

Response to interactive comments on “Biomass burning emissions and potential air quality impacts of volatile organic compounds and other trace gases from temperate fuels common in the United States” by J. B. Gilman et al.

We thank the reviewers for their thoughtful suggestions and their time improving this manuscript. Each reviewer comment is shown in *italics*. Our point-by-point responses appear after each comment in blue text.

Both reviewers were correct in noting that the emission ratios measured by the GC-MS that are presented in this manuscript were used as the basis for the emission factors presented in the synthesis paper by Yokelson et al. 2013. As described in Yokelson et al., the VOCs measured by the GC-MS instrument were scaled by the VOC-to-methanol ratio in order to estimate fire-integrated emission ratios from the discrete measurements. Fire-integrated emission ratios were then used to calculate fuel-based emission factors and were grouped into different fuel categories than those presented here. While both manuscripts fundamentally rely on the same dataset from all instruments described within this manuscript, the average emission ratios to CO that are presented in Table 2 are different from (but related to) those presented by Yokelson et al. (2013) and in the companion manuscripts by coauthors Burling, Roberts, Veres, and Warneke. We feel that the discrete emission ratios presented here provide complimentary information to the reader while the subsequent analysis of the dataset as a whole is entirely new.

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Anonymous Referee #1

General comments:

One aspect merits special attention though. If I have understood this correctly, the data presented in Table 2 are the same (ERs instead of EFs) as already given by Yokelson et al. 2013. The data are analyzed in a different context though (OH reactivity, SOAP), which is new. The former work also briefly touches upon methodical aspects (discrete sampling vs. continuous monitoring) conveying the same message as in the present work. I personally think that the manuscript conveys information in a concise and useful way even though a significant part of it is not truly new.

We have added additional language throughout the abstract, manuscript, and Table 1 further clarifying the relation between this study and concomitant manuscripts.

Specific comments:

Title: “temperate fuels”: Fuels cannot be temperate. Reformulate. Removed “temperate”.

Table 1:

As previously indicated to me by reviewers, “MS” should be used as an abbreviation for “mass spectrometry” and not for “mass spectrometer”. In other words, the term “MS” refers to the method and not to the instrument itself. When referring to the instrument, the phrase “MS instrument” (e.g. PIT-MS instrument) should be used.

Corrected. We have incorporated these changes throughout the manuscript where appropriate. In order to reduce occurrence of the word “instrument” after every mention of GC-MS, OP-FTIR, PIT-MS, PTR-MS or NI-PIT-CIMS we have defined within the text that these acronyms refer to the instrument identifiers in Table 1.

The term “sampling limitations” is incorrect. Other compounds are sampled but they are not or detected.

Corrected. We have changed the Table 1 column header from “Sampling Limitations” to “Detection Qualifications” in order to better describe the qualities of the species that can be detected by each instrument.

The use of the unit “a.m.u.” is deprecated.

Corrected. We removed all instances of “amu” when referring to mass to charge ratios.

“Protonated molecular mass” → “protonated molecule”

We keep the original phrasing “protonated molecular mass” which we equate to “the mass to charge ratio of the protonated molecule.” We have removed the phrase “or mass fragment” from the detection qualifications for the PTR-MS and PIT-MS.

“mass fragment” → “fragment ion” Corrected.

“protonated ion” → “protonated molecule” Corrected.

“deprotonated ion” → “deprotonated molecule” Corrected.

It is incorrect to use the term “identification” when using PTR-MS, PIT-MS, NI-PT-CIMS. These methods are not capable of identifying ions. Use “detection of the protonated molecule”, “detection of deprotonated molecule”.

Corrected. We have changed the word “identification” to “detection” when referring to the PTR-MS, PIT-MS, and NI-PT-CIMS instruments.

“Infrared Spectrometer” → “Infrared Spectroscopy” Corrected.

For details on MS nomenclature see: Murray et al., Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013), Pure Appl. Chem. 85(7), 1515–1609, 2013.

We thank the reviewer for this reference. This was very helpful!

Table 2: Does it make sense to report four significant digits after the decimal point?

