High DMS and monoterpene emitting big leaf Mahogany trees: discovery of a missing DMS source to the atmospheric environment

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Abstract. Biogenic volatile organic compounds exert a strong influence on regional air quality and climate through their roles in the chemical formation of ozone and fine mode aerosol. Dimethyl sulphide (DMS), in particular, can also impact cloud formation and the radiative budget as it produces sulfate aerosols upon atmospheric oxidation. Recent studies have reported DMS emissions from terrestrial sources, however their magnitudes have been too low to account for the observed ecosystem scale DMS fluxes. Big-leaf Mahogany (*Swietenia macrophylla*) is an agro-forestry and natural forest tree known for its good quality timber and listed under the Convention on International Trade in Endangered Species (CITES). It is widely grown in several South American, Central American, North American and Asian atmospheric environments (> 2.4 million km² collectively). Here, we investigated emissions of monoterpenes, isoprene and DMS as well as seasonal carbon assimilation from four big-leaf Mahogany trees in their natural outdoor environment using a dynamic branch cuvette system, high sensitivity proton transfer reaction mass spectrometer and cavity ring down spectrometer. The emissions were characterized in terms of environmental response functions such as temperature, radiation and physiological growth phases including leaf area over the course of four seasons (summer, monsoon, post-monsoon, winter) in 2018-19. We discovered remarkably high emissions of DMS (average in post monsoon: ~19 ng/g leaf dry weight/hr) relative to previous known tree DMS emissions, high monoterpenes (average in monsoon: ~15 µg/g leaf dry weight/hr which are comparable to oak trees) and low emissions of isoprene. Distinct linear relationships existed in the emissions of all three BVOCs with higher emissions during the reproductive phase (monsoon and post-monsoon seasons) and lower emissions in the vegetative phase (summer and winter seasons) for the same amount of cumulative assimilated carbon. Temperature and PAR dependency of the BVOC emissions enabled formulation of a new parametrization for use in global BVOC emission models. Finally, using the measured seasonal fluxes, we provide the first estimates for the global emissions from Mahogany trees which amount to circa 210-320 Gg yr⁻¹ for monoterpenes, 370-550 Mg yr⁻¹ for DMS and 1700-2600 Mg yr⁻¹ for isoprene. Finally, through the results obtained in this study, we have been able to discover and identify Mahogany as one of the missing natural sources of ambient DMS over the Amazon rainforest as well. These new emission findings, seasonal patterns, and estimates will be useful for initiating new studies to further improve the global BVOC terrestrial budget.

1 Introduction

Biogenic volatile organic compound (BVOC) emissions contribute to 90% of total annual VOC emissions (Guenther et al., 1995; Fehsenfeld et al., 1992). Of the total BVOC emissions of 1000 Tg yr⁻¹ estimated by MEGAN 2.1, terpenoids like isoprene, monoterpenes, and sesquiterpenes contribute about 70% to the total and are emitted majorly in the tropics (Guenther et al., 2012). When mixed with urban air which is typically rich in nitrogen oxides, these highly reactive BVOCs can impact regional air quality significantly by fueling formation of secondary pollutants such as ozone and secondary organic aerosols (SOA) with consequences also for the regional climate (Atkinson and Arey, 2003; Kavouras et al., 1998; Goldstein et al., 2009).
DMS plays a significant role in atmospheric chemistry as it contributes to the formation of ambient sulfate aerosol particles upon atmospheric oxidation. This new particle formation (NPF) can further contribute to direct and indirect radiative forcing by forming cloud condensation nuclei (CCN) (Andreae and Crutzen, 1997). The major biogenic source of dimethyl sulfide (DMS) in the atmosphere are marine phytoplankton (Stefels, 2000;Charlson et al., 1987;Lovelock et al., 1972;Watts, 2000).

However, a recent study from the Amazon rainforest reported high DMS mixing ratios above the forest and concluded that there is a net ecosystem source for DMS (Jardine et al., 2015). Only a few previous studies have shown trees to be potential terrestrial sources of DMS possibly by the uptake of carbonyl sulfide (COS) or from sulfur sources within the tree (Yonemura et al., 2005;Geng and Mu, 2006;Kesselmeier et al., 1993).

Terpenoids play key functional roles in chemical ecology and can be released by plants due to both biotic and abiotic stresses such as high temperature (Loreto et al., 1998;Sharkey and Singsaas, 1995), intense light (Vickers et al., 2009) and herbivory (Kappers et al., 2011). BVOC emissions are modeled (Guenther et al., 2012) using land use land cover data, temperature, light and other meteorological parameters as key inputs. However, large intra-annual and intra-species variability exist which lead to large uncertainties for annual fluxes. In specific instances where the physiological and biochemical pathways responsible for the BVOC emission are also not understood, such as for DMS (Yonemura et al., 2005), it is not even possible to model the BVOC emissions. Global warming and land use changes further complicate emission flux calculations of BVOCs in models (Peñuelas, 2003;Unger, 2014).

