Detection of biogenic VOCs emitted from common tropical plant species in the Western Ghats region of India: Chamber based experiments

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Brief subhead: VOC emission from plant species in the Western Ghats

Highlights:

Experiments using a custom-made branch-enclosure to study the emission compositions of BVOCs

Measurements of BVOC emission compositions from seven dominant tropical plants in the Western Ghats of India

First BVOC emission characterization study for two plant species of *Bambusa vulgaris* and *Saraca asoca*

All selected plant species show highest emissions of isoprene followed by light alkenes

Abstract

This study, for the first time, provides the detection of biogenic volatile organic compounds (BVOCs) emission 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 Analyzers to determine the emission composition and relative concentrations. 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 the high fractions of isoprene emissions, *Saraca asoca* showed moderate emissions, and *Manilkara zapota* and *Leucaena leucocephala* showed the lowest emissions. However, *Manilkara zapota* and *Leucaena leucocephala* showed higher emissions of both ethene and propene as compared to isoprene. This study reports the emission profiles of BVOCs from *Bambusa vulgaris* and *Saraca asoca* for the first time. This study emphasizes the importance of emission flux measurements of major plant species in different forest regions of India which is necessary to develop emission inventories of important BVOCs.

Keywords: Chamber experiment, Isoprene, Monoterpenes, Alkenes, Western Ghats, Tropical forests

1. Introduction

Emissions of biogenic-VOCs (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/yr[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%) have also been found to be 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, CO_2 and light intensity[13-15]. Therefore, the composition and fluxes of BVOCs emitted from the terrestrial plants are known to show strong species-to-specific variations[16,17]. Studies on some tropical plant species have shown that the 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 BVOC[19,20]. The South Asian region, consisting of about 15% of world's tropical forest region as of 2010[21], has a rich diversity of tropical plant species. However, very limited information is available on their BVOC emission characteristics[17,22-26]. Nonetheless, it is important to investigate the BVOC emissions from tropical vegetation in view of their key roles in chemistry-climate interactions. Among the South Asian nations, India has the largest geographical area with ~713789 km^2 of area under forest cover. About 14 major forest types occupy nearly 21% of the India's total geographical area[27,28]. The tropical-moist and tropical-dry forests cover ~65% of the total forest area of India[29]. 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)[30] is shown in Figure 1. Despite large forest areas, the efforts to measure the emissions of BVOCs from Indian plant species have not been systematic and comprehensive. A few studies[17,22-26,31-35] have reported BVOC emissions from different plant species in India. The isoprene and monoterpene emission rates from common tropical plant species of the *Amarkantak-Achankmar*-Biosphere Reserve (AABR) in central India are reported in[17].

During the last few decades, researchers have been trying to design and develop the branch-enclosure systems, both static and dynamic, to quantify the emissions of BVOCs from different plants[36-39]. Several recent advances in branch enclosures studies, using both static and dynamic enclosures, have been made. But the dynamic enclosure is more convenient and recommended for authentic measurements of BVOC emissions[40]. Unlike the static enclosure, the environment and circulation can be controlled in dynamic enclosures[11,41-43]. In addition, some studies have also shown that the changes in temperature and relative humidity inside the static enclosures. In absence of purge flow, the temperatures inside the static chamber rises, and this may affect the true estimations of BVOCs. While such uncertainties are relatively less in case of dynamic chamber-based estimations. In static chamber there is compulsion of zero air while as it is not for dynamic one. During the last few decades, the studies have been focused using the dynamic chambers in order to overcome the uncertainties associated with static chamber based studies[41,44,45]. So far, the dynamic chamber has been the most widely used system for the measurements of BVOC emissions from the plant species[46-48], and to determine its dependence on different environmental variables[10,49-52]. However, lack of pre-established and tested protocol, and thus, inconsistency in enclosure systems and deployment methods leads to large variations in emission estimates across the globe[53,54].

In this study, we have presented the descriptions of a custom-made chamber system and its performance during the field deployments for the measurements of BVOCs emission from the 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 few of the most common plant species found in the Western Ghats of India[57,58]. Among these, the BVOC emission compositions from the two selected plant species (*Bambusa vulgaris* and *Saraca asoca*) have not been reported previously in the literature. Thus, this study provides a test case investigation about the composition of BVOCs emitted from these plants in the Western Ghats region. And for the remaining five species, the BVOC emission properties have been reported for other parts/regions 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.

