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Biogeosciences Discussions

Interactive comment on "VOC emissions from dry leaf litter and their dependence on temperature" *by* L. Derendorp et al.

Anonymous Referee #3

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General comments

First of all, let me say that I do not share my fellow reviewers' notions of poor quality of this manuscript. The title is clear, the experiment sufficiently described, its execution reasonable, and the deductions and conclusions made defensible. I see no reason for rejection or even major rewriting apart from shortening. However, there are obviously some questions regarding some of the assumptions made, such as 'no' biotic influences, and regarding relevancy. A lack of clarity in parts of the manuscript may be to blame for the harsh critique by the other reviewers. I suggest to the authors to focus on clarity, stick to what the data clearly tells, and remove speculative statements.<p>

Specific comments

1. There is some confusion between the authors and their audience as to what the terms "precursor" and reservoir mean. The authors may want to elaborate that the 'precursor' is a molecule (pool) on which oxygen "operates" to create the hydrocarbons that are eventually observed outside the leaf litter, in the gas phase, from which they are sampled and analyzed. If this is not their definition, than the elaboration is even more important … In my opinion, the mechanics and thermodynamics of the hydrocarbons' transport after production is entirely irrelevant for this study with the possible exception of comparing intact with ground leaves. I concur with the authors that, based on the trace amounts emitted, the 'precursor' is always available in vast excess. In fact, this is the first time I see a relationship in which emissions "decay" over time suggesting a 'pool depletion' effect. The authors' explanation (exhaustion of the precursor pool) seems straightforward but it may not be so simple. If the authors' used my precursor definition above, then the literature can be consulted to evaluate what the precursor availability ("membrane fatty acids of the plant cells") actually is. My guess is that it will dwarf the measured emissions, aka it does not deplete under the given conditions. If so, the authors' explanation has to be modified, namely such that a multi-step mechanism (with overall activation energy as measured) is likely responsible for hydrocarbon production, in which the rate-limiting step produces that specific intermediate which can be reduced to such low amounts that the emission rate of the terminal product (hydrocarbon) is reduced, as far as below the detection limit … food for thought.

2. I also concur with the authors that the process is (mostly) "abiotic", aka not influenced by microbial activity. Much of the presented data is evident in that respect (material dryness, activation energies, continued increase of emissions beyond 40 deg C). Nevertheless, a measurement of CO_2 production would have been useful in determining whether air-drying was indeed sufficient to eliminate microbial activity under the experimental conditions. My own experience with dry leaf litter is that it is not, aka some activity remains. Whether that is relevant for the measurements made is another question though.

In this respect, I suggest to drastically cut the introduction section and stick to the relevant papers for your study. Your experimental work covers a small niche and ultimately shows the irrelevancy from the atmospheric perspective, hardly justifying the lengthy intro plus some parts of the other sections.

3. I would remove all speculations about hydrocarbon adsorption. While there may have been some relevance of this for VOCs with hydroxyl and carbonyl groups, this is not the case here. Most of the investigated hydrocarbons are permanent gases, which do not significantly adsorb to most surfaces. To verify this, a simple experiment could have been done, fumigating the leaf material at high loads using your calibration gas, and then re-measuring emissions. The authors relied too heavily on Warneke's work, which had its own questionable assumptions.

4. Relevancy: The global emissions estimate, though very small, is likely a large overestimate because: (i) 30 deg C was used to extrapolate, which is hardly an average temperature outside the tropics, (ii) 7E16 g annual biomass decay is a sum value of dry mass for all ecosystems and does not take timing of litter-fall and its microbial decay into account, reducing the availability of the 'precursor' to less than 365 days as a function of ecosystem, and (iii) your experiment likely maximized the abiotic emission flux by minimizing microbial activity and maximizing the possible leaf-to-air hydrocarbon gradient. In my opinion, it is likely that the actual hydrocarbon emissions are another order of magnitude lower than calculated. I suggest therefore highlighting the relative irrelevancy of this process as a source of hydrocarbons to the atmosphere. That may save others a lot of time looking into this . . .

Instead, relevancy could be shown through field measurements, which are missing in this case and are a notable shortcoming of this study.

5. Methyl-chloride: This is a different story altogether, and I suggest the authors focus a bit more on these results. However, field measurement data to support the conclusions would be useful, as would be leaf material analyses (or literature data) on pectin and

chloride contents.

6. Format: I do agree with another reviewer that the figures need attention: Axis labels and captions need to have larger fonts, point sizes should be increased, titles eliminated, and necessity of gridlines reviewed. Finally, I noticed that present tense was used throughout large parts of the manuscript where past tense is needed. That needs to be fixed.

Interactive comment on Biogeosciences Discuss., 7, 823, 2010.