Swietenia macrophylla King commonly called the Big-leaf Mahogany is a neotropical tree species which occurs naturally in both the northern hemisphere and southern hemisphere spanning across regions from Mexico (23°N) to the southern Amazon (18°S) and covering an area of circa 150 million hectares (Blundell, 2004). Due to its highly-valued best quality timber, plantations of this species are also widespread in several parts of South Asia and Southeast Asia (Mayhew et al., 2003). The area under this tree in South American, Central American, North American and Asian atmospheric environments collectively exceeds 2.4 million km² of land area. This tree species is listed in the Convention on International Trade in Endangered Species (CITES) of Wild Fauna and Flora Appendix II as it faces a threat due to widespread unsustainable logging (Groagan and Barreto, 2005). New silviculture and agroforestry of Mahogany are on an upsurge to sustainably comply with the demand for its timber due to the strict law enforcement, that prohibits the illegal logging from natural forests which had met the market requirements before the CITES listing (Ward et al., 2008). Varshney et al. 2003 were the first group in India to screen forty tropical Indian trees in terms of their isoprene emission potential, and there now exists a fairly large worldwide database for trees in terms of their isoprene and monoterpane emission potential (http://www.es.lancs.ac.uk/ cnhgroup/iso-emissions.pdf). However, to the best of our knowledge, Swietenia macrophylla King BVOC emissions have not been investigated previously.

In this study, we investigated emissions of monoterpenes, isoprene and DMS and carbon assimilation from four big-leaf Mahogany trees growing in north India in their natural outdoor environment using a dynamic branch cuvette system, a high sensitivity proton transfer reaction mass spectrometer (PTR-MS) and a cavity ring down spectrometer (CRDS). The emissions were characterized in terms of environmental response functions such as temperature, radiation and physiological growth phases including leaf area over the course of four seasons (summer, monsoon, post-monsoon, winter) during 2018-19. Using
the derived relationships, a new parametrization for use in global BVOC emission models is proposed. Finally, using the measured seasonal fluxes and currently documented natural and planted Mahogany tree cover areas, we provide the first estimates for the global annual emissions of monoterpenes, DMS and isoprene from Mahogany trees.

2 Materials and Methods

2.1 Sampling, branch cuvette experiments and flux calculation methodology

Sampling and biogenic VOC emission measurements were performed during four seasons: 2018 summer from 22-24 May (n>3000 measurements), 2018 monsoon (n>12400 measurements) from 25 September-4 October, 2018 post-monsoon (n>10300 measurements) from 15-22 November, and 2019 winter from 24-29 January (n>7300 measurements). A total of four big leaf Mahogany (*Swietenia macrophylla*) trees growing in the natural outdoor environment in the north west Indo-Gangetic Plain (30.667° N, 76.729° E, 310 m a.s.l.) were sampled using a dynamic branch cuvette sampling system. Monoterpenes, isoprene, dimethyl sulfide (DMS) were measured using a high sensitivity proton transfer reaction mass spectrometer (PTR-MS; HS Model 11-07HS-088; Ionicon Analytik Gesellschaft, Austria) while carbon dioxide was measured using a cavity ring down spectrometer (CRDS; Model G2508, Picarro, Santa Clara, USA). The same tree was sampled to obtain the inter-seasonal variability. Since observations showed significant DMS emissions we sampled three additional trees, two of which were growing within 10 m of each other and the third of which was growing approximately 250m away, during wintertime. While two of the three trees were sampled at high temporal resolution continuously in an online manner (n> 1000 measurements per day), offline sampling for collection of whole air samples from the dynamic branch cuvettes was carried out in passivated steel canisters from the distant tree. Below we describe the dynamic branch cuvette system and trace gas measurements.

Custom-made polyvinyl fluoride bags (PVF, Tedlar®; 95% transmittance, Dimension: 24” × 36”, 2 mil thickness. Avg. capacity: 54 L; DuPont, USA) were used as the cuvette material. Previous studies have already discussed its advantages for both analytical and practical purposes (Ortega and Helmig, 2008; Ortega et al., 2008). The bag has one open end and two Jaco fittings (6.3 mm) for inlet and outlet air flow Teflon tubing (3.2 mm, 6.3 mm, 12.8 mm and 19.2 mm O. D., 60-65 m). The Mahogany branch was equipped with a temperature (T) and relative humidity (RH) sensor (No: 201403513, HTC easy Log, India) to monitor the cuvette temperature and RH. Ambient meteorological parameters and soil moisture (SM) were also measured using sensors for temperature and RH, PAR and soil moisture (Decagon devices, USA), placed adjacent to the tree. A schematic of the dynamic branch cuvette system can be found in Fig. S1. Branches with similar leaf age were selected also ensuring that the cuvette received sunlight throughout the day. The cuvette was suspended carefully on the tree branch to minimize the weight stress on the tree and avoid foliage contact within the cuvette. Input air was generated from ambient air using a series of traps containing steel wool, silica gel, and activated charcoal. Measurements of ozone using a portable ozone monitor (PO3M, 2B Technologies, Colorado, US) and the target VOCs in the input air showed that the traps worked quite well with concentrations below detection limit or extremely low values in the input air. A high capacity Teflon VOC pump (N145.1.2AT.18, KNF Germany) was used to ensure a constant flow of air into the cuvette via a mass flow controller.
used inside the facility. All flows were measured using a NIST calibrated flow meter (BIOS Drycal definer 220). The input air was sampled at regular intervals by diverting the air flow such that it bypassed the branch cuvette. After installation of the cuvette, we allowed the branch to acclimatize overnight before starting the measurements. This is significantly longer than the steady-state attainment time of circa 5 minutes recommended by Niinemets et al. (2011) and was done to ensure acclimatization/conditioning of leaves to the flows and chamber. After completion of the measurements, the leaves were destructively harvested from the enclosed branch to measure the total leaf area (m²) inside the cuvette and dried at 60 °C to also measure the leaf dry weight (ldw). Data for the same is available in Table S1.

