

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

This manuscript presents 24 (+6 in SI) days of measurements of monoterpene, isoprene and DMS emissions from Mahogany in India. The measurements were conducted using a PTR-Quad and a dynamic branch chamber. The results were compared with modelled emissions and then globally upscaled. The measurements identify Mahogany as one of the missing sources of DMS in the rainforest.

The presented data is novel and even though isoprene and monoterpene emission measurements are more and more common, DMS emission measurements are rare. Therefore I see the result as interesting for the scientific community and recommend the paper to be accepted.

However, I would like that the Authors addressed following comments before publication:

- One major flaw in the manuscript is the missing discussion about the challenges when measuring DMS (and isoprene). Even though the authors have cited literature (de Gouw et al., 2006; Jardine et al., 2015) which extensively discuss the problem of acetaldehyde clusters' possible influence on mass 63, there is no evidence in this manuscript that this influence was ruled out. Even though, Jardine et al. (2015) stated that in their setup no influence could be seen, their instrumental settings seemed to have been optimized to suppress waterclusters ( $\frac{H_2O \cdot H_3O^+}{H_3O^+} < 4\%$ ; E/N > 145 -> please see my comment P6 L13).  
There is a sentence (P6 L10-16) stating that isoprene and DMS can be measured at their respective masses without much fragmentation, which is true. As long as the PTR-MS is frequently calibrated under measurement conditions, fragmentation losses (of e.g. isoprene or DMS) are corrected by the sensitivity (this is just the case if the measured and calibrated compound are identical and the signal is above the limit of detection). However, other compounds fragmenting/clustering on the same mass (e.g. M69, M63) are a major source of uncertainty. And therefore identifying/ruling out a possible influence of acetaldehyde to the DMS signal (M63) is crucial. There is a similar issue with MBO, which fragments to M69.
- It is not very clear when the offline sampling was used. The only references to the offline sampling are in the methods part and in the SI. I concluded, that all data used in the main manuscript were online. Therefore, I would recommend, moving the description of the offline sampling to the SI.
- P2 L6-8 (also P3 L20-22): Please rephrase (South, Central and North America -> Americas; atmospheric environments -> environments).
- Refer from using the word 'fluxes' (= bidirectional) when you discuss your measurements. As your setup cannot capture deposition, use the word 'emissions' instead (e.g. P4 L2, P4 L5, P6 L28, P6 L31,...)
- P4 L6-8: The number of measurements sounds impressive, however it is not clear what those measurements are. Is a measurement the measured 1 s dwell time data point? Is it one cycle through all measured compounds? ... If the authors want to state the amount of data at all, I would suggest to state the number of 1 h data points, shown e.g. in Fig. 1.
- P4 L9: Omit outdoor (there is no natural indoor environment for Mahogany, I assume).

- P4 L29: ... *using a series of traps containing steel wool, silica gel and activated charcoal*. If those traps were custom build, please state so, otherwise please add the type and brand (this information can be very helpful for people who want to use a similar setup).
- P5 L2: ... *using a second pump by ensuring to have a small positive pressure inside the chamber*...How was this positive pressure achieved (by regulating the flow with a MFC or does this pump have a flow lower than 30 L min<sup>-1</sup>) and how large was the flow flushing the 60-65 m inlet line?
- P5 L8: *This is significantly longer than the steady-state* ... this statement is correct, however, after installing the chamber a longer equilibration time is necessary to prevent measurement artefacts of physical stress or small injuries of the branch (caused by the installation of the cuvette).
- P6 L6: ...*dwelt time of 1 s at each m/z channel*. Which channels were measured (stated are M63, M69, M81, M137, however I assume also instrumental background peaks (e.g. M21, M25, M32, M45, M39, M87) were measured for quality assessment) and what was the measurement cycle time (or what was the sampling frequency)?
- P6 L8: Please state the compounds in the calibration gas, as well as the uncertainty of the calibration gas. Furthermore please state average sensitivities with standard deviation and limit of detection (concentration and emission) for the main compounds (Isoprene, DMS and the calibrated monoterpene compound).
- P6 L9: *The total measurement uncertainty was less than 10% for isoprene and DMS and less than 15% for the sum of monoterpenes* ...This low uncertainty seems for me very optimistic for the used setup, especially after addressing my first comment. If I remember correctly the calibration gas from Appel-Riemer has an uncertainty of 5% (valid for 1 year after filling of the gas bottle), then adding uncertainties for 3 MFCs (1 for the inlet at the chamber, 2 for calibration, I assume), 60 – 65 m of tubing, an extra pump, as well as only 1 calibration per season (up to 20 days before measurements). Could the authors please provide the uncertainty calculations for those numbers? Also, are the same values valid for the offline sampling?
- P6 L13: I could not find any statement about the used E/N in Jardine et al. (2015). However, from the stated values in their paper ( $p_{\text{drift}}= 2.0$  mbar,  $V_{\text{drift}}= 600$  V) it seems to be either 145 Td (if the drift temperature was 50°C, like their heated inlet) or 149 Td (if the drift temperature was the more common 60°C). Therefore, their measurements did not fall under the standard operational conditions between 130 and 135 Td. Could the authors please provide average and maximum  $\frac{H_2O \cdot H_3O^+}{H_3O^+}$  ratios during this measurement campaign (i.e. was it comparable with the 4% in Jardine et al., 2015)?
- P6 L17: Also state the used drift voltage.
- P7 L3-4: Please add that this statement is valid for winter, as below it is stated that *photosynthetically fixed carbon* (normally associated with PAR) *may be more important than emissions from storage pools* (normally associated with T).
- P7 L20: Remove the space in the hyperlink (...ac.uk\cnhgroup...)
- P7 L29: Add the year to the Jardine et al. citation.
- P8 L24-25: *It is also evident that DMS has a strong dependence on temperature, but not on PAR*. The PAR dependency is very hard to see in Fig 2(b). It seems to me quite difficult to state anything about DMS, as there is a rather high offset at low PAR and T (it seems that temperature has no effect at low PAR), there is a huge decline at high T when PAR is around 500  $\mu\text{mol m}^{-2} \text{s}^{-1}$ .
- P10 L12: Omit outdoor (see earlier comment).

