Detection of biogenic volatile organic compounds emitted from common tropical plant species in the Western Ghats region of India: chamber-based experiments

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This study deals with emission of biogenic volatile organic compounds (BVOCs) from some common plant species found in the Western Ghats of India using branch-enclosure experiments. A custom-made dynamic chamber system was deployed to collect samples from seven different plant species. Analysis of speciated BVOCs was performed using C_2–C_6 and C_6–C_{12} VOC analysers to determine the emission composition and relative concentration. Isoprene was the most abundant compound, followed by ethene, propene, α-pinene and β-pinene. Among the plant species, *Tectona grandis*, *Bambusa vulgaris* and *Psidium guajava* showed high fractions of isoprene emission, *Saraca asoca* showed moderate emission, and *Manilkara zapota* and *Leucaena leucocephala* showed the lowest emission. However, *M. zapota* and *L. leucocephala* showed higher emission of both ethene and propene compared to isoprene. This study emphasizes the importance of emission flux measurements of major plant species in different forest regions of India, which is necessary to make emission inventories of important BVOCs.

Keywords: Biogenic volatile organic compounds, chamber experiment, emission composition, relative concentration, tropical forests.

EMISSIONS of biogenic volatile organic compounds (BVOCs), including alkenes, isoprenoids (isoprene: C_5H_8, monoterpenes: $C_{10}H_{16}$, sesquiterpenes: $C_{15}H_{24}$) and oxygenated VOCs (organic acids, aldehydes, ketones, alcohols, etc.) have a substantial impact on the global atmosphere[1,2]. Emissions from terrestrial plants have been estimated to be a major source of BVOCs, with an annual global emission of ~1150 Tg/year (ref. 3). Among BVOCs, isoprene (~70%) and monoterpenes (11%) are the most abundant compounds emitted from the terrestrial vegetation[1,3–6]. Among the other BVOCs, alkane and alkene (~30%) and oxygenated volatile species (~60%) are the major compounds in some forest regions[7,8]. These reactive trace compounds play a key role in regional atmospheric chemistry and climate[7,9]. BVOCs are an important component of plant physiology and are involved in plant growth, reproduction and defence mechanisms[10–12]. The emissions are sensitive to abiotic environmental factors like temperature, relative humidity (RH), carbon dioxide (CO_2) and light intensity[13–15]. Therefore, the composition and flux of BVOCs emitted from the terrestrial plants are known to show strong species-to-species variations[16,17]. Studies on some tropical plant species have shown that climate change (global warming) can bring a change in BVOC emissions in response to induced stress[18].

Emissions from the tropical regions contribute more than 70% to the global budget of total BVOCs[19,20]. The South Asian region, consisting of about 15% of the world's tropical forests region as of 2010 (ref. 21), has a rich diversity of tropical plant species. However, limited information is available on their BVOC emission characteristics[6,17,22–25]. Nonetheless, it is important to study the BVOC emissions from tropical vegetation in view of their key role in chemistry–climate interactions. Among the South Asian nations, India has the largest geographical area with ~713,789 sq. km under forest cover. About 14 major forest types occupy nearly 21% of India's total geographical area[26,27]. The tropical-moist and tropical-dry forests cover ~65% of the total forest area of India[28]. Figure 1 is a map of the different forest types and land use/land cover of India prepared using forest-type data at 5 km resolution from the Bhuvan geo portal (https://bhuvan.nrsc.gov.in)[29]. Despite the large forest area, efforts to measure emissions of BVOCs from Indian plant species have not been systematic and comprehensive. A few studies have reported BVOC emissions from different plant species in India[6,17,22–25,30–34]. The isoprene and monoterpene emission rates from common tropical

