 2011). Meanwhile, significant adsorption of BVOCs, especially MTs and SQTs,

TABLE 2 Comparison of E_s for isoprene and monoterpenes (MTs) with previous studies in this subtropical region.

Species	BL/NL	m/s	Enclosure	Isoprene	MTs	References
<i>Acacia auriculaeformis</i>	BL	m	D	0.12 ± 0.04	1.60 ± 0.79	This study ^a
		m	S	0.27	0.84	Yang et al., 2001 ^b
		m	L	0.00	0.22	Klinger et al., 2002 ^c
		m	S	0.27	2.60	Zhao et al., 2004 ^d
<i>Acacia confusa</i>	BL	m	D	0.42 ± 0.37	0.08 ± 0.03	This study ^a
		m	D	0.17	n.r.	Baker et al., 2005 ^e
		s	S	0.00	n.r.	Tsui et al., 2009 ^f
<i>Caryota maxima</i>	BL	m	D	4.06 ± 0.77	BDL	This study ^a
		m	D	56.1 ± 37.7	n.r.	Bai et al., 2001 ^g
		m	L	250.00	1.49	Klinger et al., 2002 ^c
		m	S	1.88	n.r.	Huang et al., 2011 ^h
<i>Eucalyptus urophylla</i>	BL	m	D	26.47 ± 3.70	1.02 ± 0.65	This study ^a
		m	S	0.45	0.18	Yang et al., 2001 ^b
		m	S	1.40	0.45	Zhao et al., 2004 ^d
<i>Ficus hispida</i>	BL	m	D	20.74 ± 1.78	BDL	This study ^a
		m	L	29.90	0.04	Klinger et al., 2002 ^c
		m	S	12.10 ± 2.30	2.50 ± 0.70	Zhao et al., 2004 ^d
		s	S	3.30 ± 0.70	n.r.	Tsui et al., 2009 ^f
<i>Ficus microcarpa</i>	BL	m	D	5.44 ± 0.07	BDL	This study ^a
		m	L	1.41	0.68	Klinger et al., 2002 ^c
		s	S	0.00	n.r.	Tsui et al., 2009 ^f
		m	S	5.39	n.r.	Huang et al., 2011 ^h
<i>Schima superba</i>	BL	m	D	0.31 ± 0.15	1.44 ± 1.31	This study ^a
		m	D	0.5 ± 0.3	n.r.	Bai et al., 2001 ^g
		m	S	0.15	0.16	Yang et al., 2001 ^b
		m	L	0.00	119.00	Klinger et al., 2002 ^c
		m	S	0.15	0.16	Zhao et al., 2004 ^d
<i>Pinus massoniana</i>	NL	m	D	0.11 ± 0.07	0.20 ± 0.03	Leung et al., 2010 ⁱ
		m	D	0.19 ± 0.08	5.21 ± 2.26	This study ^a
		m	S	0.70	0.96	Yang et al., 2001 ^b
		m	L	11.90	11.50	Klinger et al., 2002 ^c
		m	S	0.70	1.00	Zhao et al., 2004 ^d
<i>Pinus elliottii</i>	NL	m	S	n.r.	1.39	Huang et al., 2011 ^h
		m	D	0.4 ± 0.1	n.r.	Chang et al., 2012 ^j
		m	D	BDL	2.72 ± 0.77	This study ^a
		m	S	0.20	24.6	Yang et al., 2001 ^b
		m	D	0.3 ± 0.1	n.r.	Chang et al., 2012 ^j

BL/NL, broad-leaved tree/needle-leaved tree; m/s, mature trees/seedlings; S/D, static/dynamic enclosure; L, leaf cuvette; n.r., not reported; BDL, below detection limits.

a: This study, field measurements were conducted in Guangzhou; b: Yang et al. (2001), field measurements were conducted in Guangzhou; c: Klinger et al. (2002), field measurements were conducted in Dinghu Mountain; d: Zhao et al. (2004), field measurements were conducted in Guangdong and Yunnan; e: Baker et al. (2005), field measurements were conducted in south China; f: Tsui et al. (2009), laboratory measurements were conducted in Hong Kong; g: Bai et al. (2001), field measurements were conducted in Dinghu Mountain; h: Huang et al. (2011), field measurements were conducted in Shenzhen; i: Leung et al. (2010), laboratory measurements were conducted in Hong Kong; j: Chang et al. (2012), field measurements were conducted in Hangzhou.

could occur in the inner surface of the static enclosure (Ortega and Helmig, 2008; Niinemets et al., 2011; Zeng et al., 2022), also leading to a lower E_s .