Whole air was sampled actively for offline measurements in commercially available 6 L passivated SilcoCan air sampling steel canisters (Restek, USA) and then analyzed with PTR-MS and CRDS within 6 hours of sample collection as described in our previous work (Chandra et al., 2017). Briefly, air was sampled into the canisters over a period of 30 minutes at a flow rate of 500 ml/min to final pressure of 30 psi using a Teflon VOC pump (Model – N86 KT.45.18; KNF Germany) and mass flow controller (Max. capacity: 500 sccm; Bronkhorst High-Tech; stated uncertainty 2%).

Emission fluxes for the sum of monoterpenes, isoprene and dimethyl sulfide normalized to leaf area were obtained using Eq. (1) (Sinha et al., 2007; Niinemets et al., 2011)

$$\text{EF}_{\text{BVOC}} \left( \text{nmol} \text{ m}^{-2} \text{ s}^{-1} \right) = \frac{m_{\text{out}, \text{BVOC}} - m_{\text{in}, \text{BVOC}}}{V_m} \times \frac{Q}{A} \left( \text{m}^3 \text{ s}^{-1} \right)$$

where, $$m_{\text{out}, \text{BVOC}} - m_{\text{in}, \text{BVOC}}$$ is the difference in the mixing ratios of the BVOC between output and input air, Q was the flow rate of air passing through the cuvette system in m³ s⁻¹, $$V_m$$ was the molar volume of gas calculated using the cuvette temperature.

The carbon assimilation rate, $$A_{\text{net}}$$ (μmol m² s⁻¹) was calculated using Eq. (2) (Huang et al., 2018)

$$A_{\text{net}} \left( \text{nmol} \text{ m}^{-2} \text{ s}^{-1} \right) = \frac{[\text{CO}_2\text{in}]-[\text{CO}_2\text{out}]}{V_m} \times \frac{Q}{A} \left( \text{m}^3 \text{ s}^{-1} \right)$$

where $$[\text{CO}_2\text{in}] - [\text{CO}_2\text{out}]$$ is the effective $$[\text{CO}_2]$$ taken up by the leaves inside the cuvette. Q and $$V_m$$ were the same as used in Eq. (1). By comparison with ambient air measurements for the week just before and after the cuvette experiments, it was found that $$[\text{CO}_2\text{in}]$$ was equivalent to ambient $$[\text{CO}_2]$$ for the corresponding hour of the day and thus the ambient CO₂ values were used as $$[\text{CO}_2\text{in}]$$ in Eq. (2).

2.2 Isoprene, monopentene, dimethyl sulphide and carbon dioxide measurements

The output air from the cuvette was sub-sampled into a high-sensitivity proton transfer reaction quadrupole mass spectrometer (PTR-MS; HS Model 11-07HS-088; Ionicon Analytik Gesellschaft, Austria) for the measurements of isoprene, DMS and sum
of monoterpenes. The instrument has been previously characterized in detail elsewhere (Sinha et al., 2014; Chandra et al., 2017; Kumar et al., 2018). In this technique, most analyte molecules having a proton affinity greater than water vapour (165 kcal/mol) undergo soft chemical ionization with reagent hydronium ions (H$_3$O$^+$) inside a drift tube to form protonated organic ions which are typically detected at mass to charge ratios (m/z) = molecular ion + 1. The product ions are then separated using a quadrupole mass analyzer and detected using a secondary electron multiplier. Measurements were conducted in the ion selective mode with a dwell time of 1s at each m/z channel. Compound-specific sensitivities (ncps/ppb) were determined using calibration experiments involving dynamic dilution of a VOC gas standard (Apel–Riemer Environmental, Inc., Colorado, USA; containing the VOCs at circa 500 ppb) on 4 May 2018, 4 October 2018, 14 November 2018 and 22 January 2019. The total measurement uncertainty was less than 10% for isoprene and DMS and less than 15% for the sum of monoterpenes also accounting for the instrumental background (determined by sampling VOC free air) at these m/z ratios. Extensive reviews (de Gouw and Warneke, 2007; Yuan et al., 2017) of previous PTR-MS studies including inter-comparisons with other more specific techniques as well as more recent validation experiments for DMS detection (Jardine et al., 2015) have demonstrated that under standard PTR-MS operational conditions ranging from 130-135 Td, isoprene and dimethyl sulfide can be detected at m/z 69 and m/z 63, respectively without any significant fragmentation and that as monoterpenes fragment their quantification can be accomplished by taking the sum of the major ions formed, namely m/z 81 and m/z 137 (Lindinger and Jordan, 1998; Tani et al., 2003). We, therefore, operated the instrument under standard operating conditions of drift tube pressure of 2.2 mbar and temperature of 60 degrees which yields a Townsend ratio of 135 Td.