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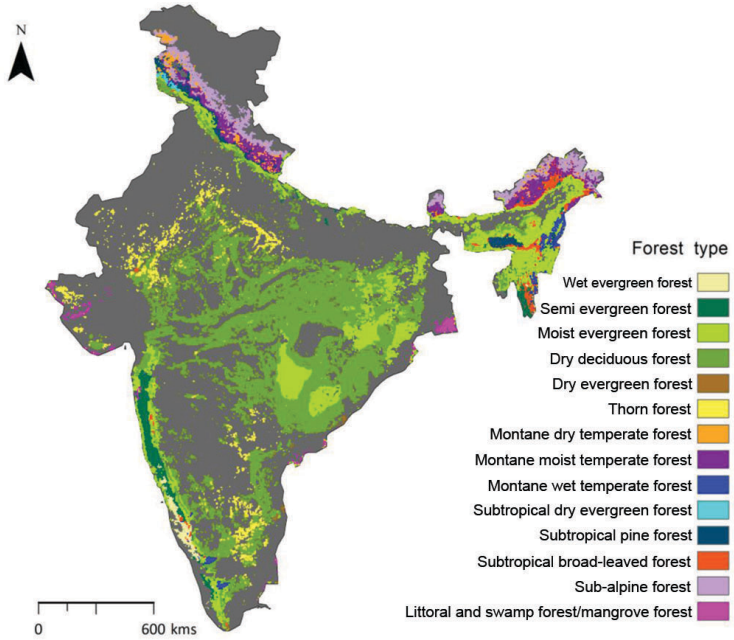

Figure 1. Different forest types and land use/land cover map of India using forest type 5 km grid data from the National Remote Sensing Centre, Hyderabad, India, using the Bhuvan geoportal (https://bhuvan.nrsc.gov.in).

plant species of the Amarkantak–Achankmar Biosphere Reserve in Central India are reported in Malik *et al.*[17].

During the last few decades, researchers have been attempting to design and develop branch-enclosure systems, both static and dynamic, to quantify BVOC emissions from different plants[35–38]. Several recent advances have been made in branch-enclosures studies using both static and dynamic enclosures. The dynamic enclosure is more convenient and recommended for authentic measurements of BVOC emissions[39]. Unlike the static enclosure, the environment and circulation can be controlled in dynamic enclosures[11,40–42]. In addition, some studies have shown changes in temperature and RH inside static enclosures. In the absence of purge flow, temperature inside the static chamber increase and this may affect the accurate estimation of BVOCs. Such uncertainties are relatively less in case of dynamic chamber-based estimations. During the last few decades, studies have mainly used dynamic chambers in order to overcome the uncertainties associated with static chamber-based analysis[40,43,44]. So far, the dynamic chamber is the most widely used system for measurements of BVOC emissions from plant species[45–47], and to determine its dependence on different environmental variables[10,48–51]. However, lack of a pre-established and tested protocols, and thus inconsistency in enclosure systems and deployment methods have led to large variations in emission estimates across the globe[52,53].

In this study, we describe a custom-made chamber system and its performance during field deployments for the measurements of BVOC emissions from seven different plant species. The seven selected species in this study, namely: *Bambusa vulgaris*, *Saraca asoca*, *Gliricidia sepium*, *Psidium guajava*, *Tectona grandis*, *Leucaena leucocephala* and *Manilkara zapota* are some of the most common plant species found in the Western Ghats of India[54,55]. Among these, the BVOC emission composition from two plant species (*B. vulgaris* and *S. asoca*) have not been reported previously in the literature to the best of our knowledge. For the remaining five species, the BVOC emission properties have been reported from other regions of India, but not for the Western Ghats. The main objectives of chamber-based experiments include detection and identification of the most dominant isoprenoid and alkene compounds emitted from the selected plant species in the Western Ghats of India.

Experiments and results

Study region

The Western Ghats of India is a global biodiversity hotspot covering the states of Maharashtra, Goa, Karnataka and Kerala[9,56]. Its geographical area is ~160,000 sq. km, of which ~57,000 sq. km (35.6%) is forest cover[57]. The Western Ghats forests are dominated by moist deciduous, semi-evergreen, dry deciduous and wet evergreen trees[29,54]. The present study was conducted in the campus of the National Institute of Oceanography (NIO; 15.5°N, 73.84°E), Goa. The area experiences typical tropical monsoon climate with annual average precipitation of approximately 3800 mm, most of which is concentrated between mid-June and September[26]. In this region, *Peltophorum pterocarpum* (peela

