

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

**Anonymous Referee #2**

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### General comments

The manuscript by Darendrop et al. aims to investigate the temperature dependence of volatile organic compounds (VOCs) emitted from dry leaves belonging to some selected plant species. The overall manuscript appears confused and even puzzling at some points due to the continuous mixing up of the different sections (especially m&m, results and discussion). 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 principle, an emission is always a result of enzyme synthesis and can be driven in leaves by “abiotic” FACTORS such as temperature, light, pollutants

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gases (ozone, NO<sub>x</sub>, 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. 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. 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/hydrophobicity) than to the enzymatic activity response (that 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. 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. 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. 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. I recommend the author a careful reading of the paper of Romanik et al. 2007, where 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

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and support all the statements with suitable references. A particular attention should be also given in redrawing the figures presented and their description in the respective captions.

#### Specific comments/technical corrections

1) 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 of Di Carlo et al. 2004 about the "OH reactivity". - 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!

- 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?

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 25°C; \*) how was grinded the material; \*) how much material has been used for the analysis; - When items such as Suprasil

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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.). - 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.

3) Results and discussion - 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. - The results must be reorganized and neatly presented following the numerical order assigned to the respective figures. - 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. - What is (badly) written is lines 11-14 page 830 again makes no sense! What is the meaning of "precursor reservoirs"? - 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? - 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

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under control. - 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!! - 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? - 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. - What the author states in lines 25-27 page 835 contributes to make lose the reliability of the experiments done. - The author should definitely read the paper of Hatanaka 1993 before going into such an absurd conclusions (line 10-16 page 839).

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.

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