Carbon dioxide measurements were performed by sub-sampling air from the cuvette into a cavity ring down spectrometer (CRDS; Model G2508, Picarro, Santa Clara, USA) which has been described in previous works from our group (Chandra et al., 2017). The overall uncertainty for measurements of CO$_2$ was below 4%. The instrument was calibrated by dynamic dilution of a gas standard mixture (1998 ppm CO$_2$ in Nitrogen traceable to NIST, USA, 2% uncertainty; Sigma gases, India) on 8 June 2018, 26 October 2018 and 24 January 2019.

3 Results and discussion

3.1 Emission of BVOCs from Mahogany including light and temperature dependency

Figure 1 shows the measured hourly averaged emission flux from big leaf Mahogany normalized to leaf area for the sum of monoterpenes and isoprene (top panel), DMS (middle panel), photosynthetically active radiation, along with the temperature (bottom panel) during summer, monsoon, post-monsoon and winter. Clear diurnal variation was observed in the emission profiles of all three compounds in all seasons with emissions reducing to zero/negligible fluxes in all seasons at night when PAR was zero. Average temperatures were highest in summer (~35 °C), followed by the monsoon (~30 °C), post-monsoon (~21 °C) and winter season (~13.5 °C). Peak hourly PAR ranged from 0-1200 µmol m$^{-2}$ s$^{-1}$ in all seasons except the post-monsoon where maximum hourly values remained below 900 µmol m$^{-2}$ s$^{-1}$ on all days of sampling. Thus, fluxes obtained in
this study covered a fairly large range of ambient temperature and light conditions. Winter was associated with the lowest BVOC fluxes for monoterpenes and isoprene (avg for both < 0.05 nmol m\(^{-2}\) s\(^{-1}\)) as well as DMS (avg 1.7 pmol m\(^{-2}\) s\(^{-1}\)), even though PAR values in winter were comparable to other seasons. Thus, temperature was a major driver for emissions of all three compounds. Average monoterpane fluxes were highest in the monsoon season (2.3 nmol m\(^{-2}\) s\(^{-1}\)) followed by the post-monsoon (~1.7 nmol m\(^{-2}\) s\(^{-1}\)) and summer season (~1.5 nmol m\(^{-2}\) s\(^{-1}\)), revealing that Mahogany is a high monoterpane emitter comparable to the highest monoterpane emitting trees in the world such as oaks (http://www.es.lancs.ac.uk/ cnhgroup/isoemissions.pdf) and actively so throughout the year. Average DMS fluxes were highest in summer season (~8.2 pmol m\(^{-2}\) s\(^{-1}\)), closely followed by post-monsoon season (~7.1 pmol m\(^{-2}\) s\(^{-1}\)) and monsoon season (~5.3 pmol m\(^{-2}\) s\(^{-1}\)), with lowest emissions during the winter season (~1.8 pmol m\(^{-2}\) s\(^{-1}\)). As most previous studies in the literature have reported emission fluxes of different tree species normalized to the leaf dry weight per hour in Table 1 we provide the average fluxes for each season in these units as well. In comparison, isoprene fluxes were significantly lower with average emission fluxes of only 0.03 nmol m\(^{-2}\) s\(^{-1}\) being observed during summer, monsoon and post-monsoon. The time series of the measured BVOC mixing ratios have also been provided in Fig. S2 for perusal. The emission profiles of monoterpenes and isoprene co-varied and correlated strongly in all seasons (r\(^2\) ≥ 0.8 with r\(^2\) ≥ 0.9 during summer and monsoon). This indicates that their emissions arise from common pathways in Mahogany and that fresh photosynthetically fixed carbon may be more important than emissions from stored pools (Monson et al., 1995). DMS emissions also correlated with the terpene emissions in all seasons except winter (r\(^2\) = 0.2) but were much weaker (0.4 ≤ r\(^2\) ≤ 0.5).

