

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 #2

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General comments

In this paper VOC and NO emissions from two soils are measured over a range of soil moistures (soil drying out process) and at two temperatures (20 and 30°C) using the PTR-TOF-MS technique. VOC emission responses to moisture and temperature are used to identify biological or abiotic mechanisms of emission. The goals are to improve our understanding on soil VOCs emissions mechanisms and to find links be-

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tween VOCs and NO production. The paper address a relevant scientific question, given the scarce information on soil VOCs emission rates, environmental controls and potential impact on atmospheric chemistry and the importance of NO. The use of the PTR-MS-TOF technique provides powerful, accurate and instant measurement of several volatile compounds, this is a valuable point of this work. The paper also presents a novel concept, the link between soil VOCs and NO through a series of distinct microbial populations emitting VOCs and NO (NO emitted hypothetically by different processes than those producing VOCs, but concomitant, like nitrification and denitrification, although this point is not satisfactory clear) at different moisture levels. The idea is very appealing, and the VOC and NO emission data fit well, however the empirical evidence provided is not enough to “assert” that different microbial groups are the origin of the VOCs and different NO peaks. First because, as the authors say, no molecular methods have been applied, therefore, the results are not conclusive, and second because within the 4 VOCs identified (representing different groups of microbes) 2 of them (hexanol and 1,3-butadiene) have not been demonstrated to have a biological origin with its Q10 (following the author’s rationale and data presented in Figure 3). It could be argued for example, that the peak of 1,3-butadiene (Fig 2) coincident with low soil water content is due to increased gas diffusivity resulting from decreased soil water content. The other 2 VOCs (isoprene and DMS) have been shown to have a Q10 of 2-3, but in a different soil type (different microbial community, activity and physico-chemical properties), which furthermore has received a different treatment prior measurements. Finally, the production of NO involves a sequence of biological and abiotic reactions, the later depending also on water content, temperature and pH. There could be a differential effect of water content (and other factors) on the biological and abiotic component of NO production, thus the link between VOCs and NO release could not be so straightforward (additive effect) as the authors propose. In summary, this paper gives important but preliminary data for further experiments aimed to specifically link VOC and NO soil emissions.

Regarding the experiment with the SR soil (Fig. 3) designed to investigate the Q10

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responses of different VOCs, it is not clear if the soil moisture was constant or if the soil was drying out, similarly to the experiment with the SC soil (Fig. 2). Perhaps the authors have assumed that at each single pair of points (e.g. time 1h, temp 20°C and 30°C) the soil moisture was the same throughout the measurements (80h). This point could be clarified in the text and discussed whether this may affect Q10 values. In general the paper is well written, and clearly presented. However, the methods section should be improved with a more exhaustive description of the experiments and methodology. The explanation of some ideas in the text should be more specific (see comments below).

Specific comments:

P.12012 Lines 8-10: what is the difference between (i) [...] abiotic decomposition in soil and (ii) originate from abiotic decomposition in soil? Lines 20-24: The paper Inamdar and Bennett, 2014 shows that exposure to a VOC, 1-octen-3-ol, led to an increase in the nitrite levels in the head, body and whole *Drosophila* extracts. Given the differences with the soil system, I think this study does not suggest that "biogenic release mechanisms of these gases are closely linked". A better reference linking VOCs and NO emissions in soils should be provided.

P. 12014 Lines 1-5: The authors say that studies in natural conditions are needed, but this work does not deal with natural systems. Maybe it should be better present this study as a first step to the understanding of more complex natural systems.

P. 12015 Lines 6-8: Why the soils were not treated similarly? Line 20: If a LI-COR 840 was used, why CO₂ was not measured together with the H₂O? Lines 28-29: Which was the temperature in Experiment 1 (SC soil) and the moisture in Experiment 2 (SR soil)?

P. 12016 Lines 3-10: The SC soil (air-dried and stored at 4°C) was not acclimated (i. e. brought to WHC and incubated at 20°C) prior to measurements shown in Fig. 2. This may explain the initial flush of VOCs after soil rewetting, the authors should explain this

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when discussing Fig. 2. Lines 5-6: Which are "pF" units for field capacity?

P. 12017 Line 2: Flow rate when sampling 8.3 x10⁻⁶ m³ s⁻¹, but in page 12015 flow rate when actively sampling was 4.2 x 10⁻⁵ m³ s⁻¹ (line 16)

P. 12020 Lines 7-10: As it is written, explanation (ii) seems an extension of (i), rather than a different mechanisms. Could you please clarify why interpretation (ii) explains better your results? Lines 13-14: Sterilization was not mentioned in the methods, was it actually done or is it an error?

P. 12021 Lines 10-11: Soil was drying out as in experiment 1 or was moisture constant? Lines 26-27: But later, about at 60h, the Q10 turns about 2, is this indicating microbial activity then? But which was the soil moisture again? This information is needed. Line 27: It is difficult to see an initial pulse of 2-butanone and acetone in Fig. 3 (at least not clear as in Fig. 2). Rather, it seems more like emissions are decreasing and peaking after 10h.

P. 12022 Lines 1-3: Which abiotic processes are exactly involved in points (ii) and (iii)? And which is the role of extracellular enzymes and intracellular solutes in these processes which can explain abiotic release of 2-butanone and acetone?

P. 12023 Overall the section "Co-emission of VOC and NO" should include a discussion of the potential weak points of the experiment and data presented, as suggested in the general comments.

P. 12030 Line 18: "aromatic"

P. 12036 Upper panel: The Y axis on the left is %WHC, should be ng Kg⁻¹ s⁻¹ Bottom panel: It might be that the left Y axis (ng Kg⁻¹ s⁻¹) is actually %WHC? Isoprene emissions, hypothetically with biological origin, are quite high. That is surprising and interesting result. Is there any other study showing similar isoprene emission rates from soils?

P. 12037 Emissions from this rainforest soil are extremely low as compared to the

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arid soil (e.g. isoprene 1.5 vs 200 ng Kg⁻¹ s⁻¹). Is the different handling of the soils explaining this? Again, the moisture is needed to understand the results.

P. 12038 Emission rates for DMS, isoprene and hexanol do not correspond with data shown in Fig. 2. Isoprene here is 2 orders of magnitude lower. Is data shown in Figure 4 another set of measurements performed with the SC soil?

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