

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

L. Derendorp et al.

l.derendorp@uu.nl

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We thank reviewer 2 for his/her efforts for providing an extensive review. Unfortunately we cannot follow most of the points that have been raised. We understand that we obviously were not able to communicate our results with the necessary clarity and we aim at improving this in the revised version. However, many of the key points of criticism raised in this referee report originate from an unfortunate misconception: The goal of our study is not investigating emissions from living plants. We are investigating emissions from plant litter. This is a field where only very few studies were published in the literature, and we do cite the relevant work. For many of the compounds investigate here, this is the first study at all! Therefore, we clearly do not “reinvent the wheel”. In this first study, we can show that some small hydrocarbons are emitted

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from plant litter (and others not), how these emissions depend on temperature and we give a rough assessment on whether the emissions may be significant for the global budget. The additional references and many of the critical remarks that the referee makes in the report show her/his in-depth knowledge of the subject and are very relevant for emissions from living plants and the underlying processes, but they do not directly relate to our study on plant litter. We will show this in the detailed replies below, where we address the specific points raised in order of their appearance:

Page C187:

The overall manuscript appears confused and even puzzling at some points due to the continuous mixing up of the different sections (especially mm, results and discussion).

Answer:

There is certainly need for improvement – will be done.

Besides that, my main concerns regard the presence of relevant scientific flaws and the use of an erroneous terminology. Indeed, starting from the abstract the author introduces the emission of some VOCs of “abiotic origin”. The term “abiotic” is inconsistent with the literature since it has never been referred to a plant emission. In principles, an emission is always a result of enzyme synthesis and can be driven in leaves by “abiotic” FACTORS such as temperature, light, pollutants gases (ozone, NO_x, etc.) and other environmental constraints (for example drought); an emission can also be elicited in leaves by “biotic” factors such as insects feeding, fungi or bacteria activity. I think the meaning and the definition of a plant emission has been completely misunderstood and the physical properties of the VOCs are wrongly mixed up with the VOCs biological control. Therefore I absolutely suggest the author to thoroughly study at least the comprehensive paper of Niinemets et al. 2004 to gain a better insight of VOCs issue.

Answer:

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In living vegetation emissions of VOCs are generally a result of enzymatic activity. In this paper, we are not investigating emissions from living vegetation, but from leaf litter. The results presented in this paper show that the emissions from leaf litter are not a result of enzymatic processes, which is indicated by emission rates that keep increasing with temperature until 80 °C, and high activation energies. Furthermore, it has been clearly shown that air-dried leaves that were sterilized using gamma radiation and compared with untreated leaves produced similar amounts of chloromethane and some other VOCs (e.g. Hamilton et al. 2003, Keppler et al. 2004, 2005). Because the emissions are not produced by enzymes, we call them abiotic. We examine how this abiotic, non-enzymatic emissions are influenced by temperature (an abiotic factor). The paper by Niinemets et al, 2004 is also about living vegetation.

Page C188:

Other big scientific flaws regard the claim for adsorption/desorption processes beside the one of emission in order to justify some results. The concept of VOCs emission is mixed up with the one of membranes adsorption/desorption and results in a series of absurd conclusions.

Answer:

The claim of adsorption/desorption is probably too speculative and there are probably more likely explanations for the observed behavior (see referee 1 comments). The revised version will be improved in this respect. Nevertheless we do not think that our conclusions are absurd.

Moreover, the goal of this study is badly described and it looks like the author is “reinventing the wheel” since it is well known the temperature dependency of VOCs emission as direct consequence of both the VOCs physical-chemical properties (volatility, surface tension, lipo/hydrophylicity) than to the enzymatic activity response (that

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usually positively correlate with the increasing temperature up to a certain threshold). Therefore I definitely invite the author to clearly describe the objectives of this investigation and to point out the novelties arisen from the results achieved and their original contribution for the VOCs field of study improvement.

Answer:

Apparently, the goal of our work is at least not well understood, although we tried to formulate it clearly, but we will make this clear in the revised version. As mentioned in the general reply, our work is definitely not reinventing the wheel. Again, our research is not on living plants, and the referee here explicitly mentions the temperature threshold for enzymatic activity that we do not see. So implicitly the referee even states the different nature of the emissions reported here from emissions mediated by enzymatic activity. There is very little research on VOC emission from plant litter, as stated above, so the results are novel. Our research showed that plant litter is not a significant source for the atmospheric budget of the observed hydrocarbons. However, plant litter emissions of methyl chloride most likely need to be taken into account to understand the atmospheric budget of this compound. This actually supports other recent studies (Keppler et al., 2004, 2005, Hamilton et al., 2003).