The twenty tree species measured in this study could be divided into five categories by cluster analysis according to their emission rates of isoprene, MTs and SQTs (Figure 2). Twelve tree species (*A. cunninghamii*, *B. ceiba*, *A. confuse*, *C. fortune*, *C. lanceolata*, *F. macrocarpa*, *S. jambos*, *C. maxima*, *P. elliottii*, *S. superba*, *A. auriculaeformis*, and *B. ventricosa*) are classified as the low BVOC emission potential group with much lower E_s of isoprene, MTs and SQTs. Two tree species (*C. hystrix* and *P. massoniana*) are identified as low isoprene and SQT emitters but moderate MT emitters. Four species (*E. urophylla*, *F. hispida*, *S. hainanense* and *C. equisetifolia*) show low emission potential of both MTs and SQTs but high emission potential of isoprene. *M. indica* is identified as having low MT and SQT emissions but moderate isoprene emissions, and *M. denudata* is identified as having low isoprene emissions but high MT and SQT emissions. Regional emissions of BVOCs depend on the coverage of dominant trees and their emission potentials. These results can have implications in the selection of tree species for urban greening plans, as more emissions of highly reactive BVOCs in urban areas would enhance photochemical ozone formation and therefore would not benefit ozone pollution control (Gu et al., 2021; Wang et al., 2022). In the subtropical regions, such as Guangdong Province, *E. urophylla* is the most dominant broad-leaved tree (24.11%; Figure 1B) and has a high isoprene emission rate, making it a major source of regional isoprene emissions; therefore, it should be avoided as a tree species for urban or rural greening in this region afflicted with ozone pollution (Willis and Petrokofsky, 2017; Wang et al., 2022). *M. indica*, *F. hispida* and *S. hainanense* are common tree species for urban greening (Jim and Liu, 2001; Singh et al., 2014). They have moderate to high isoprene emission potentials and thus might not be good choices for widely planted tree species in urban areas when ozone air pollution is serious.

3.2 Compositions and emission rates of MT and SQT monomers

Table 3 shows the E_s of 11 MTs and 3 oxygenated MTs emitted from 15 tree species (Supplementary Figure 3), and their compositions are shown in Figure 3. Overall, α -pinene, β -pinene, and limonene were the most common MT species emitted. *M. denudata* showed the highest E_s of α -pinene ($8.33 \pm 2.05 \mu\text{g g}^{-1} \text{h}^{-1}$) and limonene ($3.11 \pm 1.07 \mu\text{g g}^{-1} \text{h}^{-1}$), while *C. hystrix* had the highest E_s of β -pinene ($5.29 \pm 3.24 \mu\text{g g}^{-1} \text{h}^{-1}$). α -Pinene was the most abundant MT emitted from *C. lanceolata* (62.1 %), *B. ventricosa* (59.5 %), *E. urophylla* (57.7 %), *M. denudata* (47.3 %), *M. indica* (45.4 %), and *P. massoniana* (36.5 %) (Figure 3), β -pinene was the dominant MT from *S. superba* (76.9 %), *C. hystrix* (73.8

%), *P. elliottii* (49.8 %), and *C. fortune* (41.7 %), limonene was the major MT in emissions from *A. auriculaeformis* (76.6 %) and *S. hainanense* (37.1 %), camphene was the most abundant MT from *B. ceiba* (65.2 %), and oxygenated MTs were the most abundant species from *A. cunninghamii* (87.2%) (Supplementary Table 4). Compositions of MTs from *C. lanceolata*, which covers a large forest area (10.41 %) in south China, were not characterized before, and in this study, its MT emissions were found to be dominated by α -pinene (62.1 %).

