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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.

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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 #2 Received and published: 24 September 2014

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 30C) 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-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.

Response: We thank the reviewer for highlighting the strengths of this work. Indeed the larger focus of this work is to present a new powerful technique to integrate into studies designed to probe microbial emissions from soils. As we attempted to integrate the reviewer's suggestions, we have made a focused effort to better represent the relationship between VOCs and NO as concomitant and not necessarily produced via identical processes. For example we have added the following to section 3.3 "We would like to point out that implying this relationship does not infer a direct link between the processes emitting both VOC and NO, but is suggestive of common microbial guilds responsible for the production." We acknowledge that the use of the word "assert" was too powerful to describe our understanding of these soil systems. Rather we are using

the results of these experiments to make hypothetical connections or 'suggest' origins of VOC and NO in the soil. This language has been changed in the revised manuscript.

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.

Response: Unfortunately, we are limited in the types of data that could be collected on given soils as the experiments continuously evolved over the lifetime of this particular study. As such, the reviewer is correct in pointing out some of the differences in how the two presented soil samples have been treated. One step towards correcting these deficiencies has been to add the peak fitting analysis to the second soil where temperature probing has been performed to better understand the biological origin of the VOCs. As for our discussions on the potential origin of the VOCs observed, we have, through our edits, attempted to make it clear that we are merely speculating as to the origin of these VOC, and future studies using these methods and the PTR-TOF-MS technique should be applied to better identify the origin of these VOC, as well as to provide quantitative and ecosystem representative emission estimates. This in fact is the core of this paper that the techniques used here give us a new method for analyzing the gaseous emissions of soils and that the novel combinations of VOC and NO yields new insights into source behavior.

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 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.

Response: We agree with the reviewer that the connection between VOC release and NO production could be very complex. However, given the evidence we have from these experiments, see that there could be a relationship between the groups or processes responsible for VOC release and those contributing to NO production. Using a very simplistic mathematical approach (multi-peak Gaussian fitting) relating the VOC to NO emissions, we show that this new technique and methodology could potentially be used to simplify this complex system into smaller more focused steps. However, as the reviewer points out, this is only a first step towards simplifying these systems.

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

Response: We have attempted to clarify this portion of the method. In our opinion, perhaps the most helpful edit has been to add the soil moisture content to Figure 3. The soil moisture content was not constant, reducing throughout the experiment. Aside from the temperature modulation from 20°C to 30°C the experiment was performed in an identical manner as the SC soil sample. We do assume that for each pair of points (e.g. 1h, 20°C, 30°C) the soil moisture is constant, but it is not constant for all sets of points throughout the entire experiment (80h).

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.

Response: We thank the reviewer for pointing out the error in lines 8-10, this is a repetition and item (i) and (ii) are equivalent. Those lines have been edited to read "There is evidence that the enzymes responsible for soil emissions of NO are unspecific and thereby can react with various volatile organic compounds (VOC) that might be (i) naturally produced by microbial or abiotic decomposition in soil (Arp and Stein, 2003;Hymann et al., 1988;Keener and Arp, 1994;Insam and Seewald, 2010)." On the comment pertaining to lines 20-24, at the time we are unable to find an alternate publication that proposes a link between NO and VOC soil emissions. We would be happy to add or replace this reference if the reviewer has another one to recommend.

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.

Response: The reviewer's suggestion is an excellent one, and one that it seems like we fell short of conveying. In fact, we would like to present this study as a starting point presenting a technique to help simplify complex natural systems in the laboratory. Due to the complexity of field systems and the continuing discussions on the differences between field and laboratory studies, the complex reality must be simplified to progress

our understanding of soil systems. In order to address this shortcoming, we have added in several sections throughout the manuscript with an emphasis on this work as a starting point and new technique for breaking down this complexity.

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)?

Response: The soils were treated differently as a result of the availability of each sample. The SR soil sample was shipped during the experiments and measured immediately upon receipt while the SC soil sample was already in our soil sample archives from a previous experiment. The missing CO2 measurements are explained in detail in Behrendt et al., 2014. Briefly, CO2 can only be measured if the amount of soil is large enough (we used only 20-60g), and the flow rate is low maybe in the order of a few hundred ml. We were limited to a minimum flow of 2.5 l min-1 to support enough flow for all of the analyzers used. Furthermore during most experiments where CO2 is measured the soil is sampled in a static chamber so that sufficient CO2 concentrations are present, while in these experiments a dynamic chamber design was used. The moisture measurement has been added to Figure 3 and the following line has been added after line 28 and 29 to elaborate on the soil temperatures "During a given experiment, the incubator, including the soil chambers, could be modulated between incubation temperatures (20°C and 30°C) in order to determine the relationship between soil temperature and trace gas emissions, while the SC experiments were conducted at a constant temperature of 30°C."

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

Response: The entirety of section 3.1 “Pulsing of VOC and NO” is dedicated to the discussion of this initial flush of VOC. In this discussion we address the potential of abiotic VOC re-volatilization as observed in Warneke et al. 1999, which we believe is the process to which the reviewer is referring. The unit “pF” is a commonly used metric to describe soil water potential.

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).