2. Experiments and Results

2.1 Study region

The Western Ghats of India is a global biodiversity hotspot covering the states of Maharashtra, Goa, Karnataka, and Kerala[9,55]. The geographical area of the Western Ghats is ~160,000 km^2, out of which ~57000 km^2 (35.6%) is forest cover[56]. The Western Ghats forests are dominated by the moist deciduous, semi-evergreen, dry deciduous, and wet evergreen trees[29,57]. The 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 the annual average precipitation of approximately 3800 mm, most of which is concentrated between the months of mid-June and September[27]. In this region, *Peltophorum pterocarpum* (Peela gulmohar/Copper pod), *Ficus religiosa* (Peepal tree), *Ficus amplissima* (Nunurki tree), *Mangifera indica* (Mango tree), *Gliricidia sepium* (Mexican Lilac/Saranga), *Cocos nucifera* (Coconut palm), *Terminalia catappa* (Indian almond), *Saraca asoca* (Ashoka), *Tectona grandis* (Teak/Saguan), *Tamarindus indica* (English tamarind), *Leucaena leucocephala* (Kubabul), *Opuntia ficus* (Indian fig), *Psidium guajava* (Guava), *Manilkara zapota* (Chikoo), *Bambusa arundinacea* and *Bambusa vulgaris* (Bamboo) are the dominant tree species[57,58]. Among these, we have selected seven species of *Bambusa vulgaris*, *Saraca asoca*, *Gliricidia sepium*, *Psidium guajava*, *Tectona grandis*, *Leucaena leucocephala* and *Manilkara zapota* to investigate their BVOC emission characteristics (Figure 2). These selected species were mature and not affected by any pests and diseases.

2.2 Design of custom-made chamber

We have designed a dynamic chamber for the direct sampling of BVOCs emitted from selected plant species as shown in Figure 3. The chamber is constructed from a transparent acrylic cylinder with a length of 0.60 m and a diameter of 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. About 4 m long teflon tube (6 mm id) was connected to inlet for the supply of zero-air and a 50 cm long teflon tube was 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. The schematic diagram and onsite deployment of the chamber setup are shown in Figure 3. We collected the samples in tedlar bags (10×15 inch) made from 2 mm thick tedlar film with a capacity of 5 L (SKC Inc., catalogue no. 232-05, PA 15330-9613, USA). A polytetrafluoroethylene (PTFE) hose valve and an injection port containing a teflon fluorocarbon resin septum are attached to the bag for the sample collection and analysis without contamination or loss of species in the sampling volume.

2.3 Chamber experiments and analysis of BVOCs

The chamber experiments were performed in the daytime (between 10:30 and 15:30 hr) during 13-17 October 2022. The details of sampling and ambient conditions for each experiment are summarized in Table 1. 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 the shaded (non-sunlight) leaves[59]. For each plant species, an exposed branch at heights of 1-2 m from the ground was selected and enclosed in the chamber. To avoid the impact of any physical stresses, the chamber enclosure was held stationary using a supporting platform. The branches with leaves were carefully placed inside the chamber to minimize the contact with the inner wall of the chamber. After enclosing the branch, the open back-end of the chamber was tightly wrapped using teflon foils. After that, a continuous zero-air (99.9999%) flow was supplied from the cylinder at a 15 psi (1034.21 hPa) (outlet pressure) i.e. slightly higher than the ambient atmospheric pressure for 20 min into the 30 L volume of the chamber. This continuous flow of zero-air into the chamber provides uniform mixing of BVOCs emitted from the branch[41]. The enclosure system was not completely airtight and a continuous flow of zero-air was required to avoid the inward flow of ambient air. Due to this, some pressure might be generated in the chamber, but due to the non-availability of pressure sensor, this pressure was not measured. The flow of VOC-free zero-air was 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, by using a pocket pump (SKC Inc., catalogue no. 22-2301, PA 15330-9613, USA) through a teflon/silicone line extended from the outlet of the chamber. The ambient air (background) samples were collected at the location of sampled species before the start of the chamber experiment. During our experiment, we carefully inserted the branches inside the chamber to avoid any injury or breaking.