In fact the author run their experiments at too high temperature to claim an importance for the global climate change since a temperature of 70 C will never be reached in any natural environments.

Answer:

We run the temperature experiments to higher temperatures for two reasons: (1) to prove that the emissions are not of enzymatic origin and (2) to investigate the temperature dependency of abiotic release of some VOCs from leaf litter. The global extrapolations have been done using measured emission rates at 30 degrees Celsius. This is clearly stated in the text and in Table 4. We emphasize in the revised version that this is only a first and very rough estimate, but it already enables us to qualitatively

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assess the relevance of plant litter emissions for different compounds (in terms of whether the emissions can possibly be relevant for the global budgets).

In addition, I have serious problems with the technique used by the author to extract and quantify the VOCs from the leaves material that result in a non standardized methodology where too many variables are not controlled.

Answer:

It is not clear to which variables the referee is referring to. Our setup is quite straightforward and all relevant variables are controlled. Basically, plant material is put into a temperature controlled tube the flow through which can be controlled as well. The volume mixing ratios of the VOCs of interest are measured in the airstream before and after the interaction with the plant. The calculation of the emission rate is thus very simple. Basically this represents a dynamic chamber system which is a widely used for measurements of VOC emission from living vegetation or soil, and is standardized methodology. The methods of drying and grinding were also standardized: We air-dried the leaves for two months at 25°C. After drying, part of the leaf litter is grinded, and then stored in 50 ml vials. The fraction used as whole leaves was stored in plastic zip bags. As stated above we realize that the method section has to be improved.

As a consequence, the experimental results might have been easily impaired by the uncertainties due to the methodology used thus creating a series of artifacts.

Answer:

It is not clear what exactly the concerns are. We do not see significant uncertainties in the simple setup employed. Therefore we cannot address them specifically.

I recommend the author a careful reading of the paper of Romanik et al. 2007, where

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the VOCs extraction methodology is reviewed. In conclusion, the manuscript by Darendrop et al. is not ready for publication in a scientific journal. I warmly suggest the author first to improve their experimental protocols before repeating a new set of experiments and then to rework the manuscript by properly (re)organizing all the sections. . .

Answer:

Different extraction methodology such as described in Romanik et al. 2007 would be required if the goal was entangling the different processes leading to VOC emission. However, in this first study, the goal was to constrain the overall emission capacity of plant litter into the atmosphere. For this goal we used the appropriate method and we got clear results. Given the severe misunderstandings it is logical that the referee must come to a negative conclusion on our manuscript. But the replies hopefully make clear that the major points of criticism are not relevant for our goal. We clearly realize that this goal was not communicated well. In addition, some valuable suggestions for improvements were pointed out by the referee and will be included in the revised version of the manuscript. However, we are convinced that the underlying scientific basis of our paper is strong and within the scope of BG. The experimental protocols are reasonable and yielded solid results which we feel are worth being published.

Page C189:

Introduction - This section basically appears as a confused list of different VOCs and some of the important up-to-date references are missing; when speaking about the meaning of VOCs emitted by plants (line 1, page 825) it should be mentioned the work of Vickers et al. 2009, Baldwin et al. 2006, Dicke et al, 2009, Loreto et al. 2006, and so on: : ; the work of Huve et al. 2007 should be included when introducing the issue of methanol emission from leaves. I suggest the author to deepen the bibliographic research in order to provide a better set of references (that is an essential part for a scientific publication). - The role of VOC in the atmosphere must be definitely better explained (line 24, page 825) and the author should mention the important contribution

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of Di Carlo et al. 2004 about the "OH reactivity".

Answer:

Writing the introduction for this paper was indeed not straightforward, because we cannot give a comprehensive overview of all aspects of VOC emissions from living plants. This is clearly beyond the scope of this paper. Our attempt was to concentrate on the aspects that are relevant for our goal and we included the relevant references. We will re-evaluate our references and further improve the referencing of existing related research in view of the referee comments.

