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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Laboratory measurements of trace gas emissions from biomass burning of fuel types from the Southeastern and Southwestern United States" *by* I. R. Burling et al.

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Response to anonymous referee #2

We thank referee #2 for the positive comments and suggestions. Many of the comments and suggestions have been taken into account and were helpful in improving the manuscript. See below for specific comments

RC - I have some general recommendations for the authors to improve the manuscript as they prepare it for resubmission. I found the paper to be lengthy relative to the material presented. In particular I feel that 13 figures and 3 large tables is somewhat excessive for a paper of this sort and that the manuscript could be trimmed without losing any important content while making the manuscript more succinct and readable. Specific suggestions for doing this are below.

AC - In referee #2's general comments, it was suggested to shorten the paper by removal of any unnecessary figures and/or tables. We agree that the paper is indeed long and have removed figures 5 and 11 (see specific comments). On the other hand, we do believe that the three tables, while large, are vital to this paper. Table 1 lists a summary of the burns and includes important information such as species burned, number of replicates, and some limited fuel characteristics. Tables 2 and 3 show the emission factors of the southeast and southwest fuels, respectively and although large, are necessary for summarizing our results and also demonstrate the scope of this work.

RC - . . .Another general comment is that linear regressions are used in the paper with minimal regard for the uncertainty associated with the fits – generating fit confidence intervals or uncertainties in fit parameters is part of many linear regression routines and these values should be used when comparing fits within this work or from previous work. This latter issue is of course is not a fault only with this paper, but I would like to see this work present details of fits and not over-interpreting regression results.

AC - The referee suggested the use of fit confidence intervals. We will report the fit uncertainties (1σ) in the graphs and also use these values for comparison of data sets in the discussion (see also specific comments).

Specific Comments (p16427, l5 refers to line 5 on page 16427):

RC - p16428, l23: A reference or references pointing the reader to evidence for, and the importance of, our poor understanding of HONO sources would be helpful. Is there evidence that direct emission from biomass burning may be an important source?

AC - The text has been changed to: "HONO is an important photolytic source of hydroxyl (OH) radicals; however, the mechanisms of HONO formation are not fully understood (Stutz et al., 2010; Kleffmann, 2007). Knowledge of the HONO formation mechanisms is important for modeling of the chemical processes as a plume ages. HONO has been observed as a direct emission from combustion processes (Finlayson-Pitts and Pitts (2000) and references therein)".

RC - p16431, l12: What was the approximate size of the wood chips?

AC - Previous text: The chipped understory hardwood ("cuh") samples were mostly larger diameter hardwood species (red maple (Acer rubrum), red bay (Persea borbonia) and loblolly bay (Gordonia lasianthus) that had been recently mechanically masticated into small chips. Changed to "...recently mechanically masticated. Our samples were of the smaller diameter pieces (less than ~5 cm) of various lengths (up to ~30 cm) as these are the components that are most likely to burn in a prescribed fire.

RC - P16435, l18 – 20: Were low-consumption fires included in emission factor calculations? Were any systematic differences observed in burns with similar fuels that had different fuel consumptions (e.g. the vertical/horizontal ceanothus burns)? Will burn extent have large effects on fire-integrated emission factors for different fuels? Are there implications for using these emission factors for modeling actual wild fires?

AC - The two replicates with the lowest fuel consumption, the vertically oriented ceanothus (3% fuel consumption) and chamise/scruboak (9.5%) were omitted from the analysis when determining average emission factors. The smoke from the biomass of these 2 burns was difficult to distinguish from the ignition sources. While there may be correlation between emission factors and fuel consumption, we do not believe we have enough data to provide a rigorous statistical analysis of the potential correlation. The fuel consumption could have an impact on the emission factors since the components of the vegetation burned (eg. foliage, grass, litter, woody material) may be related to fuel consumption, as we observed for HCl. These low consumption fires can occur naturally. We will add a few sentences regarding the effect of fuel consumption on EFs,

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specifically we will add the following: “The two replicates with the lowest fuel consumption, the vertically oriented ceanothus (3% fuel consumption) and chamise/scruboak (9.5%) were omitted from the analysis since the smoke from the biomass of these two burns was difficult to distinguish from the ignition sources. While there may be a correlation between emission factors and fuel consumption, we do not have enough data to probe the correlation statistically.“

RC - P16436, l3-4: What is meant by ‘higher mass loading and better heat transfer’? Is this because the fuel bed was more tightly packed? Is this a realistic burning geometry? This could bear more discussion.