The analysis of speciated BVOCs including ethene, propene and isoprene present in the collected samples was performed using a C_2-C_6 VOC analyzer (AirmoVOC Model: A12000, Chromatotec®, Saint-Antoine, France). While monoterpene compounds including α-pinene and β-pinene were measured using a C_6-C_{12} VOC analyzer (AirmoVOC, Model: A22022, Chromatotec®, Saint-Antoine, France). Both these instruments are based on the 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 via a 1 m long stainless steel (SS) tube (0.25" ID). In the C_2-C_6 VOC analyzer, BVOCs samples pre-

concentrated on the adsorbent trap are desorbed into a PLOT column (Al_2O_3/Na_2SO4, 25 m× 0.53 mm, 10 μm film thickness, Restek Corp., USA). In the C_6-C_{12} VOC analyser, the desorbed samples were transferred into an MXT30CE column (30 m × 0.28 mm, 1 μm film thickness, Restek Corp., USA). 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[60].

We performed multipoint calibrations on our 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©, France). The calibrations were performed at five different mixing ratio values between 0-10 ppb (generated using a gas calibration unit, dynamic dilution system). The sensitivity was determined as the slope of the calibration curve and the detection limit (DL) was calculated using calibration curve through the following formula (according to guidelines of International Conference on Harmonization (ICH)).

$$DL=3.3\times\frac{\sigma}{S}$$

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

For analysis of α- and β- pinenes, system default sensitivity (response factors calculated with reference to benzene) was used. The detection limit (ppb) of ethene, propene, and isoprene were determined to be 0.167, 0.139 and 0.195, respectively.

Although many VOC compounds were detected using this analysis, we focused our study on the emissions of major BVOCs including ethene, propene, isoprene, α-pinene and β-pinene. Typical chromatograms obtained from the analysis of samples collected from the chamber experiments on different selected plant species are shown in Figure 4.

2.4 Plant specific emissions of BVOCs

Concentrations of ethene, propene, isoprene, α-pinene and β-pinene measured during the chamber experiments for seven selected plant species are given in Table 1. Among the plant species, emissions from the five plant species (*Bambusa vulgaris*, *Saraca asoca*, *Gliricidia sepium*, *Psidium guajava*, and *Tectona grandis*) show high levels of isoprene, followed by

ethene, propene, α-pinene and β-pinene (Figure 5). The sum of the concentrations of these measured BVOCs was highest for *Tectona grandis* and the lowest for *Leucaena leucocephala*. Among the plant species, *Tectona grandis*, *Bambusa vulgaris*, and *Psidium guajava* showed higher isoprene emissions; *Bambusa vulgaris* and *Saraca asoca* showed moderate emissions; and *Manilkara zapota* and *Leucaena leucocephala* showed the lowest emissions. *Manilkara zapota* and *Leucaena leucocephala* both showed high emissions of alkenes (ethene and propene) as compared to isoprene. However, all the selected plant species showed lower monoterpene emissions compared to isoprene and alkenes.

In order to have an idea about 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. (1998)[61] 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 highest emissions 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[62-65]. The emissions of isoprene and monoterpenes from some of the plant species selected in this study are also reported in previous studies[17,24,26,31,35,66]. Similar to present study, high BVOCs emissions are reported from *Tectona grandis* in the previous studies[22,24]. We also found significant BVOCs emission from *Psidium guajava.* On contrary, previous studies have reported lower BVOCs emissions[17,25].

The emission composition of BVOCs from *Bambusa vulgaris* mainly consists of isoprene. Okumura et al. (2018)[66] have reported the BVOCs emissions from 14 different bamboo species with significant fractions of isoprene from all. The BVOC emission profiles of two tropical plant species (*Bambusa vulgaris* and *Saraca asoca*) have been reported for the first time in this study. However, genus and family-level studies are available in the literature (genus-level: *Bambusa vulgaris*; family-level: *Saraca asoca*)[17,66]. This study also revealed that the leaves of different species within the same genus are likely to exhibit similar isoprene emission characteristics. The comparison of studies for genus and family-level studies shows considerable differences in their emission characteristics[17,66]. Okumura et al. (2018)[66] have reported *Bambusa oldhamii* and *Bambusa multiplex* as significant isoprene emitters only. Whereas in the present study, we found that *Bambusa vulgaris* also emits smaller amounts of other BVOCs (ethene, propene, isoprene, α-pinene and β-pinene). These variations in BVOCs emission characteristics could be due to the differences in their leaf structures, physiological

characteristics and genetic makeup. There could be some other reasons like different environmental conditions, use of different measurement methods, growth forms and stage, age, etc. might influence BVOCs emission and composition. Overall, the sum of measured BVOCs as well as relative composition of individual compound showed large variations from plant-to-plant. The result indicates that isoprene is the dominant BVOC in major plant species found in the Western Ghats. Consistently, previous studies also support the fact that tropical as well as broad-leaved species are mainly isoprene emitters, while coniferous or needle-like leaves are monoterpene emitters[10,67]. A comprehensive study is required to quantify the emission fluxes of BVOCs from different tropical plant species by taking account of the seasonality in key environmental parameters.