As shown in Supplementary Table 5, α -pinene and 1,8-cineole are the two most abundant MTs emitted from *E. urophylla*, consistent with those reported in previous studies for Eucalyptus trees (Street et al., 1997; He et al., 2000; Winters et al., 2009). The E_s of α -pinene for *E. urophylla* ($0.60 \pm 0.36 \mu\text{g g}^{-1} \text{h}^{-1}$) from this study was very close to that for *E. calophylla* ($0.64 \mu\text{g g}^{-1} \text{h}^{-1}$), *E. cladocalyx* ($0.57 \mu\text{g g}^{-1} \text{h}^{-1}$), *E. robusta* ($0.55 \mu\text{g g}^{-1} \text{h}^{-1}$), and *E. rudis* ($0.58 \mu\text{g g}^{-1} \text{h}^{-1}$) reported by He et al. (2000), but lower than that for young *E. globulus* ($0.89\text{--}2.47 \mu\text{g g}^{-1} \text{h}^{-1}$; Evans et al., 1982; Street et al., 1997; He et al., 2000; Purser et al., 2020). The E_s of 1,8-cineole for *E. urophylla* ($0.30 \pm 0.37 \mu\text{g g}^{-1} \text{h}^{-1}$) was within the range of the E_s for Eucalyptus trees in previous studies (Supplementary Table 5), but significantly lower than that for young *E. globulus* ($1.67\text{--}8.56 \mu\text{g g}^{-1} \text{h}^{-1}$; Evans et al., 1982; Street et al., 1997; He et al., 2000; Purser et al., 2020). For the main MTs emitted from both *P. massoniana* and *P. elliottii* (Table 3), the E_s of α -pinene and β -pinene for *P. massoniana* (1.49 ± 0.84 and $0.88 \pm 0.53 \mu\text{g g}^{-1} \text{h}^{-1}$) and *P. elliottii* (0.96 ± 0.25 and $1.35 \pm 0.42 \mu\text{g g}^{-1} \text{h}^{-1}$) were higher than those measured in Europe for pine trees (Tarvainen et al., 2005; Hakola et al., 2006; Bracho-Nunez et al., 2011; Staudt et al., 2017) and in the United States (Helmig et al., 2013; Supplementary Table 6), but lower than those for pine trees (e.g., *Pinus griffithii*, *Pinus armandii*) in northern China (Jing et al., 2020). In this study, *P. massoniana* showed higher E_s of limonene ($0.89 \pm 0.21 \mu\text{g g}^{-1} \text{h}^{-1}$) than most other pines except for *P. griffithii* ($3.7944 \mu\text{g g}^{-1} \text{h}^{-1}$; Jing et al., 2020), and the E_s of limonene for *P. elliottii* ($0.28 \pm 0.10 \mu\text{g g}^{-1} \text{h}^{-1}$) from this study were within those reported for other pines (Helmig et al., 2013; Jing et al., 2020). These differences also demonstrated geographical and intraspecific variabilities in MTs emissions (Staudt et al., 2001; Tarvainen et al., 2005; Loreto et al., 2009; Welter et al., 2012), implying that more field measurements are necessary to overcome the variability.

In this study, fourteen tree species were found to be emitters of SQTs (Table 4), and β -caryophyllene was the most commonly detected among the nine species of SQTs measured in this study (Supplementary Figure 3), with 12 tree species being β -caryophyllene emitters. *M. denudata* had the highest E_s of the SQTs ($1.10 \pm 0.41 \mu\text{g g}^{-1} \text{h}^{-1}$) with a dominance of α -gurjunene (72.2 %) (Supplementary Table 7). Two SQTs, longicyclene and β -caryophyllene, were observed

TABLE 3 Emission factors ($\mu\text{g g}^{-1}\text{h}^{-1}$) of different monoterpene (MT) species emitted from the measured trees.

