



## Supplement of

## Significant emissions of dimethyl sulfide and monoterpenes by big-leaf mahogany trees: discovery of a missing dimethyl sulfide source to the atmospheric environment

Lejish Vettikkat et al.

Correspondence to: Vinayak Sinha (vsinha@iisermohali.ac.in)

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Figure S1: Schematic of the dynamic branch cuvette setup. Offline canister collection scheme is depicted in the dashed rectangle. MFC: mass flow controller. PTR-MS: proton transfer reaction mass spectrometry. CRDS: cavity ring-down spectroscopy. PAR: photosynthetically active radiation.



Figure S2: Results of calibration experiments performed on 4 May 2018 and 4 October 2018 for DMS, isoprene and  $\alpha$ -pinene illustrating the excellent linearity and low drift in the sensitivity of the PTR-MS for these compounds

- 5 The instrument was calibrated at least four times during the period of study on 4 May, 4 October, 14 November 2018 and 22 January 2019 at different humidities (~ 40 % RH, 60 % RH and 70% RH) using a VOC standard (Apel-Riemer Environmental, Inc., Colorado, USA) by dynamic dilution with zero air at four different mixing ratios (in the range of 2–20 ppbv) for each VOC. The measured m/z ion signals in counts per second (cps)  $(I_{R_lH^+})$  for each VOC was converted to normalized cps (ncps) with respect to the sum of reagent H<sub>3</sub>O<sup>+</sup> ion signal  $(I_{H_3 O^+})$  and the first water cluster H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O) signal  $(I_{H_3 O^+(H2O)})$  using the
- 10 following normalization equation:

$$ncps = \frac{I_{R_iH^+} \times 10^6}{I_{H_3 0^+} + I_{H_3 0^+(H20)}} \times \frac{2}{p_{drift}} \times \frac{T_{drift}}{298.15}$$

The normalized counts per second (ncps) thus calculated was corrected for dilution using zero air using the equation (2):  $ncps \times Total \ flow = (ncps_{zero} \times Zero \ air \ flow) + (ncps_q \times Standard \ gas \ flow)$  (1)

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$$ncps_g = \frac{(ncps \times Total flow) - (ncps_{zero} \times Zero air flow)}{Standard gas flow} \quad (2)$$

These ncps corrected for dilution (ncps<sub>g</sub>) were converted to sensitivity (ncps/ppb) by plotting it in y-axis with the introduced concentration of gas standard of each VOC in x-axis. The slope of the graph yielded the sensitivity factor for each VOC which was then used to calculate the mixing ratio (in ppb) from the measured counts per second of each VOC. The standard deviation in ncps<sub>g</sub> along with the error in the flows during calibration gives the uncertainty of each VOC measurement. The percentage instrumental uncertainty was then calculated using the root mean square propagation of individual uncertainties like the 5% accuracy error inherent in the VOC gas standard concentration, the 2σ instrumental precision error while sampling 10 ppbv of the VOC and error in the flow reproducibility (2%) of the two mass flow controllers.

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The overall uncertainty in fluxes was calculated by propagating the error in each term in the flux calculation formula and the drift in sensitivity:

$$EF = \frac{m_{out} - m_{in}}{V_m} \times \frac{Q}{A}$$
(1)

where, EF is the emission flux,  $m_{out} - m_{in}$  is the difference in mixing ratios of the BVOC between input and output air, Q is

20 the flow rate of air passing through the cuvette system in  $m^3 s^{-1}$ ,  $V_m$  is the molar volume of gas calculated using the cuvette temperature and ideal gas law.

Following are the major steps in calculating the overall uncertainty of fluxes:

Step 1: Let the error in measurement of  $m_{out}$  and  $m_{in}$  be  $s_{out}$  and  $s_{in}$  respectively. Since the percentage uncertainties associated with measurement of  $m_{out}$  and  $m_{in}$  are equal, we can say that  $\frac{s_{out}}{m_{out}} = \frac{s_{in}}{m_{in}}$ .

25 Step 2. Uncertainty in measurement of BVOC of difference of input and output air from cuvette.

Let, 
$$y = m_{out} - m_{in}$$
,  $s_y = \sqrt{s_{out}^2 + s_{in}^2}$  (2)

Since we have percentage uncertainties instead of individual absolute uncertainties,  $s_y$  can be written as:

$$s_{y} = \sqrt{m_{out}^{2} \left(\frac{s_{out}}{m_{out}}\right)^{2} + m_{in}^{2} \left(\frac{s_{in}}{m_{in}}\right)^{2}} = \sqrt{(m_{out}^{2} + m_{in}^{2}) \left(\frac{s_{out}}{m_{out}}\right)^{2}} = \sqrt{(m_{out}^{2} + m_{in}^{2}) \frac{s_{out}}{m_{out}}}$$
(3)

Further simplifying equation (3) we obtain that the maximum relative uncertainty (if  $m_{out} = m_{in}$ ) as: Therefore the maximum uncertainty (if  $m_{out} = m_{in}$ ) is given as:

$$s_{y} = \sqrt{2} m_{out}$$
(4)

$$\frac{s_y}{y} = \sqrt{2} \frac{s_{out}}{m_{out}}$$
(5)

In the case of plant chamber experiments,  $m_{out} \gg m_{in}$ , therefore the maximum uncertainty in difference (y) is 1.4 times the instrumental uncertainty,  $\frac{s_{out}}{m_{out}}$ .