- P14 Figure 1: It seems the PAR axis label has a different color than the PAR graph, please use the same color.
- P15 Figure 2:
  - o (a) Please provide the slopes for the linear fits
  - o (b) Sadly, these plots are not very clear. They give an idea of the temperature dependence, however, the PAR dependence cannot be seen. I recommend either turning these 3D plots to have the origin (0-point) at the bottom middle and PAR and T axis going with the same angles left and right (=symmetrical) or changing the plot style altogether. Depending on the changes, please state in the figure caption that the color corresponds to the respective VOC flux. Also to make that more obvious, the color bars could be stretched to cover the whole axis (then maybe one set of axis labels would be enough).
  - o (c) Here I would recommend changing all y axes labels to Modeled flux (with respective unit) and state the compound as a title (centered above each plot)
- P16 Table 2: I recommend renaming the variables in the *Reproductive phase modeling fn*:  $f(T, PAR) = a * PAR + c * \exp(d * T)$  to make it easier to compare to the vegetative phase modeling fn.
- P17 Table 3: ( $\times 100 \text{ nos./km}^2$ ); Please use 100 (or  $10^2$ ) if  $\times 100$  is a multiplication, similar as in the second column in this table. Please clarify 'nos.' Is it a unit? If so, please explain it in the table caption.
- PS2 Figure S1: The offline canister sampling is twice in your schematic (once at the KNF pump2 and once behind it). Normally the tubing is marked by 2 lines (e.g. between MFC and Tedlar bag), however right before the instruments it changes to normal arrows, please use only one style.
- PS3 & 5, Figure S3 & S5: The figure caption seems to be wrong, as it says that BVOC emissions are shown, but the y axis unit is ppb. Assumingly it should state Time series of BVOC concentrations in the chamber with corresponding... (in case there are actually emissions shown, please calculate background emissions and change the label).
- PS4 & 5, Figure S4 & S5: As there is no reference in the main manuscript to these figures, could you please provide some context to the figures.

Technical:

(see: [https://www.atmospheric-chemistry-and-physics.net/for\\_authors/manuscript\\_preparation.html](https://www.atmospheric-chemistry-and-physics.net/for_authors/manuscript_preparation.html))

Use SI units (e.g. P4 L19: change to metric)

[For units of **physical quantities**, the metric system is mandatory and, wherever possible, SI units should be used.]

State the inner diameters of tubing (instead of outer diameters), as those are the crucial parameters for volume, residence time, line losses.

Follow the recommendations of the journal for the format of your units (e.g. P2 L13&14, P5 L1,...)

[Regarding the **notation**, if units of physical quantities are in the denominator, contain numbers, and are abbreviated, they must be formatted with negative exponents (e.g.  $10 \text{ km h}^{-1}$  instead of  $10 \text{ km/h}$ )]

Unify the way you state instruments (often type, company, country are stated, sometimes not; e.g. P4 L13, P4 L25, P5 L1, P5 L5,...)

Please use either L or l for the unit of liter (e.g. P5 L1, P5 L15,...)

Sometimes spaces are missing between values and units (e.g. P4 L15,P9 L21,... )