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Atmospheric Measurement Techniques Discussions

Interactive comment on "Dynamic Infrared Gas Analysis from Longleaf Pine Fuelbeds Burned in a Wind Tunnel: Observation of Phenol in Pyrolysis and Combustion Phases" *by* Catherine A. Banach et al.

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Response to Interactive comment on "Dynamic Infrared Gas Analysis from Longleaf Pine Fuelbeds Burned in a Wind Tunnel: Observation of Phenol in Pyrolysis and Combustion Phases" by C. A. Banach et al.

Anonymous Referee #2 Received and published: 29 October 2020 General Comment Referee Comments: This work focused on gases emissions, and in particular volatile organic compounds (VOCs), by plants materials burned in a wind tunnel, simulating

in laboratory a field scenario. The experiments allowed isolating and characterizing pre-combustion phase (pyrolysis) with its specific VOCs sign employing two different methods (FTIR and IR thermal imaging), to validate findings. Moreover, the other fire phases and phenol temporal profiles were characterized. Topic is of relevant interest, characterizing an always more spread process in the world, focusing on VOCs emissions, which are increasingly key factor in atmosphere chemistry and dynamics worldwide. Manuscript is qualitatively satisfactory, fitting journal topic and carrying new useful knowledges to the scientific community. I only have some doubts about the experimental/technical part about VOCs sampling system, based on my experience in VOCs experimental campaigns. I am going to report these perplexities in the specific detailed comments below. However, I recommend accepting this manuscript with some minor revision in structure and specific observation for the technical part. Author response We thank the referee the constructive suggestions to improve the readability, utility and strength of the paper. We will try to address the concerns regarding the VOC sampling system in the responses below. Thank you again.

Specific Comments Referee Comments: 1. Line 60, 73. Typing error. There is a dot and then brackets with references and another dot after. Author response Corrected. Thank you.

Referee Comments: 2. From line 72 to 128. There is too much space to explain the entire project into the introduction, respect to the specific goals of the paper. I would summarize the details of the whole project. Indeed, at a first reading it was little bit confusing for me, because I did not find connection in the results. Author response The referee is correct that this section is too long and distracting. We have greatly shortened this section, particularly in regard to context of the larger project. It is now nearly 25% shorter.

Referee Comments: 3. Line 136. I would specify '1 m s-1 wind condition'. Could be confusing. Author response Corrected. Thank you.

Referee Comments: 4. Line 149. I do not know how FTIR Spectrometer works in details, but based on my experience in VOCs measurements with PTR-TOF-MS and cartridges, the best option for VOCs sampling is to use PTFE (Teflon) for sampling line. This is because it is the most inert and least reactive material, avoiding the loss of the sticky compounds as many VOCs could be. It is true that the high temperatures of the gas inside the probe mitigates sticking of compounds on probe walls (showing an average gas temperature inside the probe could be useful, it is available), but I would insert few lines that would take into account consequences of using a stainless steel probe. Because of the stickiness, some compounds could be lost, they could react and become something slightly different from what is primarily emitted by pyrolysis and combustion, or they could be underestimated. This concept is valid in the same way also for the White cell. This is noticed at line 279 for the ammonia in the results. Author response This has been addressed. Stainless steel was used for the sampling probe and much of the transfer line as Teflon melts at these temperatures (> 327 C). It is also true that stainless steel is a bit more “sticky” but this is really not problematic for this application, save for amines. See the revised text.

Referee Comments: 5. Line 154-156 and Table 1. Why if in the manuscript are reported only the 21 experiments carried out in November 2018, at the beginning of the paragraph all measurement were reported? This could be confusing. I would mention only the experiments showed in the paper.

Author response The referee is correct; the misleading text that was in lines 131-133 has been removed such that only the 21 burns of interest are discussed.

Referee Comments: 6. All of Chapter 2. Experimental. Always based on my experience in VOCs sampling, I wonder how you took into account the possible contribution to VOCs identification and quantification of the Wind Tunnel, white cell and other canisters? Some compounds could be already present because released by one of these sources and not from the processes that you are surveying in this work, or both could emit them and bias your quantitative estimation. In my experience it is always needed

a blank (zero) measurement of the surveying matrix and means. This is important also for the ceramic plant holders. What they emit? What they emit when they burn? This could bias your results. Author response That is correct, but as opposed to e.g. GC, TOF-MS or other VOC sampling methods, the infrared experiment is always effectively “self-ratioing” in that the sample spectrum of intensity I is always ratioed against a zero or blank measurement Io thus having every absorbance spectrum [which is -log(I/Io)] divide out the effects of ambient background / sampling device gases. We have added a few sentences at lines 186-190 to make this more clear. The are reproduced here: “For both acquisition modes (static / dynamic), a single Io reference spectrum at the appropriate resolution was collected by flowing ambient gas into the cell at the start of each day to form the single (static) or multiple (dynamic) decadic absorbance spectra using Beer’s law: - log10(I/Io). Acquiring such a blank or zero Io spectrum effectively accounts for any trace VOC emissions from the White cell, wind tunnel, tubing etc. “

Referee Comments: 7. Table 2. I would report standard deviation, since reported mixing ratios come from multiple scan averaging of 30 minutes. In this way, it is possible to observe the mixing ration variation during process observation. Author response This is a bit more difficult to address as the 30 minutes’ data collection all are averaged to form just one interferogram in the FTIR software (automatically). This single interferogram is transformed to generate just one spectrum (see above). Thus, there are no multiple sets of data from which a standard deviation can be derived. As discussed in our earlier papers (Scharko et al. 2019a, b), however, what can be derived are the residuals from the MALT fit to the spectroscopic data and the multiple fits to the same spectrum using different spectral microwindows. The latter is more informative and has been shown to generate variance ranging from ca. 2 to 20% depending on the molecule and signal strength.

Referee Comments: 8. Line 466-480, paragraph 3.3 . This is a state of art about phenol emissions by burns. It should stay in introduction defining the background knowledges at the base of this study. Author response While there is some merit to this statement

that the current state of the art information about phenol could be lodged in the introduction, we respectfully disagree with this reviewer and believe that it adds more merit to the discussion to juxtapose the new results with the prior results of others. To analyze phenol was not the motivation for the experiment, it was simply one of the results that appeared upon analyzing the data and the discussion regarding these results belongs there - in the discussion.

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