Whereas databases now exist concerning isoprene and monoterpane emission potential of trees, and also many studies have shown that monoterpane and isoprene emissions depend on the plant functional type, PAR availability, temperature and to a lesser extent soil moisture (Kesselmeier and Staudt, 1999; Guenther et al., 1996) (http://www.es.lancs.ac.uk/ cnhgroup/isoemissions.pdf), there are very few studies in the literature reporting DMS emissions from terrestrial plants and ecosystems (Kesselmeier et al., 1993; Yonemura et al., 2005; Geng and Mu, 2006), with even less known about the factors that control DMS emissions (Jardine et al., 2015). Hourly averaged DMS emission flux from Mahogany was found to vary between a maximum of 15.7 pmol m\(^{-2}\) s\(^{-1}\) in winter to 48.2 pmol m\(^{-2}\) s\(^{-1}\) in the post-monsoon seasons and were much higher than the maximum flux of 26 pmol m\(^{-2}\) s\(^{-1}\) observed from Hibiscus sp (Yonemura et al., 2005) or the DMS branch emission measurements made from seven tropical plant species (max ~6 pmol m\(^{-2}\) s\(^{-1}\)) within a large, enclosed rainforest mesocosm in Arizona, USA (Jardine et al., 2015) and the Geng and Mu (2006) study in China (max ~2 pmol m\(^{-2}\) s\(^{-1}\)). We note that in all these previous studies the range of temperature and PAR covered while measuring the DMS were significantly lower, with the temperature never exceeding 30 °C and PAR lower than 140 µmol m\(^{-2}\)s\(^{-1}\) in the Jardine et al. study and less than 500 µmol m\(^{-2}\)s\(^{-1}\) in the Yonemura et al., 2005 study, respectively.

To investigate the factors driving the emissions of monoterpenes, isoprene, and DMS in different seasons from Mahogany, we examined the relationship between the cumulative BVOC emission flux of these compounds with respect to the cumulative CO\(_2\) assimilation flux (A\(_{net}\)) starting from the sunrise of each day. Cumulative fluxes were calculated for every hour of the day and accumulated from sunrise until that hour. This is helpful as A\(_{net}\) is a good proxy for the rate of photosynthesis and a recent
13C-pulsed labeling study has shown that newly assimilated carbon can be emitted as monoterpenes within one hour (Huang et al., 2018). Further, depending on whether the tree’s growth is in the reproductive or vegetative phase, the assimilated carbon can be allocated differently impacting the emitted BVOC flux. For example, one could expect that in the constitutive growth phase, emissions of BVOCs would be lower whereas, in the reproductive phase, when flowering and fruiting occur, due to the important functional roles BVOCs play in attracting pollinators and for plant defence, there would be increased emissions of BVOCs (Peñuelas, 2003). Mahogany is known to bear fruits during the monsoon season (Gullison et al., 1996) and trees emit odorous compounds like terpenes for defence purposes especially against herbivores and abiotic stresses like high-intensity light, temperature. Hence the enhanced emission of BVOCs during the monsoon and post-monsoon seasons is likely due to these reasons. This diversion of the carbon allocation for such purposes can decrease growth by diverting photosynthates from the production vegetative structures (Herms and Mattson, 1992). Henceforth, the two distinct phases are referred to as the vegetative growth phase when the carbon allocation to BVOC synthesis is low and reproductive growth phase, when the carbon allocation by the tree to synthesize BVOCs is high. The results are shown in Figure 2(a) for monoterpenes, isoprene, and DMS. Distinct linear relationships were observed for the emissions of all three BVOCs with higher emissions during the reproductive phase (monsoon and post-monsoon seasons) and lower emissions in the vegetative phase (summer and winter seasons) for the same amount of cumulative assimilated carbon. It is interesting to note that DMS flux also shows this pattern in the two phases which suggests that DMS emission could be linked to these functional roles as well, in addition to being dependent upon the uptake of COS, the latter of which has been previously reported to be similar to uptake of carbon dioxide during photosynthesis (Jardine et al., 2015).

Global BVOC emission models such as MEGAN - Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2012) use PAR and ambient temperature dependence of major plant functional types to calculate BVOC emissions. Thus, it is meaningful to examine if one can obtain a parametrization of the monoterpane, isoprene, and DMS flux from big leaf Mahogany trees in terms of PAR and temperature. Figure 2(b) shows 3-D surface plots illustrating the dependence of BVOC emission flux as a function of instantaneous chamber temperature and PAR in the vegetative growth phase. In the vegetative phase, terpenes varied exponentially with respect to the two meteorological drivers. It is also evident that DMS has a strong dependence on temperature, but not on PAR. DMS peaked during high temperatures even when PAR was only 200 μmol m⁻² s⁻¹. However, the dependence of DMS flux on temperature is not always followed possibly because the DMS flux is dependent upon the uptake of COS or on the internal sulphur content. We constructed best bivariate fit functions by expressing the emission flux as an exponential function of both temperature and PAR for the vegetative growth phase and as a linear function of PAR, and an exponential function of temperature in the reproductive growth phase to better formulate the dependence of the BVOC emissions on these meteorological parameters.

Table 2 shows the fit functions and their coefficients for BVOC flux paramterizations as a function of PAR and temperature in both the reproductive and vegetative phases of Mahogany. The temperature dependent coefficient in the reproductive growth phase (c) is much lower than the temperature dependent coefficient in the vegetative growth phase (d). This implies that during the reproductive phase plant emits higher BVOCs with less temperature increment than during the vegetative phase and is in
agreement with our earlier observation regarding the higher carbon allocation for the BVOC synthesis and emission during the reproductive growth phase.