Compounds	<i>Acacia auriculaeformis</i>	<i>Acacia confusa</i>	<i>Bambusa ventricosa</i>	<i>Bombax ceiba</i>	<i>Castanopsis hystrix</i>
α -pinene	0.12 \pm 0.05	0.02 \pm 0.01	0.98 \pm 0.72	0.01 \pm 0.01	0.78 \pm 0.44
Camphene	BDL	0.004 \pm 0.001	0.11 \pm 0.04	0.14 \pm 0.13	0.05 \pm 0.03
β -pinene	0.06 \pm 0.02	0.02 \pm 0.01	0.07 \pm 0.03	0.004 \pm 0.004	5.29 \pm 3.24
β -myrcene	0.11 \pm 0.07	0.01 \pm 0.00	0.06 \pm 0.02	0.01 \pm 0.01	0.24 \pm 0.14
α -phellandrene	BDL	BDL	BDL	BDL	0.04 \pm 0.03
3-carene	BDL	0.01 \pm 0.01	0.25 \pm 0.18	0.002 \pm 0.001	BDL
Limonene	1.22 \pm 0.61	0.01 \pm 0.01	0.19 \pm 0.09	0.003 \pm 0.002	BDL
1,8-cineole	BDL	BDL	BDL	BDL	0.37 \pm 0.22
<i>cis</i> -ocimene	BDL	BDL	BDL	BDL	BDL
Trans- β -ocimene	BDL	BDL	BDL	BDL	BDL
γ -terpinene	0.08 \pm 0.08	0.02 \pm 0.01	BDL	0.005 \pm 0.004	0.35 \pm 0.20
Terpinolene	BDL	BDL	BDL	0.003 \pm 0.001	0.05 \pm 0.03
Linalool	0.004 \pm 0.003	BDL	BDL	0.04 \pm 0.04	BDL
Camphor	BDL	BDL	BDL	BDL	BDL
	<i>Eucalyptus urophylla</i>	<i>Magnolia denudata</i>	<i>Mangifera indica</i>	<i>Schima superba</i>	<i>Syzygium hainanense</i>
α -pinene	0.60 \pm 0.36	8.33 \pm 2.05	0.31 \pm 0.18	0.14 \pm 0.1	0.20 \pm 0.02
Camphene	0.03 \pm 0.02	0.45 \pm 0.40	0.01 \pm 0.00	0.01 \pm 0.01	0.06 \pm 0.02
β -pinene	0.04 \pm 0.04	3.38 \pm 0.49	0.05 \pm 0.01	0.90 \pm 0.72	0.22 \pm 0.13
β -myrcene	BDL	0.53 \pm 0.15	0.02 \pm 0.01	0.03 \pm 0.03	BDL
α -phellandrene	BDL	BDL	BDL	BDL	0.09 \pm 0.11
3-carene	BDL	0.56 \pm 0.26	0.03 \pm 0.02	0.01 \pm 0.01	BDL
Limonene	0.04 \pm 0.05	3.11 \pm 1.07	0.16 \pm 0.07	0.06 \pm 0.02	0.55 \pm 0.15
1,8-cineole	0.30 \pm 0.37	0.22 \pm 0.03	BDL	BDL	0.16 \pm 0.03
<i>cis</i> -ocimene	BDL	0.11 \pm 0.01	0.01 \pm 0.00	BDL	0.02 \pm 0.02
Trans- β -ocimene	BDL	0.56 \pm 0.07	0.06 \pm 0.01	BDL	0.10 \pm 0.02
γ -terpinene	0.02 \pm 0.01	0.04 \pm 0.01	0.01 \pm 0.00	0.01 \pm 0.00	0.04 \pm 0.01
Terpinolene	BDL	0.09 \pm 0.03	0.01 \pm 0.00	0.01 \pm 0.01	0.04 \pm 0.02
Linalool	BDL	0.15 \pm 0.03	0.02 \pm 0.00	BDL	BDL
Camphor	BDL	0.06 \pm 0.02	BDL	BDL	BDL
	<i>Araucaria cunninghamii</i>	<i>Cryptomeria fortunei</i>	<i>Cunninghamia lanceolata</i>	<i>Pinus elliotii</i>	<i>Pinus massoniana</i>
α -pinene	0.002 \pm 0.001	0.20 \pm 0.03	0.33 \pm 0.08	0.96 \pm 0.25	1.49 \pm 0.84
Camphene	BDL	0.01 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.01	0.08 \pm 0.07
β -pinene	BDL	0.22 \pm 0.03	0.02 \pm 0.01	1.35 \pm 0.42	0.88 \pm 0.53
β -myrcene	0.01 \pm 0.00	0.04 \pm 0.00	0.02 \pm 0.01	0.05 \pm 0.02	0.10 \pm 0.05
α -phellandrene	BDL	BDL	0.01 \pm 0.01	0.01 \pm 0.01	0.04 \pm 0.01
3-carene	BDL	0.004 \pm 0.001	BDL	BDL	BDL
Limonene	BDL	0.05 \pm 0.01	0.14 \pm 0.05	0.28 \pm 0.10	0.89 \pm 0.21
1,8-cineole	BDL	BDL	BDL	BDL	0.005 \pm 0.004