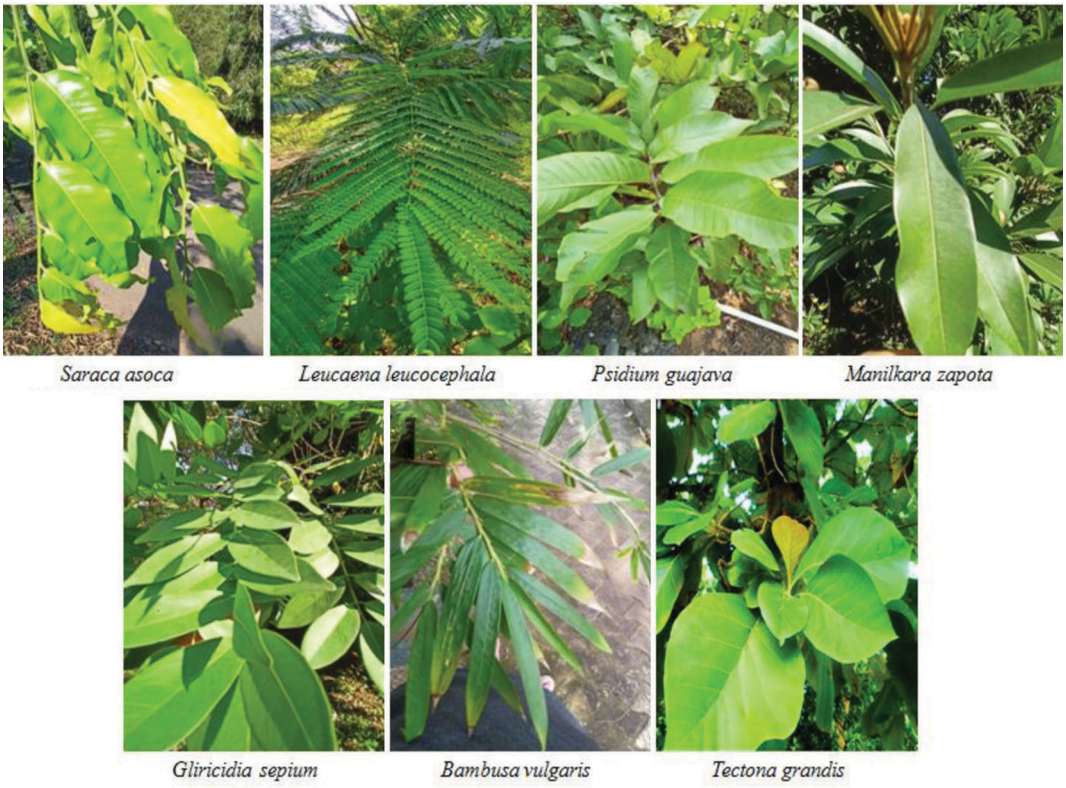

Figure 2. Photographs showing the leaves of seven different plant species selected for the chamber experiments which are dominant in the Western Ghats of India.

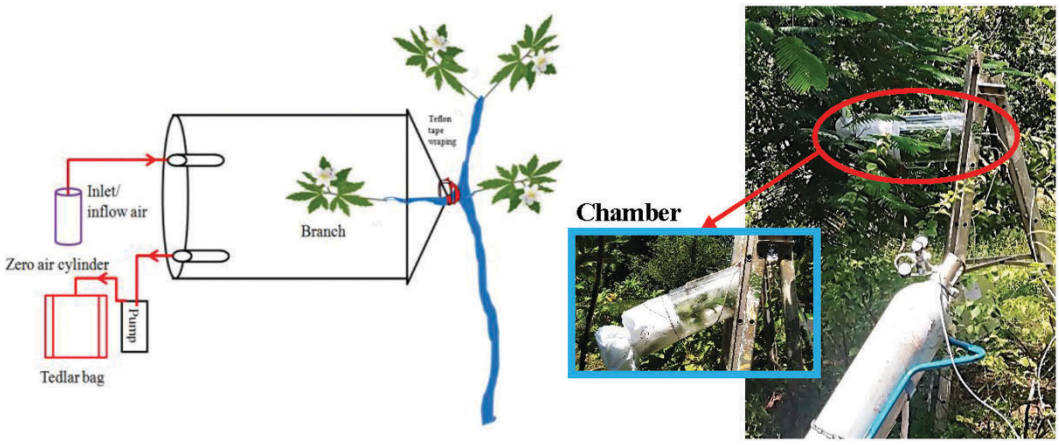

Figure 3. Schematic diagram (left) and field deployment (right) of the dynamic chamber system for sampling of biogenic volatile organic compounds (BVOCs) emitted from different plant species.