Figure 2(c) shows the modeled BVOC fluxes and measured BVOC fluxes for all the seasons. The observed temperature and PAR data during the experiments were used to calculate the modeled flux using the bivariate fit function for the two growth phases. We found that the measured flux can be predicted only if both the functions are used to calculate the modeled flux of the respective phase. Modeled DMS showed deviations from measured flux which may be attributed to irregularity in the dependence on high temperature but currently in the absence of knowledge concerning the exact pathways responsible for DMS emission, the reasons remain unclear. Still, the finding that vegetative growth and reproductive growth phases require different modeling functions, point to the need for considering the phenological cycle changes of plants in annual emissions as these can result in a significant increase or decrease in the modeled BVOC emissions from similar vegetation. These parametrizations provide a way to simulate Mahogany emissions even in global BVOC emission models that already use the PAR and temperature data for simulation of BVOC emissions.

3.3 Estimates of global annual emissions of monoterpane, isoprene, and DMS from Mahogany

Table 3 shows the distribution of Mahogany in natural forests and in plantations in terms of ground area, density, leaf area and calculated annual emission fluxes of monoterpenes, isoprene, and DMS for several countries, based on the documented area under Mahogany tree cover. First, the Mahogany tree cover was estimated using the available data regarding the natural forest and plantation cover in different countries around the globe (Blundell, 2004; Lugo et al., 2003; Mohandas, 2000). Forest cover was multiplied by the density of Mahogany trees reported in those countries (Gullison et al., 1996; Lugo et al., 2003; Gillies et al., 1999; Grogan et al., 2008; Kammesheidt et al., 2001) to estimate the total number of Mahogany trees in the world. The total crown size was calculated using the equation provided by a pioneering study by Gullison et al. (1996), assuming the median diameter at breast height (DBH) to be 80cm in forests. This was multiplied by leaf area index (LAI) (Jhou et al., 2017) to obtain the leaf area. For plantations where density was unavailable, the plantation area was multiplied by LAI to obtain the leaf area. The annual fluxes were calculated assuming six months of reproductive and vegetative phase each, and the average measured fluxes normalized to leaf area obtained in our study for each of these phases. The Table lists both natural and plantation area cover for Mahogany, and it can be seen that Brazil and several other regions in South America stand out with Brazil alone having more than 1.4 million square kilometres of Mahogany tree cover. In terms of large planted tree areas, several regions in Asia such as Indonesia and the Philippines stand out. We would like to point out that this list is by no means comprehensive and there may be many more areas from where data are not currently available but where Mahogany trees are being cultivated on large scales for the wood industry or as natural forest reserves such as the Jim Corbett national park in India. The list is nonetheless useful to identify regions where the influence of DMS and monoterpane emissions from Mahogany are important to consider for regional air quality and climate, through aerosol and oxidant chemistry feedbacks. In this context, recent ecosystem scale DMS emissions reported over the rainforest in South America (Jardine et al., 2015) could
indeed be partially explained by the contribution of DMS emissions from Mahogany growing in the rainforest and surrounding areas. Further, high monoterpane and DMS emissions from Mahogany would also contribute through the formation of aerosol particles. Our estimates indicate global yearly DMS emissions of 370-550 Mg from Mahogany alone. Further, as the cultivation of Mahogany is gaining popularity in southern Asia and are already significant in Indonesia and Fiji due to huge plantations, focused studies on the regional impact of these plantations through BVOC feedbacks to climate and air quality are warranted. Based on results obtained in this study, *Swietenia macrophylla* is estimated to also emit 210-320 Gg yr\(^{-1}\) of monoterpenes globally, with most of the emissions concentrated in specific regions of South America, Asia, and North America. The total isoprene emission flux does not seem to be of much consequence for the global budget of isoprene as it amounted to only 2600 Mg yr\(^{-1}\) but could still be of significance regionally as a dominant isoprene source, and require further investigations.