3. Summary

A custom-made chamber (branch-enclosure) was deployed to detect the BVOC emission profiles from seven dominant plant species (*Tectona grandis, Bambusa vulgaris*, *Psidium guajava*, *Saraca asoca*, *Manilkara zapota*, *Leucaena leucocephala* and *Gliricidia sepium*) in the Western Ghats of India. The experiments show that the newly designed dynamic chamber is well suited for the detection of BVOCs emissions using offline TD-GC-FID and online VOCs analysers. The emission samples obtained from the branch-enclosure experiments were analysed to determine the composition and concentrations of major BVOCs including light alkenes, isoprene and monoterpenes. Two plant species (*Bambusa vulgaris* and *Saraca asoca*) were investigated for the first time for the measurements of BVOC composition. *Tectona grandis*, *Bambusa vulgaris* and *Psidium 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 measure the dependence of key environmental variables like temperature, light intensity, CO_2 concentration, and relative humidity, as they play an important role in controlling BVOC emissions. The studies of emissions from tropical tree species in the Western Ghats are important for the inventory developments and subsequent use in atmospheric chemistry modelling studies. Although this is a preliminary study in the Western Ghats, the experiments clearly highlight the potentials of BVOC emissions from major plant species and provide scope for comprehensive study in future.

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492 Table1. Concentrations (mean ± standard deviation) of different BVOCs and values of
493 environmental parameters measured during the chamber experiments from seven different
494 plant species.

Plant species	Ethene (ppbv)	Propene (ppbv)	Isoprene (ppbv)	α-pinene (ppbv)	β-pinene (ppbv)	Sampling date and time	T (°C)	RH (%)	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