Response: The flow rate on p. 12015 (4.2 x 10-5 m3 s-1) refers to the flow rate through the soil cell chamber when that specific chamber is being sampled. The flow rate on p. 12017 refers solely to the flow the PTR-TOF-MS is using to sub sample from that 4.2 x 10-5 m3 s-1 manifold flow. To clarify p. 12017, line 1 was edited to read “During laboratory experiments, the PTR-TOF-MS sub-sampled at a flow rate of 8.3x10-6 m3 s-1 (0.5 slpm) from the soil chamber manifold flow through a 1 m long, 0.0016 m o.d. PEEK inlet heated to 50°C.”

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?

Response: We thank the reviewer for bringing this to our attention; we admit that this was overlooked in the editing process. The reviewer is in fact correct that explanation (ii) is a specific example of the process described in (i). We still hold that (i) is the best manner to describe the processes observed, as it is the more general statement and not enough evidence was collected to definitively attribute the VOC emission process observed. However, we have rewritten this section to first state that process (i) is a good description of this observation and then detail (ii) as an example of such an emission process.

Lines 13-14: Sterilization was not mentioned in the methods, was it actually done or is it an error?

Response: We thank the reviewer for bringing this omission to our attention. Sterilization was not performed for any of the soil samples presented. We chose not to apply sterilization as previous work has shown that process highly alters the chemical surface properties of the organic and clay fraction in the soil, which are involved in chemical ad-/desorption of VOCs. This was included in error, and the section has been edited to read “Based on the results observed in this experiment alone, however, the source of the initial VOC pulse cannot be unambiguously identified as CO2 was not routinely measured nor were molecular techniques or sterilization.”

P. 12021 Lines 10-11: Soil was drying out as in experiment 1 or was moisture constant?

Response: Yes, the experiment was conducted in a manner identical to the treatment of the SC soil type presented in Figure 2, a soil drying experiment, except that the soil temperature was alternately switched between 20C and 30C while drying out. The opening sentence to this paragraph (p.12021, line 9) has been edited to read “The SR soil sample was analyzed using the temperature modulation described above during a soil drying experiment as described for the SC soil type presented in Fig. 2.” Additionally a %WHC trace was added to figure 3 to show the water content over the course of the experiment.

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.

Response: As mentioned in the above responses, the soil moisture curve has been added to Fig. 3 to give that additional necessary information. As for the initial reduction in emissions, we observe what we believe to be two concomitant processes occurring. There is a reduction in emissions over the first 20h; however, around hour 5 there is a second superimposed process (similar to the emission of Acetaldehyde over 0-

20h) that increases the emission of 2-butanone and Acetone over that time period. This initial reduction in VOC emission that is common among nearly all soil emission observed is what we are referring to as the VOC pulsing. As soil samples are wetted prior to placing in the sample cells, the peak of this initial pulse of VOC is not always observed and we catch the tail end of this process here.

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?

Response: To expound on processes (ii) and (iii), the following example/explanation has been added to the end of the mentioned paragraph. “For example, processes (ii) and (iii) could reflect the breaking of cellular walls with a subsequent efflux of carbon containing liquids, which could lead to VOC evaporation according to Henry’s law.” In general, extracellular enzymes of dead microbes can still produce new products (such as VOC) as long as the precursors are available. A potential example would be that in the presence of pyruvate, acetone could be produced not in fermentation and instead by an extracellular enzyme of dead microbes.

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.

Response: We agree with the reviewer’s suggestion, and have added content to this section discussing the weak points of the data evaluation presented here. The above paragraph was inserted into section 3.3 to address some of the deficiencies of the results and discussion. “The above represents an educated discussion on the potential processes responsible for the production of various VOC; yet as mentioned previously the new methods applied in this work cannot alone add any significant support for these assignments. The high time resolution and breadth of the PTR-TOF-MS observations do yield results, which taken in combination with other traditional soil analy-

sis techniques (e.g. pyrosequencing) can be a powerful method for elucidating these proposed formation pathways. Furthermore, while the sample size presented here is small, considering the diversity of the two soil types selected we expect to find similar relationships in the temporal emissions of VOC and NO for additional soil types. However, the magnitude of the relative ratio of VOC to NO is expected to be highly variable based on soil type, treatment as well as conditions at which observations are made.”

P. 12030 Line 18: “aromatic”

Response: This error has been corrected in the edited version.

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?

Response: We thank the reviewer for pointing out the error in the axis label in the top panel. The left axis should in fact be “ng Kg-1 s-1”. However, in the bottom panel, the left axis is used to show the emission rate of 1,3-butadiene while the right axis displays the scale for the %WHC included in the figure and are therefore labeled correctly. The isoprene included in this figure is actually multiplied by a factor of 50 to allow for inclusion on the same scale as trimethylbenzene. This was not indicated in the original figure 2 submitted and is an error that has been corrected in the edited version. Scaling back the isoprene by this factor of 1/50 yields emission rates of isoprene more in agreement with previous reports of VOC emission rates.