### 4 Conclusions

In this study, BVOC emissions of monoterpenes, isoprene and DMS were determined in four different seasons at branch level from *Swietenia macrophylla* King (also called big leaf Mahogany) growing in their natural outdoor environment in India. The emissions were characterized in terms of environmental response functions such as temperature, radiation and physiological growth phases. Branch level measurements revealed remarkably high emissions of DMS (average in post monsoon: \(~19\) ng/g leaf dry weight/hr) relative to previous known tree DMS emissions, high monoterpenes (average in monsoon: \(~15\) µg/g leaf dry weight/hr which are comparable to high emitters such as oak trees) and low emissions of isoprene (< 0.09 µg/g leaf dry weight/hr). Distinct linear relationships were observed between cumulative BVOC emissions and the cumulative assimilated carbon with higher emissions during the reproductive phase (monsoon and post-monsoon seasons) and lower emissions in the vegetative phase (summer and winter seasons) for the same amount of cumulative assimilated carbon. Temperature and PAR dependency of the BVOC emissions enabled formulation of a new parametrization that can be employed in global BVOC emission models. Using the measured seasonal fluxes, we provide the first global emission estimates from Mahogany trees of circa 210-320 Gg yr\(^{-1}\) for monoterpenes, 370-550 Mg yr\(^{-1}\) for DMS and 1700-2600 Mg yr\(^{-1}\) for isoprene. Since Mahogany has a large vegetation cover in the Mesoamerican forests and is gaining popularity in South Asia due to its economic significance, large-scale emissions through land use land cover changes from this species could have a significant impact on local and regional atmospheric chemistry. Finally, through the results obtained in this study, we have been able to discover and identify Mahogany as one of the missing natural sources of ambient DMS over the Amazon rainforest as well. These new emission findings, seasonal patterns, and estimates will be useful for initiating new studies to further improve the global BVOC terrestrial budget.
Data availability. Data is available from the corresponding author upon request

Author contributions. V.S. and B.S. conceived and designed the study. L.V. carried out this work as part of his MS thesis under the supervision of V.S.. L.V. performed PTR-MS measurements with help from H.H. and carried out preliminary analysis and wrote the first draft. V.S. revised the paper and carried out advanced analyses and interpretation of the data and supervised all experimental aspects of the work. S.D., A.K., H.H. and P.Y. contributed to the plant cuvette sampling experiments and CRDS measurements. B.S. commented on the revised draft and helped with compilation of Table 3.

Competing interests. The authors have no competing interests to declare.

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Sinha, V., Kumar, V., and Sarkar, C.: Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new air quality facility and PTR-MS: high surface ozone and strong influence of biomass burning, Atmospheric Chemistry and Physics, 14, 5921-5941, 10.5194/acp-14-5921-2014, 2014.


Figure 1: BVOC emission fluxes along with PAR and temperature. (expressed in nanomols or picomols per leaf area per second).
R: Reproductive growth phase V: Vegetative growth phase.
Figure 2: Cumulative BVOC fluxes versus cumulative CO$_2$ assimilation, (b) 3-D plot showing the correlation of the fluxes with instantaneous chamber temperature and PAR for vegetative growth phase and (c) Modeled versus measured VOC fluxes using parameterization presented in Table 2.

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Table 1. Average seasonal BVOCs fluxes from big-leaf Mahogany in different seasons normalized to the leaf dry weight

<table>
<thead>
<tr>
<th>Season</th>
<th>Monoterpene $\mu$g/g/hr</th>
<th>Isoprene $\mu$g/g/hr</th>
<th>DMS ng/g/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer-Avg</td>
<td>6.82</td>
<td>0.06</td>
<td>19.16</td>
</tr>
<tr>
<td>Monsoon-Avg</td>
<td>14.65</td>
<td>0.09</td>
<td>17.06</td>
</tr>
<tr>
<td>Post-monsoon-Avg</td>
<td>7.84</td>
<td>0.09</td>
<td>18.80</td>
</tr>
<tr>
<td>Winter-Avg</td>
<td>2.23</td>
<td>0.02</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Table 2. Bivariate fit functions and their coefficients for BVOC flux parameterizations as function of PAR and temperature in both the reproductive and vegetative phases of Mahogany

<table>
<thead>
<tr>
<th></th>
<th>Vegetative phase modeling fn: $f(T,PAR) = a \times \exp(b \times PAR) + c \times \exp(d \times T)$</th>
<th>Reproductive phase modeling fn: $f(T,PAR) = a \times PAR + b \times \exp(c \times T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoterpenes</td>
<td>$0.14 \quad 0.003 \quad 0.27 \quad 0.10$</td>
<td>$0.009 \quad 0.66 \quad 0.01$</td>
</tr>
<tr>
<td>Isoprene</td>
<td>$0.01 \quad 0.002 \quad 0.000008 \quad 0.20$</td>
<td>$0.0001 \quad 0.003 \quad 0.05$</td>
</tr>
<tr>
<td>DMS</td>
<td>$1.89 \quad 0.00001 \quad 0.02 \quad 0.16$</td>
<td>$0.01 \quad 5.89 \quad 0.01$</td>
</tr>
</tbody>
</table>
Table 3. Distribution of Mahogany in natural forests and in plantations in terms of ground area, tree density, leaf area and calculated annual emission fluxes of monoterpenes, isoprene and DMS.

