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Interactive comment on "Volatile Organic Compound emissions from soil: using Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) for the real time observation of microbial processes" *by* P. R. Veres et al.

Anonymous Referee #1

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General comments

The paper presents an interesting method and shows some potential of combined soil VOC and N trace gas measurements, but it is premature and needs more elaboration on the basis of soils from a broader range of ecosystems, as well as an unambiguous elucidation of the processes responsible for the observed VOC and NO emissions. Although the authors claim that "These experiments can be used as a template for future experiments to more completely and specifically identify the active microbial guilds in soils and to characterize the impact of soil VOC emissions on the atmosphere" (last sentence of the abstract) and by this try to justify a publication of their very preliminary results, still a minimum requirement would have been to show that the VOC emission pattern observed for the arid soil can be considered as a kind of general feature. As there is no comparable information for other soils, even not for the second soil of the study, it remains completely unclear whether we deal here with a new, elegant method for detecting soil microbial activity, or whether we just see an arbitrary snapshot of a laboratory experiment which has nothing to do with natural conditions.

In particular, the paper suffers from the following points:

1. No clear mechanistic relationship between the VOC presented and soil microbiological activity has been elaborated. It remains elusive and speculative from which process(es) the VOC originate, and whether the VOC originate from the same microbiological process(es) as NO. It even remains unclear whether the VOC and the NO originate from biological processes at all, as Q10 values of 2-3 are not exclusively indicative of biological processes. Many chemical reaction have Q10 values of 2-4 over a broad temperature range. Therefore, any conclusions pertaining to the suitability of VOC for identification of soil microbiological processes are based on too weak a ground.

2. The authors present the concept of different soil microbiological "emitting guilds", but it is developed only on data of one soil (arid soil), measured only once during one rewetting–drying period. There is no evidence that the observed pattern would occur again after the second or further rewetting–drying cycles. For the second soil, no such pattern is presented. And as there are no data for other soils, it remains purely speculative whether this is a general feature, only specific for the analyzed soil, an experimental artifact, or perhaps pure coincidence.

3. The relevance of the findings is strongly relativized by the authors themselves ("The

extent to which these VOC emissions will reach the atmosphere will depend on concomitant uptake processes in the more complex soil ecosystems found in nature", p. 12022, l. 4-5). Therefore, the applicability of the laboratory method demonstrated here to the "real world" (i.e., field campaign measurements on intact soil surfaces), is questionable.

Despite the uncertainty of the relevance of the work for field conditions, the experimental data could in general still be interesting for getting a closer mechanistic insight into the role of soil microorganisms in soil VOC emissions and their relationship with soil NO emissions. However, also for this purpose the experimental design is insufficient and suffers from serious flaws due to the following reasons:

1. Only two different soils were used, of which one (rainforest soil) was measured field-moist "immediately upon receipt", whereas the other (arid soil) was air-dried, stored at 4 °C for and rewetted before analysis.

2. Only one sample per soil was measured, and each sample was measured only once. At least data of only one measurement each are presented without any information about variability.

3. No nitric oxide (NO) data are presented for the rainforest soil.

4. There is a data gap between 30-50 h for the rainforest soil.

To summarize, the design of the study needs substantial improvements. The authors make similar suggestions in the discussion section (e.g., p. 12022, l. 13-18: "Future experiments to determine the temperature optimum of VOC emissions and microbial community activity can be pursued as further evidence of biological production. . . Furthermore, similar measurements using pure cultures of the active microbiological constituents could help to identify and validate a biological source of soil VOC."; and p. 12024, l. 2-3: "Sub-samples of soil during peak activity periods have to be subjected to molecular analysis in order to better attribute these microbial processes to the release of VOC").

Specific comments

p. 12013, l. 5-6: The statement "since abiotic and biotic processes should exhibit a different response to temperature" only holds true for the same reaction which could proceed either purely chemically or also biologically (enzymatically catalyzed). Then one can determine the activation energy, compare it with chemical data tables or text-books, and then decide whether the observed reaction is a purely chemical or biological process.

p. 12012, l. 6ff.: Give examples of such "unspecific" reactions. Not every reader will be familiar with the enzymes involved in NO production in the soil, and very likely even fewer with the kind of "side reactions" these enzymes could undergo in terms of VOC turnover. Thus, name examples of VOC classes that could be involved. This will be crucial for the interpretation of the data presented, i.e. whether it is likely that the VOC data shown could be a result of microbial activity related to NO production in the soil.

p. 12015, l. 6-8: The difference in sample treatment is highly problematic with respect to microbial activity, as can be seen from the very paper cited here (Stotzky et al., 1962), where it is clearly stated that air-drying leads to a significant decline in microbial activity and changes microbial species composition (as does storage of field-moist soil in closed sample bags).

p. 12017, l. 25: NO is, unlike CO2, CH4 and N2O, not a primary greenhouse gas, but contributes to global warming through tropospheric ozone formation.

p. 12018, l. 1-2: Using clean, VOC-free zero air can lead to increased VOC release from any source (soil, leaves…) by shifting the equilibrium between release and uptake completely to the side of release. This artificial experimental effect should be taken into account and discussed.

p. 12018, l. 18: "the mechanisms described in the introduction": There are no mech-

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anisms described in the introduction. It is only mentioned there that “the enzymes responsible for soil emissions of NO are unspecific and thereby can react with various volatile organic compounds (VOC)“, but this statement is not followed by a description of the mechanisms, which would be very helpful.

p. 12020, l. 2-3: Which reaction is meant here? Reaction of NH_4^+ with hydroxylamine? NH_4^+ has the oxidation number -3, hydroxylamine has the oxidation number -1. It is not clear how the two should react to NO with the oxidation number +2 without further oxidant. Please explain.

p. 12020, l. 3-5: “It is likely that in addition to AMO, there exist other enzymes that are also nonspecific resulting in further reduction of the release rate of NO.” This statement needs more detailing, especially pertaining to potential suppression mechanisms of NO production.

p. 12020, l. 5-6: Again, it is not clear why a “high mass-loading of organics” should inhibit NO production.

p. 12021, l. 3: Also many purely chemical reactions have a Q10 value of 2-3.

p. 12021, l. 20-22: Again, Q10 values of 2-3 are not exclusively indicative of biological activity. A clear proof of biological activity would be an emission maximum at, e.g., 40°C with subsequent decline at higher temperatures due to degeneration of enzymes. Almost every chemical reaction features an increase in reaction velocity by a factor of 2-4 when the temperature is increased by 10°C.

p. 12022, l. 13-18: That’s the way to go and would have been needed to address the objectives of this paper, i.e., assessing the suitability of VOC as indicators of soil microbiological activity.

Technical corrections

p. 12011, l. 18: Change “Xinijang” to “Xinjiang”

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l. 12013, l .22: Change “are” to “be”.

p. 12013, l. 29 and p. 12016, l. 3: Change “are” to “were”.

p. 12014, l. 6-7: Change “occurring with” to “occurring in”

p. 12014, l. 25: Delete “–“ before “55.” (already indicated by “W”).

p. 12018, l. 23: “occurs”: here and in the following, use past tense for the description of your results.

p. 12019, l. 29: Change “pre-cursor” to “precursor”.

p. 12021, l. 6/7: Change “a temperatures of T1 and T2 respectively” to “at temperatures T1 and T2, respectively”

Interactive comment on Biogeosciences Discuss., 11, 12009, 2014.