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

Response: As will be pointed out in the following response, many of the VOC in figure

2 have been adjusted by a scaling factor (typically x 50) for best viewing on the scales used. It was not indicated in the original figure, as a result of an error, that the isoprene emission rate had been multiplied by 50. If we understand the comment correctly, we believe this is the reason for the discrepancy in the scale of emissions observed from the two soil types. Though we recognize there still of course remains differences in the amounts observed, the magnitude of those differences is much more realistic when that factor is taken into account.

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?

Response: We kindly disagree with the reviewer. The data used in figures 2 and 4 agree for hexanol and DMS (note that DMS is scaled by a factor of 50 in Figure 2). However, we do agree that there is an error in the isoprene data as it is currently displayed. Isoprene also was scaled by a factor of 50, however we failed to indicate that in the graph legend. We thank the reviewer for pointing this out. Figure 2 has been edited to reflect the scaling on isoprene.

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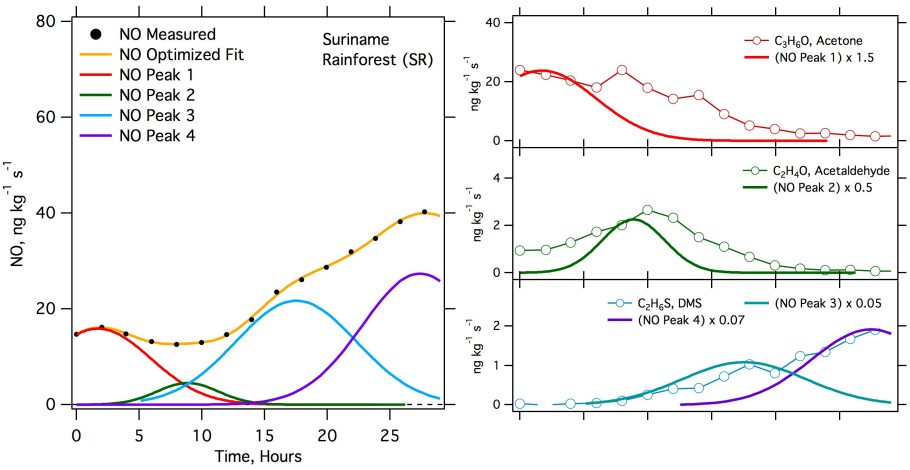

Fig. 1. Figure 5 addition

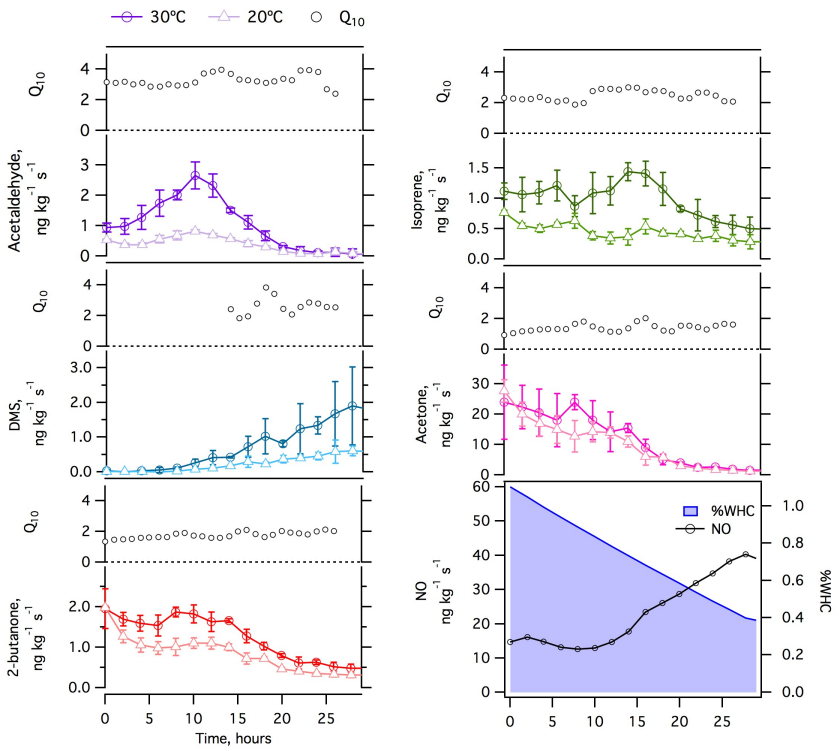

Fig. 2. Edited Figure 3

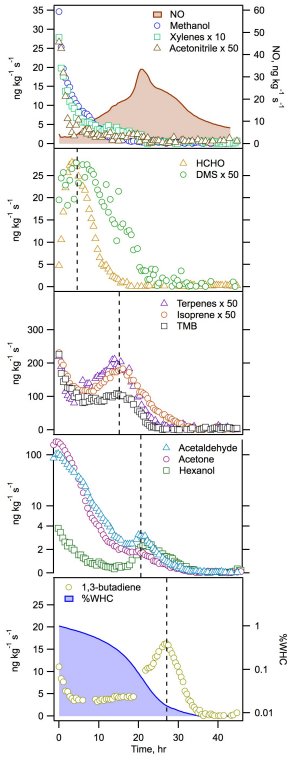

Fig. 3. Corrected Figure 2