We reported the mean and standard deviations to 4 digits after the decimal point in order to keep the table uniform and (in our opinion) easier to read.

Would it make sense to also report median ERs?

We considered this, but decided that it would make a very large table with an additional 5 columns (see comments from Reviewer #2) even more unwieldy.

Alkenes (Saturated, ..) → Alkenes (Unsaturated,..) Corrected.

HCN and HNCO are inorganic compounds.

We understand that some, including the reviewer, may classify HCN and HNCO as inorganic gases. We classified HCN and HNCO as (non-methane) nitrogen-containing organic compounds because they contain both carbon and hydrogen. This is a simplified and common definition of an organic species. Reclassification of these species would have very little effect on the overall discussion detailed in this manuscript with the exception of the molar mass emitted for non-methane organic compounds (e.g., Figure 5 a-c) where the contribution of nitrogen-containing organics to the molar mass emitted would be even smaller as HCN and HNCO would be excluded. We feel that it is better to keep these species in the discussion of non-methane organic compounds and choose to maintain our original classification of these species as organic.

Indicate in the table (e.g. asterisk or similar) which species have been calibrated and which have not!

Corrected. We have added asterisks after the species names in order to identify those where we estimated the sensitivities.

Table 3: Change unit in the VOC vs. CO (ppb/ppm)?!

Corrected. We have changed the units of the VOC to CO ratios from (ppbv/ppbv) as originally shown in Table 3 to ppbv/ppmv in order to be consistent with the units in Table 2.

Figure 1: "select gases"-> "selected gases" Corrected.

Text:

21716, 9: Health effects due to exposure to HNCO at relevant levels have not been demonstrated. Use "potentially harmful" instead of "harmful" for this compound. Corrected.

21716, 19-27; 21717, 1-10: The tutorial on tropospheric gas-phase chemistry is excessive in length and not strictly relevant for this work. I suggest shorting this paragraph and introducing the concept of OH reactivity here.

We appreciate this suggestion and had made the following changes: We have removed the text on P21716 L21-P21717 L2. We have added additional text to read, "Due to the complex relationship between O₃ production and VOC/NO_x ratios and peroxy nitrates, we use OH reactivity as a simplified metric to compare reactivity of all measured gaseous emissions by fuel region in order to identify the key reactive species that may contribute to photochemical O₃ formation."

21717, 11-27: The tutorial on SOA and SOA formation is excessive in length and not strictly relevant for this work. I suggest shorting this paragraph and introducing the concept of SOA formation potential here.

We appreciate this suggestion and had made the following changes: We have removed the text on P21717 L15- L23. We relocated the text on P21736 L8-14 to the introduction.

21718, 14: revise number of inorganic gases (HCN, HNCO).

The original number is maintained as per above discussion.

21718, 17: "spectrometer (GC-MS)"-> "spectrometry (GC-MS) instrument" Corrected.

21719, 3: "cursory". I have never seen a cursory analysis by Bob Yokelson!

The reviewer is correct! We have replaced the text, "Yokelson et al. (2013) focused on retrieving an improved set of emission factors for prescribed fires by coupling lab and field work, but they performed only a cursory analysis of the atmospheric impacts." with the following, "Yokelson et al. (2013) synthesized the results of all the measurement techniques, including the GC-MS data presented here, in an effort to compile an improved set of fuel-based emission factors for prescribed fires by coupling lab and field work."

21719, 9: "SOA potential"->"SOA formation potential" (I know the term "SOA potential" has been used previously but I still think it is incorrect). Corrected.

21719, 1: Heading: use "2 Methods" instead of "2 Experimental"; analysis methods should also be given here (see below). Corrected.

21720, 24-27: “spectrometer”->“spectrometry instrument” Corrected.