5 Step 3: Now since the equation (1) contains only products and quotients to calculate the propagation of error,

$$\frac{\mathbf{S}_{\rm EF}}{\mathrm{EF}} = \sqrt{\left(\frac{\mathbf{S}_{\rm y}}{\mathrm{y}}\right)^2 + \left(\frac{\mathbf{S}_{\rm Q}}{\mathrm{Q}}\right)^2 + \left(\frac{\mathbf{S}_{\rm Vm}}{\mathrm{V}_{\rm m}}\right)^2 + \left(\frac{\mathbf{S}_{\rm A}}{\mathrm{A}}\right)^2 + \left(\frac{\mathbf{S}_{\rm D}}{\mathrm{D}}\right)^2} \tag{6}$$

We substitute for Eq. (5) with Eq. (4) and by the propagation of individual uncertainties like 2% error in the flow measurement of MFC: (EL-FLOW; Bronkhorst High-Tech), 1.67% error in the leaf area measurement (Easy Leaf Area doi: 10.3732/apps.1400033), uncertainty of molar volume calculation: <1 % (molar volume is calculated theoretically using ideal gas law) and percentage drift in sensitivity (d).

$$\frac{s_{\rm EF}}{\rm EF}(\%) = \sqrt{\left(1.4 \times \text{instrumental uncertainty } (\%)\right)^2 + 2^2 + 1 + 1.67^2 + d^2}$$
(7)

15 For example, to calculate the total measurement uncertainty (%) in emission fluxes of DMS, isoprene and sum of monoterpenes during post-monsoon, we substitute the instrumental uncertainty in mixing ratio and percentage drift in sensitivity of PTR-MS for these 3 compounds (DMS < 3.8%; isoprene < 4.1 % and alpha-pinene < 6.1 %) obtained from calibration experiments conducted on 4 May 2018 and 4 October 2018 in Eq. (7).

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$$DMS, \frac{S_{EF}}{EF} (\%) = \sqrt{8.9^2 + 4 + 1 + 1.67^2 + 3.8^2} = 13\%$$

*Isoprene*, 
$$\frac{S_{EF}}{EF}$$
 (%) =  $\sqrt{8.9^2 + 4 + 1 + 1.67^2 + 4.1^2} = 13$  %

Monoterpenes, 
$$\frac{s_{\rm EF}}{{\rm EF}}$$
 (%) =  $\sqrt{9.9^2 + 4 + 1 + 1.67^2 + 6.1^2} = 12 \%$ 

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The total uncertainty in emissions flux measurements, while not being able to correct between 4 May and 4 October (which spans over 5 months including monsoon season) with new sensitivity, is less than equal to 13% for all the reported VOCs. Thus the calculated total measurement uncertainty can be considered as the upper limit for monsoon season as well.



Figure S3: A typical 30 min averaged PTR-MS mass scan of the output air from the branch cuvette system during the afternoon period after subtraction of input background air signals showing the ion signals observed in the mass range m/z 40 to 210.



Figure S4 (a): Correlation of m/z 63 ion signal with m/z 45 ion signal for all seasons.



Figure S4 (b): 30 min averaged PTR-MS mass scan of the output air from the branch cuvette system during the afternoon period on 22.05.2018 of m/z 63, 64 and 65; error bars reflect combined instrumental precision error and emission variability.

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Below we show the chromatographic peak for isoprene from the output air of the branch cuvette system identified based on the retention time of isoprene vapours that were sampled under identical operating conditions with the TD-GC-FID. The isoprene data co-measured with the TD-GC-FID for the monsoon season along with the isoprene data measured with the PTR-MS was found to have an excellent correlation of the PTR-MS isoprene signal but the absolute values were much lower due

10 to the suspected losses within the TD-GC-FID system.