What it is stated in lines 19-20, page 826: "Polar compounds like acetone and methanol are not emitted directly, but stick to the cell material" is absolutely wrong especially for what regard methanol that basically is emitted as a consequence of enzyme activity on membranes during leaves growth and expansion (otherwise, please support that sentence with references, if they exist); what is also written in the following sentences (lines 20-24, page 826) make really no sense!

Answer:

The referee is referring to methanol and acetone emission from living plants. AGAIN: our paper is on plant litter – dead, dry material. What is written on page 826, lines 20-24, are findings from Warneke et al. The correct reference is given in the text. It makes sense if one realizes that it is about plant litter.

- Why "To get some insight in the precursors of the VOCs, the dependence of the emissions on oxygen is examined" (lines 21-22, page 827). What is the meaning of "precursors"? What is the sense of that objective?

Answer:

The observed VOCs originate from chemical reactions of structural plant compounds such as pectin for methyl chloride and polyunsaturated fatty acids for the hydrocar-

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bons. The structural plant components from which the VOCs are produced are called precursors. The goal of the oxygen exposure experiment was to gain more insights on the underlying chemistry, i.e. whether or not oxygen is required to release the different compounds. The results clearly prove that it is worthwhile objective.

*2) Experimental methods - The author needs to describe in details the experimental protocol used, specifying: *) for how long the material has been drying; *) how was controlled and/or monitored the temperature of 25C; *) how was grinded the material; *) how much material has been used for the analysis; - When items such as Suprasil quartz tube are mentioned, the name of the provider must be given. - What is a "nafion drier"? - Please give references regarding the gas standard used to calibrate the GC device (company provider, concentration, etc.).*

Answer:

We are sorry that the manuscript was missing some important details, but this will be added in the revised version.

Page C190:

The text written starting from line 23 page 828 to line 3 page 829 are results! - Please create a separate (sub)section where more and better indications about the statistical methods used for the data elaboration are given. What is written in lines 10-13 page 829 may be suitable for a figure caption.

Answer:

The text on page 828 line 23 to page 829 line 3 characterizes our GC system and gas standard measurements. These are no scientific results and belong in this section. Unfortunately it is not clear what further information is requested here. Page 829 lines 10-13 is an important part of the description of the methodology and needs to be in the text-body not in the Figure caption.

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The "Results" section where the data collected are described must be definitely separate from the "Discussion" section where whatsoever meaning regarding the data presented is debated.

Answer:

that is a question of style. We will reconsider this but in the case of this paper with a number of different experiments and results, it seemed logical for us to present the data and discuss the implications directly, because this way we can more naturally provide the motivation for the subsequent experiments.

There is no need to show the analyzed background (Figure 1 – middle panel); in fact it should be subtracted from each samples analyzed. Moreover, if there is really the need to show the reference gas analysis (Figure 1 – upper panel), the results should be presented with the proper scientific measurements unit and not as "intensity". Since a calibrated gas standard has been used, I wonder why the author did not use units of concentration for the Y-axis.

Answer:

We think Figure 1 is useful. Including the background gives the reader an immediate impression on the quality (signal-noise ratio) and thus credibility of our results. This is much more informative than just mentioning that the background has been subtracted. The same argumentation holds for showing a chromatogram of the gas standard. The y-axis displays the proper scientific unit of a chromatogram. It is detector intensity in millivolt. The concentration is not directly related to the maximum intensity but it is derived from the integration of the compound peaks. The integrated peak areas are converted to mixing ratios via a response factor, which is different for each VOC. Therefore it is not possible to attach a concentration scale to the y-axis.

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What is (badly) written is lines 11-14 page 830 again makes no sense! What is the meaning of "precursor reservoirs"?

Answer:

The meaning of "precursor reservoirs" will be more clearly explained in the revised paper. When the emissions of hydrocarbon decrease, these precursor reservoirs are getting emptied. We do not understand what makes no sense here. In fact, this observation together with the interpretation of the Arrhenius plots shows that the first order assumption is not applicable, i.e. the pools of the emission are of limited size.