21722, 5: *Why was an ozone scrubber used? Briefly describe and discuss CO₂ and H₂O scrubbing (large CO₂ concentrations in BB samples, loss of water-soluble analytes?)*

We have added the following text, “While ozone traps were not required for these experiments, they were left in sample path in order to be consistent with other ambient air measurements and laboratory experiments using this instrument.” Details of the water, CO₂, and O₃ traps are included in the stated references (i.e., Goldan et al., 2004). All calibrations, instrument tests, ambient air measurements (e.g., stack backgrounds and Fourmile Canyon Fire samples), and biomass burning samples were collected with the same traps and trapping temperatures. Losses of lower vapor pressure and/or water-soluble species to the water trap or surface effects from the O₃ traps have been accounted for during calibration regardless of the sample type.

21722, 13: *“atomic mass units”; use of this unit is deprecated.* Corrected.

21722, 19: *How did the experimenters decide when to take the sample? Did they follow CO and CO₂ on-line and manually activate the sampler based on their experience?*

We have added the text, “...as determined by visual inspection of the fire in addition to the real-time measurements via PTR-MS.”

27125: *The Results and Discussion section contains lots of methodical information (e.g. how to calculate MCE, degree of unsaturation, emitted molar mass, OH reactivity, SOA formation potential.). The methods of data analysis should also be included in chapter 2.*

We agree with the reviewer and have incorporated the suggested changes. We added sections 2.4.2 to 2.4.6 and included all equations and descriptions of methodologies (i.e., MCE, D, OH reactivities, and SOA formation potential) that were originally included in the Results and Discussion section to the Methods section.

27128: *It is crucial to take the sample at the right time. Briefly discuss this aspect.*

Our analysis of the discrete vs. fire-integrated emission ratios (ERs) show that it was important to collect samples at various stages of the replicate burns in order to best characterize the emissions when fire-integrated sampling strategies are not possible.

21730, 2: *revise number of inorganic gases (HCN, HNCO).*

The original number is maintained as per above discussion.

21730, 16: *“degree of unsaturation”. In mass spectrometry, the use of the term “ring and double bond equivalent” (RDB, or RDBE) is recommended (see Murray et al., 2013).*

We have added the text, “The degree of unsaturation (D) is also known as “ring and double bond equivalent” (Murray et al., 2013) and is equal to...” Murray defines RDB as “the degree of unsaturation” so we have opted to keep the term “degree of unsaturation” throughout the discussion.

21732: *The authors use the term “molar mass emitted” but many gases were not measured (e.g. N₂, H₂, N₂O, SO₂, : :). It should be stated more clearly that the given percentages refer to the molar mass that was measured. Give an estimate of the percentage of non-measured gaseous species.*

The reviewer is correct in pointing out this analysis only includes the mass of the species that were detected by the suite of instruments used here. We have changed the section header to “Molar mass of measured emissions” and added additional qualifiers throughout the text where appropriate. P21732 L21-26 and P21733 L1-25 directly answer the reviewer’s questions on the nitrogen and carbon budgets. In short, about one-half of the fuel-nitrogen was unaccounted for in the emissions and ~1% of the carbon mass remains either unmeasured or unidentified and was therefore not included in this analysis.

21733, 27-28 and 21734, 1-14: *Introduce concept of OH reactivity in chapter 1 and give methodical details in chapter 2. Only present results here. Corrected.*

Text on P21734 L5-14 was moved to the methods section 2.4.5 as detailed above.

21736, 6-22: *Introduce concept of SOA formation potential in chapter 1 and give methodical details in chapter 2. Only present results here. Corrected.*

Text on P21736 L6-23 was moved to sections 1 or 2.4.6.

21738, 9-14: *This statement should go elsewhere.*

We have opted to keep this statement where it is.

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Anonymous Referee #2

General comments:

1) *The observations have already been reported in a series of papers. While the manuscript does mention these papers in the introduction, it initially appeared to me that they were just referencing previous studies that they would compare with some new observations. I had read through most of the paper before I realized these were all the same data. The authors should make it clear that ALL of the fire lab observations in the paper have previously been described.*

We have added additional language throughout the abstract, manuscript, and Table 1 further clarifying the relation between this study and companion manuscripts.