gulmohar/copper pod), *Ficus religiosa* (peepal tree), *Ficus amplissima* (nunurki tree), *Mangifera indica* (mango tree), *G. sepium* (Mexican lilac/saranga), *Cocos nucifera* (coconut palm), *Terminalia catappa* (Indian almond), *S. asoca* (Ashoka), *T. grandis* (teak/Saguan), *Tamarindus indica* (English tamarind), *L. leucocephala* (kubabul), *Opuntia ficus* (Indian fig), *P. guajava* (Guava), *M. zapota* (chikoo), *Bambusa arundinacea* and *B. vulgaris* (bamboo) are the dominant tree species[54,55]. Among these, we have selected seven species, as mentioned earlier to examine their BVOC emission characteristics (Figure 2). These selected species were mature, and not affected by any pests and diseases.

Design of custom-made chamber

We have designed a dynamic chamber for the direct sampling of BVOCs emitted from the selected plant species (Figure 3). The chamber has been constructed from a transparent acrylic cylinder of length 0.60 m and diameter

Table 1. Concentration (mean ± standard deviation) of different biogenic volatile organic compounds (BVOCs) and values of environmental parameters measured during the chamber experiments from seven different plant species

Plant species	Ethene (ppbv)	Propene (ppbv)	Isoprene (ppbv)	α-Pinene (ppbv)	β-Pinene (ppbv)	Sampling date and time	Temperature (°C)	Relative humidity (%)	Solar radiation (W/m^2)
Saraca asoca	0.73 ± 0.19	0.41 ± 0.12	0.74 ± 0.09	0.03 ± 0.008	0.03 ± 0.006	12:55 (16 October 2022)	29.22 ± 0.16	69	591.25 ± 35.38
Leucaena leucocephala	0.53 ± 0.11	0.45 ± 0.12	0.34 ± 0.11	0.02 ± 0.007	0.02 ± 0.004	12:05 (14 October 2022)	29.05 ± 0.38	62	620.08 ± 12.98
Psidium guajava	0.39 ± 0.14	0.44 ± 0.19	6.64 ± 1.82	0.01 ± 0.001	0.01 ± 0.007	13:20 (14 October 2022)	28.23 ± 0.15	70	459.83 ± 77.11
Gliricidia sepium	NA	NA	NA	0.02 ± 0.01	0.03 ± 0.001	15:10 (13 October 2022)	27.96 ± 0.19	67	216.90 ± 112.82
Manilkara zapota	0.9	0.49	0.31	0.01	0.01	11:45 (13 October 2022)	28.39 ± 0.52	76	625.34 ± 15.42
Bambusa vulgaris	0.88	0.83	0.65	0.03	0.04	11:30 (16 October 2022)	29.66 ± 0.30	63	707.20 ± 12.38
Tectona grandis	0.92	0.60	6.84	0.01	0.01	12:50 (13 October 2022)	28.33 ± 0.17	76	493.69 ± 60.11

0.25 m. The top of the chamber is closed using an acrylic plate/disk with two holes of 12 mm internal diameter (id). These holes on the plate are used to insert the inlet and outlet lines. A 4 m long teflon tube (6 mm id) is connected to the inlet for supply of zero air and a 50 cm long teflon tube is connected to the outlet for air sampling. The other open side of the chamber is wrapped with teflon foil after the plant branch is inserted. We collected the samples in tedlar bags (10 × 15 in) made from 2 mm thick tedlar film with a capacity of 5 litre (SKC Inc., PA, USA, catalogue no. 232-05). A polytetrafluoroethylene (PTFE) hose valve and an injection port containing a teflon fluorocarbon resin septum are attached to the bag for sample collection and analysis without contamination or loss of species in the sampling volume.