What is written in lines 15-20 page 830 represent one the weakest point. I am not surprise that the author noticed "at high temperatures the emission rates for whole leaves are generally much higher compared to ground leaves" (lines 15-16 page 830). In fact during grounding there might have been big losses of VOCs due both to the simple VOCs release in air than to the oxidative reactions occurring during the mechanical process of grinding itself: however these losses can be minimized by using a proper experimental protocol. My problem is how to discuss about VOCs temperature dependency in presence of such big uncertainties? Is the author sure that three replicates are enough to overcome all the big sources of uncertainties introduced and to provide scientific reliable results?

Answer:

We do not understand what is weak here. We describe results which were expected by the referee. He/she gives several good reasons that can explain our observations which are all in line with our argumentation. So what is the weakness? For the same reasons we argue that the rates from whole leaves are probably more realistic for real world conditions. We do not understand how uncertainties are introduced through something which can actually be understood! It is always desirable to have a high number of replicates. Three replicates at every temperature step is a reasonable number which allowed us to gain good and reliable results.

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Following my concern, the author states in line 1-2 page 831: "For ground leaves, there is more variability among the plant species": it is obvious if only 3 replicates are performed and if has not been used a protocol where all the different variables are kept under control.

Answer:

We think this has nothing to do with the number of replicates. Note that the statement is not about the variability within a set of three replicates. Also note that grinding and analysis of all biomaterials followed the same protocol.

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- Again, what it is written in lines 7-9 page 831 it is both obvious than puzzling; in the following sentences there is the clear indication that the author mixed up the physical properties of VOCs with their biological control!! –

Answer:

What is written on page 832 lines 7-9 is neither meant to be perceived obvious nor puzzling. It is a neutral description of our findings. The exponential increase over the full temperature range is a clear indication of abiotic origins. Enzymatic processes cease at a certain temperature. There is no mixing up of physical properties and biological controls. This is simply not an enzymatic process, and this is probably the main misconception of the referee.

The sub-section regarding the Arrhenius plots is really confused and it looks more suitable more for a text book than for a scientific paper. - What is written in lines 17-18 page 832 shows again the use of an erroneous terminology: can the author define what a "precursor reservoir" is?

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Answer:

We use the Arrhenius relation to interpret our data and therefore we introduce it. Precursor reservoir is explained above.

The sentence written in lines 7-16 page 833 is really wrong! How can the author discuss the VOCs adsorption/desorption processes from leaves surfaces? In my opinion now the author starts mixing up the concept of "emission" with the one of desorption, as it comes out again in lines 22-26 page 833.

Answer:

We think that this part is not wrong, but one possible hypothesis. However, we agree that the attempt of explaining our observation by absorption/desorption is weak and there are probably better hypothesis (see referee 1 comment). The discussion will be improved in the revised version.

- What the author states in lines 25-27 page 835 contributes to make lose the reliability of the experiments done.

Answer:

The decrease of the emission capacity over the course of one year is a point of concern and warrants further research. However this fact does not change the general results of our research. It possibly indicates that our emission estimates are too low (because most of the emission occurs from recently dried leaves). However, this needs to be investigated in future studies. Btw the depletion is less pronounced for methyl chloride.

- The author should definitely read the paper of Hatanaka 1993 before going into such an absurd conclusions (line 10-16 page 839).

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Answer:
Hatanaka 1993 does not relate to our work.

The referee mentions repeatedly in the report that we draw “absurd” conclusions. But at no point it is stated why they are absurd. Given that the emissions we report here are non-enzymatic, they do not contradict prior studies, but confirm previous studies and extend our knowledge about abiotic formation of VOCs from plant litter. We are not questioning generally accepted concepts and therefore we do not understand in what sense the results should be absurd. The referee also offers no alternative (non-absurd) interpretation of our results other than referring to non-specified potential problems with the experimental setup. But the results are clear and systematic and there is not random or systematic issue in the simple experimental setup conceivable that would lead to such results. We are puzzled by this repeated unfounded criticism and can only explain it by the fact that the referee overlooked that we report non-enzymatic emissions.

4) Figures - The figures are really raw and basics and should be definitely improved. - Please avoid the use of a text box set within a figure; the full description of the figure should be written in the respective caption. - There is absolutely no need to present a figure with a title (Figure 2); again the author should use only the captions to fully describe the figures.

Answer:
The figures are not raw. We will remove the titles, but will keep legends that make the figures self-explanatory rather than expecting readers to go always back to the caption.

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