(Continued)

TABLE 3 (Continued)

	<i>Araucaria cunninghamii</i>	<i>Cryptomeria fortunei</i>	<i>Cunninghamia lanceolata</i>	<i>Pinus elliottii</i>	<i>Pinus massoniana</i>
<i>cis</i> -ocimene	BDL	BDL	BDL	0.003 ± 0.003	BDL
Trans- β -ocimene	BDL	BDL	BDL	0.01 ± 0.00	BDL
γ -terpinene	BDL	BDL	BDL	0.01 ± 0.00	0.01 ± 0.00
Terpinolene	BDL	BDL	BDL	0.02 ± 0.00	0.01 ± 0.00
Linalool	0.05 ± 0.01	0.01 ± 0.00	BDL	0.01 ± 0.00	0.03 ± 0.01
Camphor	BDL	BDL	BDL	BDL	BDL

BDL, below detection limits.

to emit from *E. urophylla* with E_s values of 0.02 ± 0.01 and $0.03 \pm 0.02 \mu\text{g g}^{-1}\text{h}^{-1}$, respectively, higher than those from *E. yarraensis* (Sørensen et al., 2020; **Supplementary Table 8**). Four SQTs monomers were identified from *P. massoniana*, six were identified from *P. elliottii*, and β -caryophyllene and α -humulene were the common SQTs emitted from the pine trees. The E_s of β -caryophyllene and α -humulene from *P. elliottii* were 0.02 ± 0.01 and $0.01 \pm 0.00 \mu\text{g g}^{-1}\text{h}^{-1}$, respectively, but all were below $0.005 \mu\text{g g}^{-1}\text{h}^{-1}$ from *P. massoniana*. Five trees emitted α -copaene with E_s ranging from 0.002 to $0.04 \mu\text{g g}^{-1}\text{h}^{-1}$, twelve trees emitted β -caryophyllene with E_s ranging from 0.002 to $0.09 \mu\text{g g}^{-1}\text{h}^{-1}$, and five trees emitted α -humulene with E_s from 0.001 to $0.03 \mu\text{g g}^{-1}\text{h}^{-1}$. These ranges are similar to the E_s from plants in Turkey (0.0002 – $0.043 \mu\text{g g}^{-1}\text{h}^{-1}$; Yaman et al., 2015), Mediterranean plants

(0.02 – $0.20 \mu\text{g g}^{-1}\text{h}^{-1}$; Bracho-Nunez et al., 2013), and Hawaii (0.01 – $8.04 \mu\text{g g}^{-1}\text{h}^{-1}$; Llusà et al., 2010; **Supplementary Table 8**). The large variability in the E_s of SQTs from plants come from many factors, such as the diversity of plants, and seasonal changes in SQT emissions (Hakola et al., 2006). In fact, more *in-situ* measurements are needed for emissions of SQTs from plants since far fewer field campaigns are available for emissions of SQTs than for emissions of isoprene and MTs.

3.3 The Canopy-scale emission factors

The coverage-weighted EFs of the broad-leaved trees and needle-leaved trees were calculated based on the EFs of