2) *Since emissions are given as a ratio to CO, it is important that the CO emission is relevant to “real” fires. Is there any indication that this is the case? How does the CO emitted per fuel mass burned relate to what is observed in the field for fires from these different regions?*

This study utilizes VOC/CO emission ratios which are not strongly dependent on the overall mass of CO emitted per fuel mass burned (i.e., the CO emission factor). Comparison of the VOC/CO emission ratios from the Fourmile Fire (Table 3) generally agree to within a factor of 2 with the mean ERs observed for the northern fuels (a more similar compilation of fuels than the southeastern or southwestern) suggesting that the laboratory studies are adequate representations of “real” fire emissions. Further information on the comparison of fuel based emission factors from these laboratory studies and field observations is addressed by Yokelson et al. (2013) who showed that there was good agreement between laboratory and field measurements for “pine-understory fuels”, but that the EFs were lower for “semiarid shrubland fuels” in the lab.

3) *What fraction of Table 2 was quantified by each of the instruments? How did you choose which instrument to use when there was more than one choice? What would be lost if you did not have all 5 systems? For example, I see “+” listed on only 3 compounds and all of them can be analyzed by GCMS. Does this suggest that there is no need for PTRMS and PITMS for determining emission factors?*

Table 2 details what species were measured by each instrument. The vast majority of the number of compounds were quantified by the GC-MS as it provided unparalleled speciated chemical information, but on a restricted timescale. The few species that were measured by multiple instruments aided in characterizing and comparing the instrument responses. If a species was measured by more than one instrument, we reported the emission ratio from a single, designated instrument based on the number of fires sampled as well as the comparison results (e.g., Figure 2). For example, ethyne is measured by the GC-MS but the m/z 26 used to quantify ethyne was not included in total ion scans; therefore, we report ethyne from the OP-FTIR in Table 2. Another example is furan, which was quantified by the GC-MS as reported in Table 2. The OP-FTIR measurements of furan had small spectral interferences and m/z 69 measured by the PTR-MS represents the sum of several species in addition to furan. For cases where all else was equal (e.g., ethene, benzene, or methanol), then the GC-MS data was used to ensure the most consistent data set possible.

4) on P21721, line 5: I would expect it would be difficult to get these compounds through an unheated sample line? Have there been any tests to look at this?

Species such as the benzenediols, phenol, and cresols were measured by the PIT-MS or NI-PT-CIMS which both had very short inlets. Warneke et al. (2011) presented a comparison of masses measured by the PIT-MS and the PTR-MS, where the inlets were of similar design (unheated, 1/4" o.d. PFA) but of different lengths (< 2m for the PIT-MS versus 20 m for the PTR-MS) showing that there were no systematic losses for the higher molecular weight species through the longer fast-flow inlet. Additionally, all VOCs quantified by the GC-MS, including species such as benzaldehyde, were calibrated using a sample line of equivalent length and type as that used at the Fire Lab.

5) Section 3.2: Why not collect a sample for the GC that includes the whole burn? The way the GC sampling is presented in the manuscript gives the impression that the GC can only capture a discrete sample and so cannot characterize the fire integrated value. But this was the case for this study only because you didn't sample for the entire burn. It should be made clear in the text that it is possible to characterize the fire integrated value with GC if you integrated the sample over the entire burn.

The GC-MS used in this study was not designed to collect in-situ samples longer than 300 seconds. Modifying the existing instrument would have required considerable effort particularly in characterizing the trapping efficiencies of such a wide range of concentrations and highly reactive species over extended sampling times. We acknowledge that other GC-MS instruments or sampling strategies could be employed in order to collect a fire-integrated samples; however, that was not possible for this study. We have added text to section 3.2 to reflect that this was a limitation of the instrument and not the technique.

6) section 3.2: How common is this bias (discrete sampling that did not characterize the entire burn) in past studies? Would it change any of the emission factors used in models if this was accounted for? Could the biased values be adjusted and still useful?

