Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-489-RC1, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "High DMS and monoterpene emitting big leaf Mahogany trees: discovery of a missing DMS source to the atmospheric environment" *by* Lejish Vettikkat et al.

Anonymous Referee #1

Received and published: 3 July 2019

General comments:

This paper reports high volatile emissions from the big leaf Mahogany trees. Specifically, the authors have observed high emissions of volatiles identified as DMS and monoterpenes, and low from isoprene. By means of seasonal measurements, the authors describe the emissions as a function of environmental response such as temperature, radiation, and physiological growth phases and study the relationships with net assimilation. Using the seasonal fluxes, the authors provide the first global estimation of BVOC emissions from Mahogany trees and state that this tree-species is one of

the missing natural sources of ambient DMS over the Amazon rainforest. Overall, the subjects addressed in the manuscript are appropriate for ACP. However, I have some serious concerns concerning reproducibility and chemical identification that needs to be addressed. Please see my specific questions below.

Specific comments:

1) Number of biological replicates: The number of biological replicates (i.e. number of trees) is unclear. The authors state that they have used 4 different trees (P4L8). However, only one (n=1) was used for inter-seasonal variability (Figure 1). From the remaining 3 trees, 2 of them were measured "at high temporal resolution" online (P4L16) and 1 was sampled for "offline analysis". Overall, the biological variability of BVOC emissions is never given, and which data is presented in figure 1 and table 1-2. Please provide the variance of data dispersion of the BVOC emission based on either standard error or standard deviations (see also further comments later on).

2) Chemical identification of BVOCs: This is largely uncertain especially for isoprene and DMS. The chemical identification of VOC requires special attention, in particular for uncharacterized tree species and when measurements are based only on PTR-MS. Especially for DMS, the key compound of the actual paper, more evidence should be provided. First of all, there is little and sometimes unclear evidence of DMS emissions from trees. Second of all, a chemical identification based on PTR-QMS (Q: quadrupole), with $\sim$ 1 amu mass resolution is too little to certainly say that the volatile measured at m/z 63 is DMS. For instance, m/z 63 might originate from several VOCs, including those at MW $\sim$62g/mol or larger but fragmenting down to m/z 63. Some examples are the related dimethyl disulfide (CH3SSCH3, DMDS), and dimethyl trisulfide (CH3SSSCH3, DMTS), but possible any large compounds that fragment at m/z 63. Similarly, m/z 69 can be other than isoprene, for instance, alkyl aldehydes such as pentanal, octanal, nonanal, decanal, etc. I personally think that a large amount of m/z 137 from plants is likely to be monoterpene, so here the result is, in my opinion, reasonable because it is extremely unlikely the large emission of other unknown biogenic volatiles

at m/z 137. Although the gold technique for VOC identification remains GC-MS, VOC might be convincingly identified using PTR-MS technology by proper additional fragmentation study, or isotopic pattern simulation study, or switching the reagent ion for VOC ionization.

3) Estimation of the global annual emission of BVOCs from Mahogany: This part is very interesting but there is a fundamental contradiction. The authors state that the biomass data available (global distribution of Mahogany trees) is "by no means comprehensive" P9L27-31. So, it is unclear why the global BVOC estimations are then "meaningful".

4) Overall there is a lack of statistical analysis. When comparing the temperature and light intensities of the different season, are those significantly different? And the corresponding BVOC emissions? These and further data should be supported by appropriate statistical analysis.

5) Relative humidity: it is necessary for the reader to see the humidity data along with figure 1, essential when comparing Monsoon with post-Monsoon data.

6) Seasonality: To describe inter-seasonal variability of BVOC emissions, the authors seem to have used one single tree (n=1). This is not scientifically acceptable. It is unclear how reproducible the experiment is and what is the intra-species variance of BVOC emissions. Either the experiments are performed with more replicates (at least n=3), or the data should be removed from the manuscript.

7) Seasonality: to describe the seasonal change of BVOC emissions, the authors have performed the measurements during summer, fall (during and post-monsoon) and winter. Why did they not consider spring? The tree phenology strongly changes in spring, which is known as an important player in changing the seasonality of BVOC emissions (e.g. (Fischbach et al., 2002; Noe et al., 2012; Grote et al., 2014; Vanhatalo et al., 2018).

8) Seasonality: I find two days of measurements of one unique tree, not representative

for describing seasonal emission during summer.

9) Methods: it appears that the authors did not make any background correction using empty cuvette. To correctly calculate the BVOC fluxes, background measurements are necessary for taking into account the chemical noise of the cuvette system. However, this point does not seem to be critical since the emissions go to nearly zero during the night. However, data should be corrected before publication.

10) Table1: what are the variability of the data?

11) Table1: In the last column, what do "5" and "10" refer to?

12) Table2: why the function is different between "vegetative" and "reproductive" phase? This makes the comparison difficult. And what it the working hypothesis behind the use of these 2 functions? If available, please cite relevant literature. Overall the rationale is not described.

13) It is unclear the calibration procedure used for VOC quantification. Which molecules have been used for the calibration of the PTRMS? Was the standard mixture passing throughout the whole cuvette and canister system during calibration? If the authors have calculated the compounds-specific sensitivities, why did they sum up m/z 81+137 for monoterpene measurements?

14) M/z 81 originate also from other compounds, in particular, LOX products and sesquiterpenes. Can the authors show the correlation between 81 and 137 to rule out that other VOC were included as monoterpenes? Alternatively, the quantification should be based using only the parent ion (i.e. m/z 137).

Technical corrections:

P5L3: How long were the Teflon tubing between cuvette and sampling? Fig1: "nmol/m2 s" should be "nmol m-2 s-1" Fig2: each individual subplot should be named (e.g. (a), (b), etc...) Fig2: the unit of light intensity is missing Fig2: please give slopes and intercepts for the linear regressions in the first raw of subplots. Fig2 legend: please add

here the time period of the cumulative BVOC flux and assimilation. P4L6-10: please remove the number of measurements, since this information is misleading. P4L26: please describe the leafage. P5: “The input air was sampled at regular interval”. It is unclear when and how often did the authors sample the inlet air. P6L29-30 Are these temperatures statistically different? P6L30-31: Are the light intensities statistically different? P8L31: “paramterization” should be “parameterization”

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Grote R, Morfopoulos C, Niinemets Ü, Sun Z, Keenan TF, Pacifico F, Butler T. 2014. A fully integrated isoprenoid emissions model coupling emissions to photosynthetic characteristics. Plant, Cell and Environment 37: 1965–1980.

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Vanhatalo A, Ghirardo A, Juurola E, Schnitzler JP, Zimmer I, Hellén H, Hakola H, Bäck J. 2018. Long-term dynamics of monoterpene synthase activities, monoterpene storage pools and emissions in boreal Scots pine. Biogeosciences 15: 5047–5060.

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