495

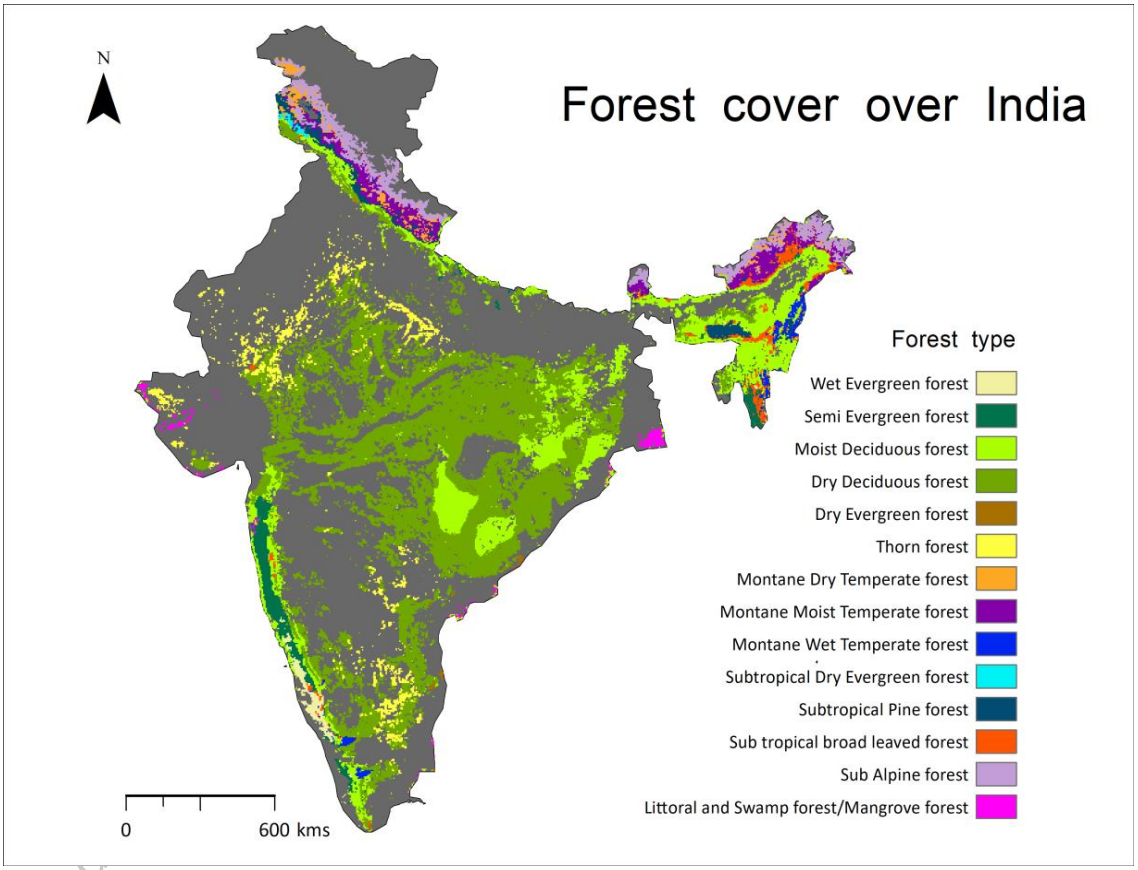

Figure 1. Different forest types and land use/land cover map of India using Forest type 5km grid data, National Remote Sensing Centre, ISRO, Government of India, Hyderabad, India, through the Bhuvan Geo Portal (https://bhuvan.nrsc.gov.in)

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

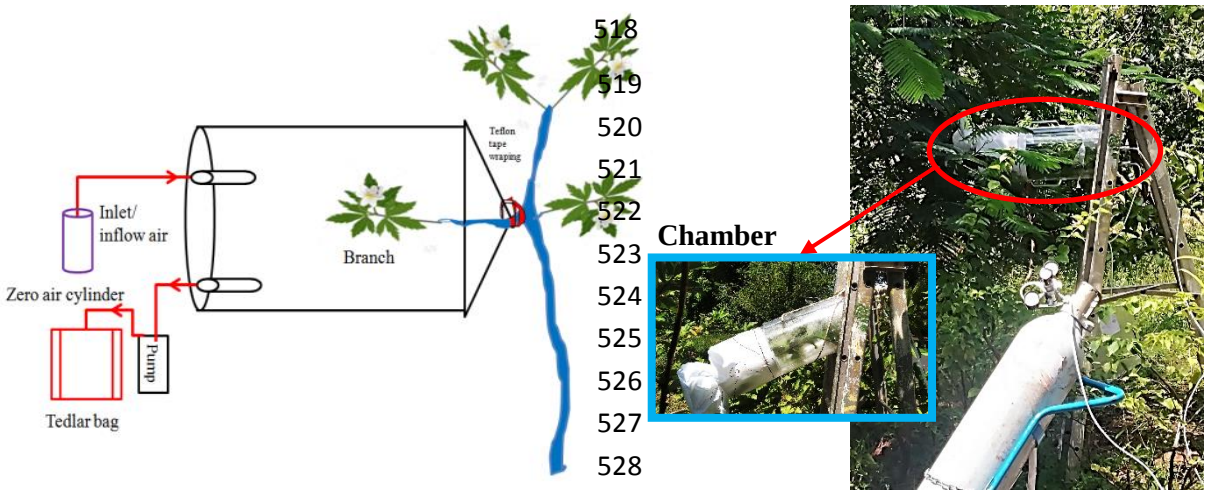

Figure 3. Schematic diagram (left) and field deployment (right) of the dynamic chamber system for the sampling of BVOCs emitted from different plant species.