AC - This statement was meant to reflect the higher mass loading and thus better heat transfer of the southeast fuels as they occur in nature. By mass-loading we are referring to the amount of biomass/area. We did not manipulate the mass loading of these fuel types in the lab. We changed the text at line 2 to read: “The southeast has higher annual rainfall and higher biomass production than the southwest, which can lead to denser fuel beds with more efficient heat transfer when the fuel is burned. Thus, most of our replicated southeast fuel beds burned well even in a vertical orientation.”

RC - P16436-37, l26-28 and l1-2: Making a comparison between your relationship and one with a R2 value of 0.15 is essentially meaningless. I’d suggest that at most you retain your comparison of average HCOOH emission factors for the two studies and note that the fuels and conditions (e.g. age of emissions) in the two studies are quite different.

AC - We agree that the HCOOH vs MCE comparison is statistically meaningless due to the high scatter. The comparison will be limited to the average values in the tables. Also, in the case of HCOOH, recent updates to the HCOOH reference spectrum have become available and while not impacting our data, will decrease the HCOOH in the other studies we referenced in the figure by a factor of 2.1. We will update the HCOOH graph accordingly, and note it in the discussion.

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RC - P16437, L23-26: The fact that a good portion of the NMOC is unidentified should be emphasized a bit earlier; otherwise your 'identified' OVOC/NMOC ratios could be misinterpreted. I think this should go after the first sentence in this paragraph, though the later discussion of the WAS results can remain further down.

AC - Agreed. We will do as the referee suggests and emphasize the unidentified NMOC earlier in the discussion.

RC - P16439, L17-23: This discussion is a bit sloppy. NOx is not 'a component of flaming combustion' – Higher NOx emissions are associated with higher temperature combustion through 'thermal' NOx production pathways. The fact that fuel nitrogen content will have a different impact on NOx production than MCE (with higher MCEs generally accompanying higher temperature combustion) should not be surprising (see e.g. http://en.wikipedia.org/wiki/NOx) and a discussion of the different NOx production pathways would be fitting here. The interaction is not simple, as you show in the figure, because fuel nitrogen content seems to be systematically related to the MCE achieved during a burn.

AC - It is not likely that thermal NOx contributes to the NOx formed in these fires and so was not considered. Thermal NOx requires flame temperatures >1,300 °C. While we did not measure the flame temperatures in these fires the flame temperatures in a high intensity biomass burning fire (such as a crown fire) are typically lower than 1,100°C (Butler et al., 2004) and the peak temperatures are usually of very short duration. We believe that the fuel nitrogen is the source for all nitrogen-containing emissions observed here. In fact, biomass is often co-fired with coal to reduce flame temperatures and decrease the NOx (and SO2) emissions from coal-fired combustion both due to the lower flame temperature and the also the lower N-content of the biomass. Sometimes fuels that tend to burn by smoldering are high in N content, which masks the MCE dependence of the NOx emissions.

RC - P16440, l3-17 and Figure 5: This figure is not necessary and doesn't contribute

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much to the manuscript. A more precise discussion of your fits (see comments in the last paragraph in the opening portion of this comment document) and that generated by Goode et al. would be more useful than the plot. Your results do not appear to be significantly different than those of Goode et al.; this can be tested statistically either by generating confidence intervals on your fit or parameter uncertainties. I'm not sure if Goode et al. provided enough information to do this for their fit as well, but it's definitely possible for your data.

AC - Upon consideration of the referee comments, Figure 5 will be removed and the discussion will be altered slightly. "(2009) plotted $\Delta NH_3/\Delta NO_x$ vs MCE compiled from other studies. While our results are similar to that of Goode et al. (2000) and the Flame 2 points of McMeeking et al. (2009) there is a large amount of scatter among the compiled data."

RC - P16442, l25-26: For context, it would be helpful to give reasoning/references to identify why you suspect this might be an important pathway for HONO production.

AC - In this discussion we were attempting to rule out the well-known production of HONO on the walls of the stack. Wall-produced HONO would yield a positive artifact that could not be explained from the fire emissions alone. The line has been changed to: "Since HONO can be formed on surfaces, we briefly examine the possibility of heterogeneous formation of HONO on the walls of the stack"

RC - P16442, L3: 'no obvious flow rate dependence' is a bit vague. Can you quantify this?

AC - It is difficult to quantify statistically as we only have a limited number of fires at lower flow rates. Only two fuels types had more than one run at both low and high flow rates. One actually showed a weak increase in HONO/NOx with flow whereas the other showed no effect on the HONO/NOx with flow rate. Thus we have no evidence that formation of HONO on the walls was significant in this experiment. This sentence will be changed to "no flow rate dependence".