Chamber experiments and analysis of BVOCs

The chamber experiments were performed during daytime (between 10:30 and 15:30 h) from 13 to 17 October 2022. Table 1 summarizes the details of sampling and ambient conditions for each experiment. During the experiments, we collected samples for each of the representative plant species as well as from the ambient (background) air. For each plant species, an open branch was selected for the experiments to avoid underestimation of emissions due to shading from overlying leaves[58]. For each plant species, an exposed branch at a height of 1–2 m from the ground was selected and inserted into the chamber. To avoid the impact of any physical stress, the chamber enclosure was held stationary using a supporting platform. The branches with leaves were carefully placed inside the chamber to minimize contact with the inner walls of the chamber. After inserting the branch, the open back end of the chamber was tightly wrapped using teflon foil. Next, a continuous zero-air (99.9999%) flow was supplied from the cylinder at 15 psi (1034.21 hPa, outlet pressure), i.e. slightly higher than the ambient atmospheric pressure, for 20 min into 30 litre volume of the chamber. This continuous flow of zero air into the chamber provides uniform mixing of BVOCs emitted from the branch[40]. The enclosure system is not completely airtight and a continuous flow of zero air is required to avoid the inward flow of ambient air. Due to this, some pressure might be generated in the chamber, but because of the non-availability of a pressure sensor, this pressure could not be measured. The flow of VOC-free zero air is preferred instead of ambient air to minimize any alteration of BVOC emissions from the plants. The samples were collected after 20 min of zero-air flow using a pocket pump (SKC Inc., catalogue no. 22-2301) through a teflon/silicone line extended from the outlet tube of the chamber. The ambient-air (background) samples were collected at the location of the sampled species before the start of the chamber experiment. During the experiment, we carefully inserted the branches inside the chamber to avoid any injury or breaking.

Analysis of speciated BVOCs, including ethene, propene and isoprene present in the collects samples was performed using a C_2–C_6 VOC analyser (AirmoVOC Model: A12000, Chromatotec®, Saint-Antoine, France). Monoterpene compounds, including α-pinene and β-pinene were measured using a C_6–C_{12} VOC analyser (AirmoVOC, Model: A22022, Chromatotec®). Both these instruments are based on thermal desorption–gas chromatography coupled with a flame ionization detector (TD–GC–FID). The collected air samples were introduced into a peltier-cooled (at –15°C) adsorbent trap using a 1 m long stainless steel (SS) tube (0.25″ id). In the C_2–C_6 VOC analyser, BVOCs samples pre-concentrated on the adsorbent trap are desorbed into a PLOT column (Al_2O_3/Na_2SO_4, 25 m × 0.53 mm, 10 µm film thickness, Restek Corp., USA). In the C_6–C_{12} VOC analyser, the desorbed samples are transferred into an

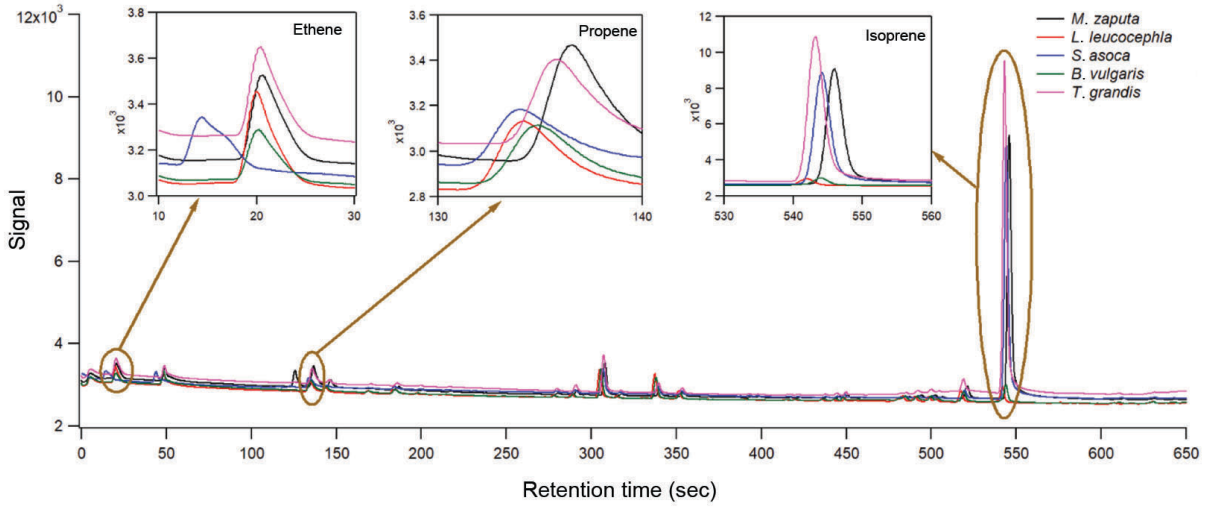

Figure 4. Typical chromatograms obtained from the analysis of samples collected during the chamber experiments on selected plant species.