These are great questions, but cannot be accurately answered without an exhaustive literature search. As noted previously by the reviewer, this is a non-issue for laboratory studies if biomass burning samples could be collected over the course of the biomass burn such as that for the real-time measurement techniques (e.g., OP-FTIR and CIMS). Discrete sampling is a common method for ambient air analysis for any instrument that requires a pre-concentration step such as that for most chromatography-based systems, so it is possible that other studies have used a similar sampling strategy. In the field this is not as important an issue because the emissions from different combustion processes are happening simultaneously and the biomass burning emissions are also mixed during transport. The primary goal of section 3.2 was to show

that the discrete sampling strategy of the GC-MS used in this study was still able to adequately characterize the emissions of a wide range of compounds.

7) Page 21730 line 24-26: *How do you know there are differences are due to region? If you had samples for different ecosystems within each region then you could investigate this. With the data presented here it can be shown that there are differences between fuels from some different landscapes but I don't see evidence that these are characteristic of the whole region.*

We have classified the fuels by the general geographical regions that they were collected in, but we did not mean to imply that the results presented here are characteristic of all ecosystems within these large geographic regions. We have added text throughout the manuscript where appropriate to help further clarify this point. For example, we have changed the text from "...the distribution of ERs are unique to each fuel region" to read "the distribution of ERs are unique for the fuels measured from each fuel region."

8) Page 21730: *The text makes it clear that emissions from these fuels are different but not why. Any ideas on why they are different?*

Generally, emissions differ for different fuel types based on the molecular structure of the fuel itself (i.e., cellulose, lignans, etc.). Additionally, different fuel types burn differently. For example, emissions from grasses and small woody fuels are typically occur due to flaming combustion.

9) Page 21734, line 15: *It is impressive that OH reactivity was found for all of these compounds. One of the most important contributions that this paper can make is to list the OH reaction rate of each compound and include this in Table 2. That would be a valuable resource for readers of this paper.*

We have added all of the OH reactivities that were used in the calculations presented here. These values appear in Table 2 under the column heading "kOH", where asterisks (*) indicate the kOHs that were estimated.

10) Section 3.3.3: *Was a SOAP calculated for each compound in Table 2? How does this compare to other reported SOAP for the most important contributors to total SOAP?*

The SOAP values in the analysis presented here are the same as those presented by Derwent et al. (2010). We have added those values to Table 2 under the column heading "SOAP", where asterisks (*) indicate estimated values.

11) Table 2: *Provide the units for the "SW" columns. It is presumably mmol(mol CO)⁻¹ but it would help the reader to make this clear in the table. Corrected.*

12) Figure 2: *When it states "GC-MS vs OP-FTIR", I assume it means the ratio of GC-MS value to the OP-FTIR value but it is not clear. If they are ratios then state this.*

As stated in the Figure caption, each marker represents the slope and correlation coefficients determined from correlation plots of all samples. We maintain our reference to the slope rather than ratio to be most accurate. Neither "slope" or "ratio" will fit into the figure legend so it was included in the figure caption.

13) Fig 7: *what is the line? It is not described. Is it needed?*

The lines in Figure 7 are the best fit lines of the Fourmile Canyon Fire samples with the slopes (S) and fit coefficients (r) listed beneath the compound names in each panel. This is now clearly stated in the figure caption.

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Summary of Major Changes

Portions of the text that originally appeared in Section 3 were moved to Sections 1 and 2, which was expanded to include calculations of modified combustion efficiency, degree of unsaturation, OH reactivity, and SOA formation potential.

Portions of Table 1 have been revised per the reviewer's suggestion.

Table 2 was expanded to include kOH and SOAP values per the reviewer's suggestion. We have revised the kOH values of furans to those published by Bierbach et al. (1992) in place of the theory-based analysis by Grosjean and Williams (1992) that was originally used in our analysis. This change results in an overall reduction in the VOC-OH reactivity of the furan subgroup by 10% for the southeastern fuels and ~30% for the southwestern and northern fuels. Overall, the total VOC-OH reactivity decreased by 2-7%. Figure 2d-f has been updated to reflect these changes. We note that our discussion and conclusions are not affected by these changes.

Table 3 has been revised to include the VOC to CO slopes in units of ppbv per ppmv CO and kOH values of furans from Bierbach et al. (1992).