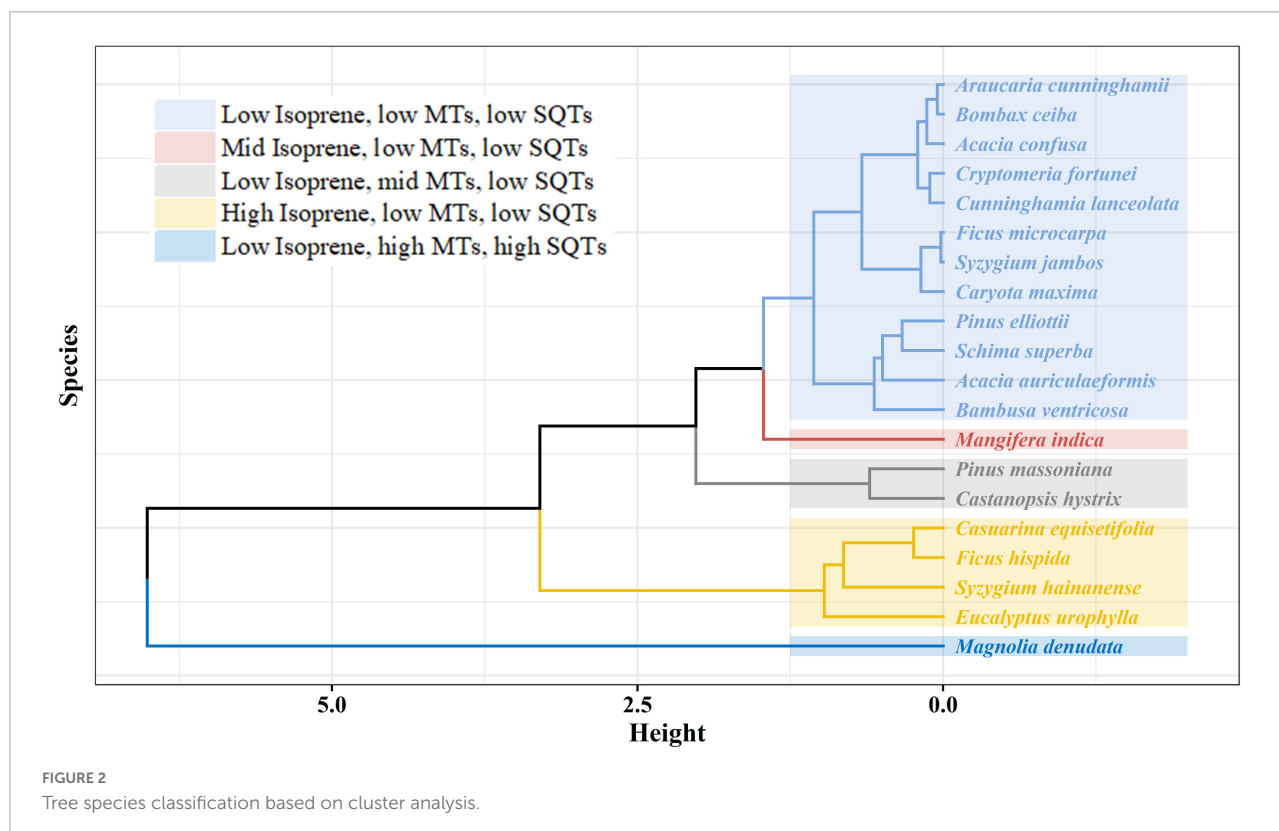


FIGURE 2
Tree species classification based on cluster analysis.

TABLE 4 Emission factors ($\mu\text{g g}^{-1}\text{h}^{-1}$) of different sesquiterpene (SQT) species emitted from the measured trees.