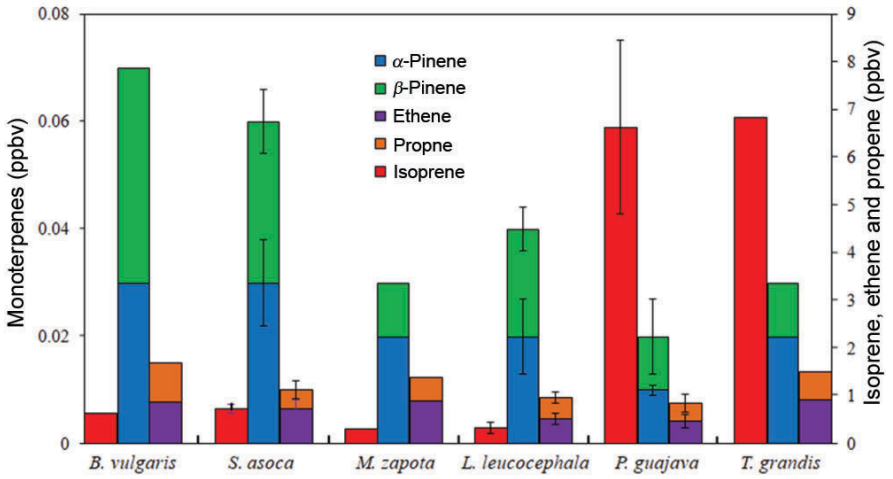

Figure 5. Concentration (mean) of alkenes (ethene and propene), isoprene and monoterpenes (α-pinene and β-pinene) in the samples collected from plant species during the chamber experiments. The error bars represent standard deviation.

MXT30CE column (30 m × 0.28 mm, 1 µm film thickness, Restek Corp.). The identification and peak area integration of different compounds were performed using VISTACHROM® software developed by Chromatotec®. Additional descriptions of VOC analyzers are provided in our previous study[59].

We performed multipoint calibrations on the system using standard gas mixture (lot no.: 1341032, Linde, USA) containing C_2–C_8 NMHCs at ~1 ppm with an analytical accuracy of ±5%, and also using a permeation tube (benzene-SN: 20170725-E703, Chromatotec©). The calibrations were performed at five different mixing ratios between 0 and 10 ppb (generated using a gas calibration unit, dynamic dilution system). The sensitivity was determined as the slope of the calibration curve and detection limit (DL) was calculated using the calibration curve and the following formula (according to guidelines of the International Conference on Harmonization).

$$\mathrm{DL} = 3.3\frac{\sigma}{S},$$

where σ is the standard deviation of the y-intercept and S is the slope of the calibration curve.

For analysis of α-pinene and β-pinene, the system default sensitivity (response factors calculated with reference to benzene) was used. DL (ppb) of ethene, propene and isoprene was determined as 0.167, 0.139 and 0.195 respectively.

Although many VOCs were detected using this analysis, we focused our study on the emissions of major BVOCs, including ethene, propene, isoprene, α-pinene and β-pinene.

Figure 4 shows typical chromatograms obtained from the analysis of samples collected from the chamber experiments on different selected plant species.