<table>
<thead>
<tr>
<th>Country</th>
<th>Natural Area (10^4 km²)</th>
<th>Plantation Area (km²)</th>
<th>Tree density^{iii} Natural/Plantation (x100 nos./km²)</th>
<th>Leaf area^{iv} (km²)</th>
<th>Monoterpenes (Gg/yr)</th>
<th>Isoprene (Mg/yr)</th>
<th>DMS (Mg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>139.6</td>
<td>-</td>
<td>0.014-1.17^{ibi}</td>
<td>1564-10756</td>
<td>10-69</td>
<td>82-565</td>
<td>17-119</td>
</tr>
<tr>
<td>Peru</td>
<td>56.5</td>
<td>-</td>
<td>-</td>
<td>9042</td>
<td>58</td>
<td>475</td>
<td>100</td>
</tr>
<tr>
<td>Bolivia</td>
<td>18.9</td>
<td>-</td>
<td>0.1-0.2^{i}/-</td>
<td>1512-3025</td>
<td>9.7-19</td>
<td>79-159</td>
<td>17-33</td>
</tr>
<tr>
<td>Nicaragua</td>
<td>5</td>
<td>-</td>
<td>0.6/-</td>
<td>2400</td>
<td>15</td>
<td>126</td>
<td>27</td>
</tr>
<tr>
<td>Mexico</td>
<td>3.6</td>
<td>-</td>
<td>1.0/-</td>
<td>2881</td>
<td>18</td>
<td>151</td>
<td>32</td>
</tr>
<tr>
<td>Ecuador</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>2801</td>
<td>18</td>
<td>147</td>
<td>31</td>
</tr>
<tr>
<td>Colombia</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>2080</td>
<td>13</td>
<td>109</td>
<td>23</td>
</tr>
<tr>
<td>Guatemala</td>
<td>2.8</td>
<td>-</td>
<td>0.2-2.0/-</td>
<td>448-4480</td>
<td>2.9-29</td>
<td>24-235</td>
<td>4.9-49</td>
</tr>
<tr>
<td>Honduras</td>
<td>1.7</td>
<td>-</td>
<td>2.0/-</td>
<td>2720</td>
<td>17</td>
<td>143</td>
<td>30</td>
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<tr>
<td>Venezuela</td>
<td>1.2</td>
<td>-</td>
<td>1.0^{d}/-</td>
<td>960</td>
<td>6.1</td>
<td>50</td>
<td>11</td>
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<tr>
<td>Panama</td>
<td>1</td>
<td>-</td>
<td>0.1/-</td>
<td>80</td>
<td>0.5</td>
<td>4.2</td>
<td>0.88</td>
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<tr>
<td>Belize</td>
<td>1</td>
<td>5.91</td>
<td>1.0-2.5/119-288^{e}</td>
<td>825-2061</td>
<td>5.3-13</td>
<td>43-108</td>
<td>9.1-23</td>
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<tr>
<td>Costa Rica</td>
<td>0.3</td>
<td>-</td>
<td>0.5-2.5/-</td>
<td>120-600</td>
<td>0.77-3.8</td>
<td>6.3-32</td>
<td>1.3-6.6</td>
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<tr>
<td>Indonesia</td>
<td>-</td>
<td>1160</td>
<td>-</td>
<td>3410</td>
<td>22</td>
<td>179</td>
<td>38</td>
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<tr>
<td>Fiji</td>
<td>-</td>
<td>420</td>
<td>-</td>
<td>1235</td>
<td>7.9</td>
<td>65</td>
<td>14</td>
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<tr>
<td>Philippines</td>
<td>-</td>
<td>250</td>
<td>-</td>
<td>735</td>
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<td>8</td>
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<tr>
<td>Sri Lanka</td>
<td>-</td>
<td>45</td>
<td>-</td>
<td>132</td>
<td>0.85</td>
<td>6.9</td>
<td>1.5</td>
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<tr>
<td>Guadeloupe</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>118</td>
<td>0.75</td>
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<td>1.3</td>
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<tr>
<td>Martinique</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>44</td>
<td>0.28</td>
<td>2.3</td>
<td>0.49</td>
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<tr>
<td>Puerto Rico</td>
<td>-</td>
<td>13.81</td>
<td>-/66.7-200^{e}</td>
<td>33-99</td>
<td>0.21-0.64</td>
<td>1.8-5.2</td>
<td>0.37-1.1</td>
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<tr>
<td>Kerala, India</td>
<td>-</td>
<td>1.7^{e}</td>
<td>-</td>
<td>5</td>
<td>0.03</td>
<td>0.26</td>
<td>0.06</td>
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<tr>
<td>Honduras</td>
<td>-</td>
<td>1.50</td>
<td>-</td>
<td>4</td>
<td>0.03</td>
<td>0.23</td>
<td>0.05</td>
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<tr>
<td>St. Lucia</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
<td>3</td>
<td>0.02</td>
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<td>TOTAL</td>
<td>237.7</td>
<td>1953.92</td>
<td>33154-49674</td>
<td>212-317</td>
<td>1740-2607</td>
<td>366-548</td>
<td></td>
</tr>
</tbody>
</table>

1^Blundell (2004), 2^Lugo et al. (2003), 3^Gillies et al. (1999), 4^Mohandas (2000), 5^Grogan et al. (2008), 6^Gullison et al. (1996), 7^Kammasheidt et al. (2001);
5 Leaf Area Index: 2.94 (Jhou et al., 2017)
Crown radius (m)= 0.139 x diameter (cm) - 2.82 x 10^-4 x [diameter (cm)]^2, r^2 = 0.97 (Gullison et al., 1996)