Compounds	<i>Acacia auriculaeformis</i>	<i>Acacia confusa</i>	<i>Bambusa ventricosa</i>	<i>Bombax ceiba</i>	<i>Castanopsis hystrix</i>	<i>Eucalyptus urophylla</i>	<i>Magnolia denudata</i>
α -longipinene	BDL	BDL	BDL	BDL	BDL	BDL	0.03 \pm 0.01
Longicyclene	BDL	BDL	BDL	0.002 \pm 0.001	BDL	0.02 \pm 0.01	BDL
α -copaene	BDL	BDL	BDL	BDL	BDL	BDL	0.04 \pm 0.00
α -cubebene	BDL	BDL	0.09 \pm 0.03	BDL	BDL	BDL	0.05 \pm 0.01
α -gurjunene	BDL	BDL	BDL	BDL	BDL	BDL	0.80 \pm 0.33
β -caryophyllene	0.08 \pm 0.04	0.02 \pm 0.01	0.01 \pm 0.00	BDL	0.02 \pm 0.02	0.03 \pm 0.02	0.09 \pm 0.03
Thujopsene	BDL	BDL	BDL	BDL	BDL	BDL	0.04 \pm 0.02
α -humulene	BDL	BDL	BDL	BDL	BDL	BDL	0.03 \pm 0.00
β -chamigrene	0.10 \pm 0.06	0.02 \pm 0.01	BDL	BDL	0.02 \pm 0.01	BDL	0.02 \pm 0.00
	<i>Mangifera indica</i>	<i>Schima superba</i>	<i>Syzygium hainanense</i>	<i>Araucaria cunninghamii</i>	<i>Cunninghamia lanceolata</i>	<i>Pinus elliottii</i>	<i>Pinus massoniana</i>
α -longipinene	0.004 \pm 0.002	BDL	0.02 \pm 0.02	BDL	BDL	0.01 \pm 0.01	0.002 \pm 0.002
Longicyclene	BDL	BDL	BDL	BDL	BDL	BDL	0.003 \pm 0.002
α -copaene	0.002 \pm 0.001	BDL	0.02 \pm 0.00	0.004 \pm 0.001	BDL	0.01 \pm 0.01	BDL
α -cubebene	0.01 \pm 0.00	BDL	0.10 \pm 0.01	0.002 \pm 0.001	0.01 \pm 0.00	0.01 \pm 0.00	BDL
α -gurjunene	0.06 \pm 0.02	BDL	BDL	BDL	BDL	BDL	BDL
β -caryophyllene	0.01 \pm 0.00	0.02 \pm 0.01	0.02 \pm 0.00	BDL	0.002 \pm 0.001	0.02 \pm 0.01	0.005 \pm 0.004
Thujopsene	0.002 \pm 0.001	BDL	BDL	BDL	BDL	0.01 \pm 0.00	0.002 \pm 0.001
α -humulene	0.004 \pm 0.001	BDL	0.01 \pm 0.00	BDL	0.001 \pm 0.001	0.01 \pm 0.00	BDL
β -chamigrene	BDL	0.04 \pm 0.04	BDL	0.002 \pm 0.001	0.004 \pm 0.002	0.02 \pm 0.00	BDL

BDL: below detection limits.

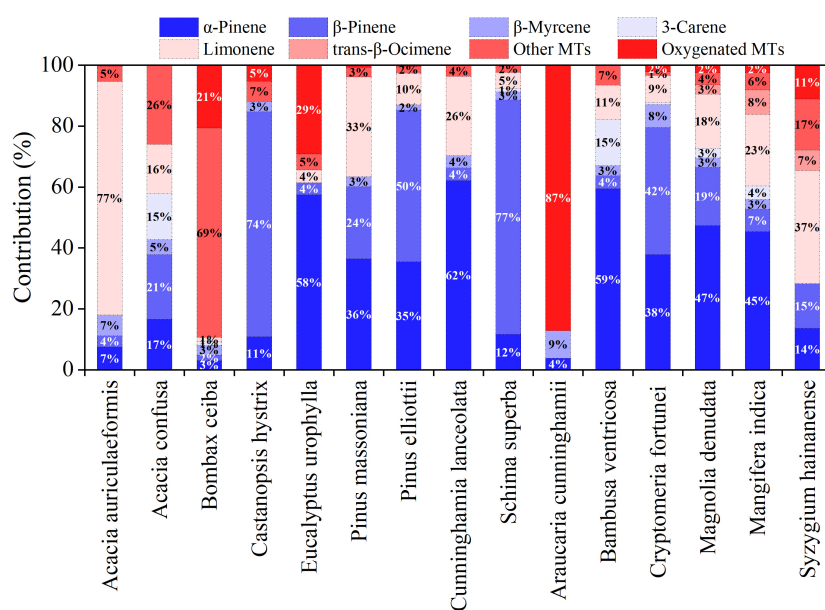


FIGURE 3
Compositions of different monoterpenes (MTs) emitted from measured trees.