## Isoprene measurements by Thermal Desorption-Gas Chromatography-Flame Ionization Detector (TD-GC-FID):

Isoprene was detected in output air from the branch cuvette using a gas chromatograph equipped with a flame ionization

- 5 detector (GC-FID 7890B, Agilent Technologies, Santa Clara, United States) which is coupled to a thermal desorption unit (CIA Advantage-HL and Unity 2, Markes International, UK) for sampling and pre-concentration. Water in the sample air was removed using a Nafion dryer which also removed the oxygenated VOCs such as alcohols, aldehydes and ketones (Badol et al., 2004; Gros et al., 2011). 1000 ml of dry sample air was then pre-concentrated at -30°C at 20 ml min<sup>-1</sup> on an ozone precursor trap (U-T17O3P-2S, Markes Internatioal, UK) which was then thermally desorbed by rapid heating to 325°C. The desorbed
- 10 analytes were then transferred onto the GC instrument via a heated inlet (130°C) line. The GC instrument consisted of a capillary column (Alumina PLOT, Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub>, 50 m x 0.32 mm, 8 μm film thickness, Agilent Technologies, Santa Clara, United States). The oven temperature was ramped from 30°C (hold for 12 min) to 200°C at the rates of 5°C min<sup>-1</sup> (upto 170°C) and 15°C min<sup>-1</sup> (upto 200°C) for resolving the peaks.
- Isoprene was resolved on Alumina PLOT column at a retention time of 37.5 min and identified based on the retention time of isoprene vapours injected into the TD-GC-FID system under identical instrument operational conditions as the sample. The eluted isoprene was then detected using the FID. Unfortunately, due to the suspected transfer losses within the GC system, which could not be corrected, the data is only semi-quantitative and hence reported in arbitrary units.





Figure S5: Sample chromatogram of the isoprene peak resolved on the Alumina PLOT column at a retention time of 37.5 min in the air collected from the plant chamber experiment overlayed with the peak from pure isoprene vapours injected to determine the retention time of isoprene.



Figure S6: Times series of hourly averaged isoprene measurements from PTR-MS and TD-GC-FID for monsoon season.



Figure S7: Correlation of isoprene data measured with PTR-MS and TD-GC-FID for monsoon season.



Figure S8: Correlation between observed m/z 81 and 137 signals from the plant chamber output air for all seasons.



Figure S9: Time series of BVOC mixing ratios (hourly averages) with the corresponding background mixing ratios in nmol mol<sup>-1</sup>. Background mixing ratios are shown as a dotted line.



Figure S10: Wintertime BVOC emission fluxes along with PAR and temperature. (expressed in nanomols or picomols per leaf area per second). Blue shaded region marks rain event.



Figure S11: Time series of wintertime BVOC mixing ratios observed for Trees 2, 3 and 4 with the corresponding background mixing ratios in nmol mol-1 Background mixing ratios are shown as a dotted line. Blue shaded region marks a rain event.

Season	Leaf area (m <sup>2</sup> )	Leaf dry weight (g)	g/m <sup>2</sup>
Summer	0.3	30.1	96.1
Monsoon	0.3	28.2	82.8
Post-monsoon	0.2	20.5	109.4
Winter	0.2	26.8	135.3
Winter (2)	0.3	27.3	102.3
Winter (3)	0.2	31.7	138.9
Winter-Offline	0.3	36.1	139.8

Table S1. Leaf area and leaf dry weight inside the cuvette during all the experiments.

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15 Table S2: Details of the VOC gas standard (Apel–Riemer Environmental Inc., Colorado, USA) used in the calibration experiments.

Compound	Mixing ratio in VOC standard (ppb);Stated accuracy 5%		
Methanol	503		
Acetonitrile	491		
Methyl vinyl ketone	479		
Methyl ethyl ketone	497		
Acetaldehyde	490		
Acetone	493		
DMS	495		
Isoprene	483		
Benzene	492		
Toluene	468		
p-Xylene	477		
α-pinene	494		
1,2,4-Trimethylbenzene	510		

Table S3: Sensitivity factor, limit of detection, instrumental uncertainty and overall uncertainty of measured VOCs from calibration experiments conducted on 4 May 2018 and 4 October 2018.

Calibration performed date (RH)	VOC	Sensitivity factor (ncps ppb <sup>-1</sup> )	Limit of detection (ppb) <sup>a</sup>	Instrumental uncertainty (%)	Overall uncertainty (%)
04.05.2018 (40%)	DMS	$10.77\pm0.14$	0.06	6	10
	Isoprene	$7.27\pm0.13$	0.10	6	10
	Monoterpenes	$8.21\pm0.13$	0.07	7	12
04.10.2018 (70%)	DMS	$10.42\pm0.21$	0.12	6	13
	Isoprene	$7.01\pm0.07$	0.04	6	13
	Monoterpenes	$7.67\pm0.05$	0.07	7	12

 $^{a}$  The limit of detection is defined as  $2\sigma$  of the measured normalized signal while measuring zero air (99.999% purity; Sigma gases, New Delhi) divided by the sensitivity.

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