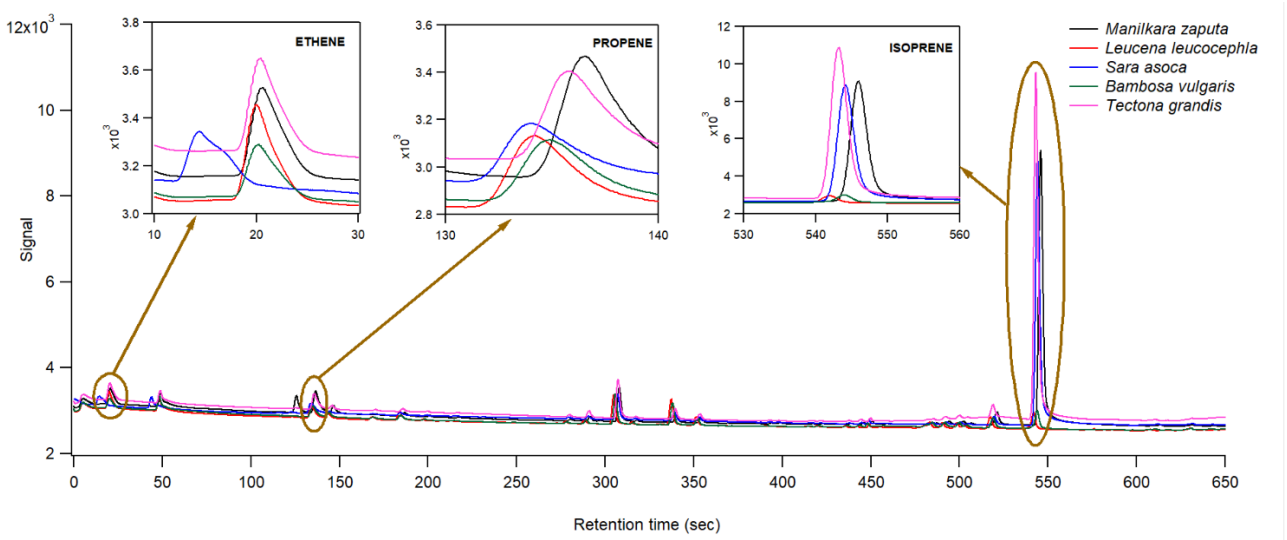

Figure 4. Typical chromatograms obtained from the analysis of samples collected from the chamber experiments on selected plant species.

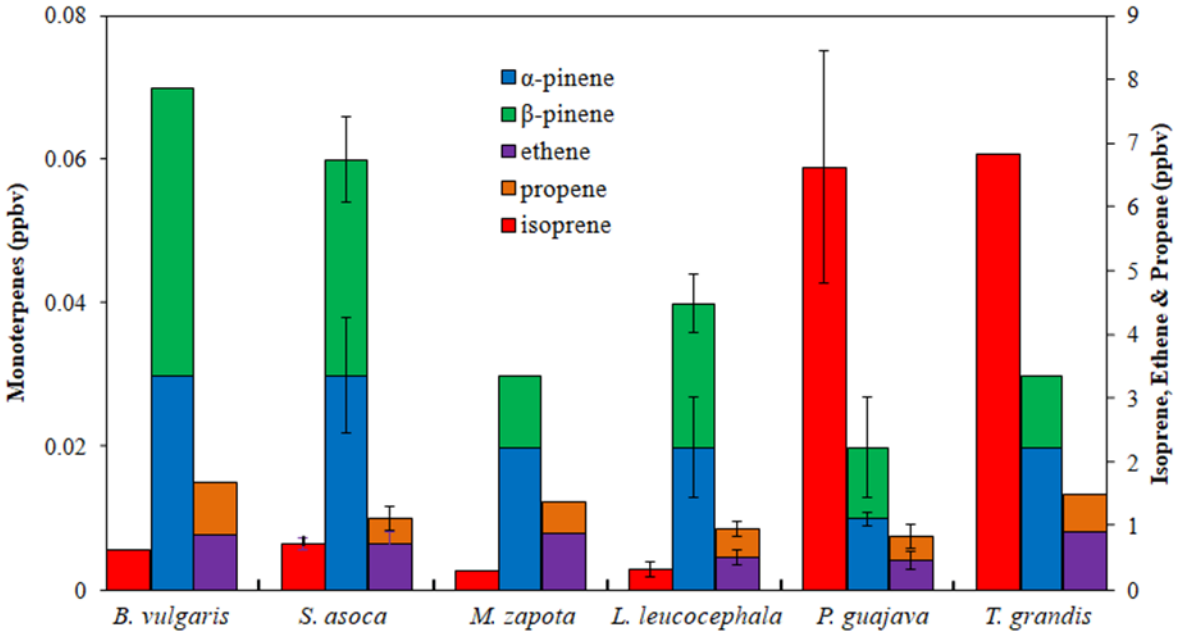

Figure 5. The concentrations (mean) of alkenes (ethene and propene), isoprene and monoterpenes (α-pinene & β-pinene) in the samples collected from plant species during the chamber experiments, the error bars represent the standard deviation.