dominant trees and their coverage proportions (Figure 1B). According to previous studies, the leaf mass area (LMA) of broad-leaved trees and needle-leaved trees were chosen to be 100 and 150 g m⁻², respectively (Guenther et al., 1995; Zheng et al., 2010; Wang et al., 2016), and the standard value of 5 m² m⁻² was adopted for the LAI (Wang et al., 2016). However, the measured LAI of Eucalyptus plantations in south China ranged from 0.65 to 3 m² m⁻² with an average of about 2 m² m⁻² (Wen et al., 2008; Ouyang et al., 2021; Zhang et al., 2021). Therefore, the LAI of Eucalyptus trees was chosen to be 2 m² m⁻² when calculating the weighted average EFs by Eucalyptus trees due to the large proportion and high isoprene E_s of Eucalyptus trees. For broad-leaved trees, the EFs of 43% of all broad-leaved trees (Figure 1B) were updated using our measured values and the EFs of the remaining broad-leaved trees (57%) adopted the default values in MEGAN v2.1. The updated localized average isoprene EFs of broad-leaved trees (7,657 μg m⁻² h⁻¹) is ~24% lower than the default value (10,000 μg m⁻² h⁻¹) for broadleaf evergreen temperate trees (BETT) in the MEGAN v2.1 (Supplementary Figure 4), indicating that the model might overestimate the regional isoprene emissions if the default EFs are used. This is consistent with results from a previous model-measurement comparison study (Zhang et al., 2020), which showed that the MEGAN estimation might overestimate isoprene emissions in south China. The overestimation of the model might be partly because the default isoprene EF (10,000 m⁻² h⁻¹) was nearly twice that of *E. urophylla* (5,294 m⁻² h⁻¹). This overestimation of isoprene emissions also occurred in Eucalyptus-dominated areas in Australia (Emmerson et al., 2016), and the default

isoprene EFs for BETT in MEGAN v2.1 were suggested to decrease by up to a factor of 4 or 5 in that area to bridge the gap. In addition, the localized canopy-scale EFs of MT and SQT monomers for broad-leaved trees were also lower than the default values in MEGAN v2.1. The localized canopy-scale EFs of the total MTs (667 μg m⁻² h⁻¹) and the total SQTs (108 μg m⁻² h⁻¹) were ~33 and ~41% lower than those of the default values for BETT in MEGAN v2.1, respectively.

For needle-leaved trees, the localized canopy-scale EFs of isoprene and total SQTs of needle-leaved evergreen temperate trees (NETT) were nearly 7 and 11 times lower than the default values in MEGAN v2.1, respectively. Nevertheless, the localized canopy-scale EFs of MTs for α-pinene, β-pinene and limonene were 30, 47, and 300% higher than the default values in MEGAN v2.1, respectively. In addition, the emissions of sabinene, 3-carene and trans-β-ocimene from the dominant needle-leaved trees (e.g., *C. lanceolata*, *P. elliotii*, *P. massoniana*) were below the detection limits (Table 3). However, the default EFs of these three MTs are 70, 160, and 70 μg m⁻² h⁻¹ for NETT, respectively. If the default EFs of BVOCs were used for NETT in the model, it may not only lead to the overestimation of isoprene, sabinene, 3-carene and trans-β-ocimene and SQTs, but also lead to the underestimation of α-pinene, β-pinene, and limonene from needle-leaved trees in south China with changed emission profiles of MTs. The results showed that the localized EFs of BVOCs may help to reduce the uncertainties of BVOC emission estimations by MEGAN or other emission models in typical regions.

4 Conclusion

In this study, BVOC emission factors from 20 tropical/subtropical mature trees, including 15 broad-leaved trees and 5 needle-leaved trees, were measured in-situ by a dynamic chamber. Concurrent dynamic and static chamber measurements revealed substantially higher emission factors by the dynamic chamber method than by the static chamber method. The localized compound-specific emission factors of isoprene, 14 MTs and 9 SQTs for the dominant tree species were obtained and applied to update and compare with default emission factors for typical tropical vegetation types in the MEGAN model. The results showed that more localized emission factors would help improve BVOC emission estimates in typical/subtropical regions and narrow their uncertainties. Nevertheless, more extensive *in situ* branch-scale and ecosystem-scale measurements of BVOC emissions with a good representation of tree species and vegetation types are urgently needed in tropical regions with globally dominant BVOC emissions.

Data availability statement

The original contributions presented in this study are included in the article/**Supplementary material**, further inquiries can be directed to the corresponding author.

Author contributions

JZ and WS: field measurement, laboratory analysis, data curation, and original draft preparation. YZ: conceptualization, methodology, visualization, writing—reviewing and editing, and funding acquisition. ZM and WP: field measurement and laboratory analysis. HZ: methodology, laboratory analysis, and validation. XW: conceptualization, methodology, reviewing and

editing, and funding acquisition. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/ffgc.2022.1089676/full#supplementary-material>

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