RC - P16446, L25-26 and Fig. 11: Graph is unnecessary – just give correlation and parameter uncertainties.

AC - Figure 11 has been removed and the corresponding fit statistics will be noted in the text.

RC - P16449, L20-21: Switch order of N2 emission and ash sink as the former is likely the dominant end point for fuel nitrogen.

AC - fixed

RC - Tables 2 and 3: Include ‘N’ (number of experiments per fuel) as a row in these tables. Also, include a footnote that the sums of NMOC and OVOC here are only those identified by OP-FTIR

AC - The number of replicate burns is already included in Table 1 and would add unnecessary clutter and size to the EF tables. We will add a footnote regarding the NMOC and OVOC to Table 2 and 3.

RC - Figure 3: I’d like to see confidence intervals on your fits

AC - 1 sigma uncertainty have been added to the linear regression parameters in the graphs.

RC - Figure 5: Remove

AC - Figure 5 has been removed. See previous comment

RC - Figure 7: Largely just aesthetic, but why only include y-axis ticks/units for one of the spectra? I would show it for both or neither. . .

AC - Since the y-axis of Figure 7 is irrelevant for this discussion, the y-axis has been removed from both the top and bottom graphs.

RC - Figure 9: Switch order of laboratory studies so that yours is the bottom as it’s the basis of comparison. What do the bars signify? Presumably 1 sigma, but it’s somewhat confusing because you discuss a range in the text of 0.025 to 0.2 (e.g. P16443, L18-19) but the bars do not cover this range.

AC - The order of data points has been switched to put ours at the bottom. The bars are the 1 sigma standard deviation and will be noted in the caption. The full range of data points as discussed in the text extends beyond this 1 sigma range.

RC - Figure 10: This figure is of limited use because there is little systematic variation in HCl EF. The current discussion of HCl coming from leafy combustion (and perhaps a listing of fuel types with higher HCl emissions is likely more useful than having a figure that distracts the reader as the actual values are all in the table.

AC - The purpose of this figure is to show the lack of systematic variation, which is easier to see in a figure than in a table. We have already removed figures 5 and 11, but prefer to keep this figure.

RC - Figure 11: Remove

AC - Agree. Figure 11 has been removed in the final version

Technical Corrections:

RC - P16428, L28: 'The advantages of OP-FTIR include the quantification of. . .' should be 'An advantage of OP-FTIR is that it is able to quantify most. . .'

AC - fixed

RC - P16437, L14: 'identical to Yokelson et al. (2003)' should read 'identical to that presented in Yokelson et al. (2003)'

AC - fixed

RC - P16440, L15: 'fire-integrated MCE, compiled from several..' – remove comma.

AC - fixed

RC - P16440, L24-25: 'flaming combustion product'? – reword.

AC - The sentence: “We also included the flaming combustion product, HNCO, as measured by the NI-PT-CIMS (Roberts et al., 2010; Veres et al., 2010).” has been changed to: “We also included HNCO, observed during flaming combustion by NI-PT-CIMS (Roberts et al., 2010; Veres et al., 2010).”

RC - P16440, L26-27: ‘. . .measured by OP-FTIR, as well as. . .’ – remove comma or rework Sentence

AC - Comma removed

RC - P16441, L3: ‘obvious regional effect on..’ – this makes no sense, replace with ‘a clear variation in the nitrogen balance with the region from which fuels were gathered’ or something similar.

AC - The sentence in question has been removed and reworded to: “From Fig. 6 the fractional contributions. . .”

RC - P16445, L16-17: ‘These two studies. . .’: Move ‘to our knowledge’ the start of the sentence.

AC - fixed

P16445, L18: ‘list’ is more appropriate than ‘recommend’

AC - fixed

RC - P16448, L1: ‘from Camp Lejeune show’ should read ‘from Camp Lejeune fuels show’

AC - fixed

RC - P16448, L8-9: ‘Four of the samples at Camp Lejeune in North Carolina represent the effects of fuel treatments. . .’ should read ‘Four of the samples collected from Camp Lejeune in North Carolina represent fuel treatments. . .’

AC - fixed

RC - P16449, L3: replace ‘values’ with ‘emissions’

AC - fixed

RC - P166449, L9-15: this section should be tightened and made more clear

AC - Reworded: The non-methane hydrocarbon species measured here are important due to their reactions with oxidants in the plume. The significance of the large amounts of OVOC is that in addition to oxidation reactions, for many of these compounds photolysis is also important. Photolysis of these OVOC can make them an important source of additional oxidants in the plume (Singh et al., 1995).

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