Plant-specific emissions of BVOCs

Table 1 gives the concentration of ethene, propene, isoprene, α-pinene and β-pinene measured during the chamber experiments for the seven selected plant species. Emissions from five plant species (*B. vulgaris*, *S. asoca*, *G. sepium*, *P. guajava* and *T. grandis*) show high levels of isoprene, followed by ethene, propene, α-pinene and β-pinene (Figure 5). The sum of the concentration of these measured BVOCs was highest for *T. grandis* and the lowest for *L. leucocephala*. *T. grandis*, *B. vulgaris* and *P. guajava* showed higher isoprene emission; *B. vulgaris* and *S. asoca* showed moderate emission, and *M. zapota* and *L. leucocephala* showed the lowest emission. Both *M. zapota* and *L. leucocephala* showed high emission of alkenes (ethene and propene) compared to isoprene. However, all the selected plant species showed lower monoterpene emission compared to isoprene and alkenes.

In order to determine the emission profile of BVOCs, the results obtained in this study have been compared with those reported for the same or other plants in previous studies. For instance, Hakola *et al.*[60] reported ethene, propene and 1-butene emissions from three tree species, i.e. tea-leafed willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*), with the highest emission from willow. Previous studies have revealed that ethene is produced in almost all plant parts in varying concentrations, and plays an important role in fruit ripening, flowering development, senescence and other physiological processes[61–64]. The emission of isoprene and monoterpenes from some of the plant species selected in this study has also been reported in previous studies[17,24,26,31,35,65]. Similar to the present study, high BVOC emissions are reported from *T. grandis* in previous studies[22,24]. We also found significant BVOC emissions from *P. guajava.* On the contrary, previous studies have reported low BVOC emissions[17,25].

The emission composition of BVOCs from *B. vulgaris* mainly consists of isoprene. Okumura *et al.*[65] have reported BVOC emissions from 14 different bamboo species with a significant fraction of isoprene from all of them. The BVOC emission profile of two tropical plant species, (viz. *B. vulgaris* and *S. asoca*) have been reported in this study. However, genus- and family-level studies are available in the literature (genus-level: *B. vulgaris*; family-level: *S. asoca*)[17,65]. The present study also reveals that the leaves of different species within the same genus are likely to exhibit similar isoprene emission characteristics. A comparison of genus- and family-level studies shows considerable differences in their emission characteristics[17,65]. Okumura *et al.*[65] have reported *Bambusa oldhamii* and *Bambusa multiplex* as significant emitters of only isoprene. Whereas in the present study, we found that *B. vulgaris* also emits smaller amounts of other BVOCs (ethene, propene, isoprene, α-pinene and β-pinene). These variations in BVOC emission characteristics could be due to the differences in their leaf structure, physiological characteristics and genetic make-up. There could also be other reasons like different environmental conditions, use of various measurement methods, growth forms and stage, age, etc. that might influence BVOC emission and composition. Overall, the sum of the measured BVOCs as well as relative composition of individual compounds showed large variations among plant species. The result indicates that isoprene is the dominant BVOC in major plant species found in the Western Ghats of India. Consistently, previous studies also support the fact that tropical as well as broadleaved species are mainly isoprene emitters, while coniferous or needle-like leaves are monoterpene-emitters[10,66]. A comprehensive study is required to quantify the emission fluxes of BVOCs from different tropical plant species by taking into account seasonality in key environmental parameters.

Summary

A custom-made chamber (branch enclosure) was deployed in this study to detect the BVOC emission profile from seven dominant plant species in the Western Ghats of India. The experiments show that the designed dynamic chamber is well suited for the detection of BVOC emissions using off-line TD–GC–FID and on-line VOCs analysers. The emission samples obtained from the branch-enclosure experiments were analysed to determine the composition and concentration of major BVOCs, including light alkenes, isoprene and monoterpenes. Two plant species (*B. vulgaris* and *S. asoca*) were considered for the measurement of BVOC composition. *T. grandis*, *B. vulgaris* and *P. guajava* were found to be strong isoprene-emitters with smaller amounts of alkenes, α-pinene and β-pinene.

Further improvements in the chamber design have been planned to determine the dependence of key environmental variables like temperature, light intensity, CO_2 concentration and RG, as they play an important role in controlling BVOC emissions. Studies of emissions from tropical tree species in the Western Ghats of India are important for inventory development and subsequent use in atmospheric chemistry modelling studies. Although this is a preliminary study in the Western Ghats, the experiments clearly highlight the potential of BVOC emissions from major plant species and provide scope for a comprehensive study in the future.

Conflict of interest: The authors declare that there is no conflict of interest.

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