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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires" *by* R. J. Yokelson et al.

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We thank both Referees for their helpful comments. We address the comments as best we can without unduly lengthening the paper. In this effort we are aided by the fact that two closely related papers cited as "in preparation" in the version of this work posted on ACPD are now submitted and in one case available on the ACPD website. Those papers provide important details relevant to this work.

Anonymous Referee #1

R1.1. In this paper, the authors perform a thorough analysis of previously published emission data from laboratory and field fires to derive an internally consistent set of emission factors for a very large number of gaseous and particulate smoke components. The results can be expected to provide a substantially better data base for emissions from prescribed burning, and should be very useful for air quality modeling. Of great interest is the fact that emission estimates for a large number of unidentified, but potentially important substances, which showed up in the mass spectra, are included. I recommend publication with just a few minor revisions.

Specific comments and technical corrections:

Page 21529, line 10ff: The airborne PM2.5 measurements used an indirect technique (measurement of the scattering coefficient). I would like to see a quantitative assessment of the errors and uncertainties that arise from this technique. If this is detailed in the reference given (Burling et al., 2011), at least a brief summary would be desirable.

A1.1. The uncertainty in the nephelometer based PM2.5 is discussed in detail in Yokelson et al 2007 and again in Burling et al., 2011, which is the supplied reference. The details of that assessment are summarized in our final response below, but in the interests of not lengthening the paper we plan to simply modify the text to include that the uncertainty in the nephelometer-based field measurements of PM2.5 is about 20%.

P21529, L11-13: Original text: The airborne field measurements of PM2.5 were based on the ratio of light-scattering to CO2 and a gravimetric calibration of the nephelometer as described by Burling et al. (2011).

New text: The airborne field measurements of PM2.5 were based on gravimetrically-calibrated light-scattering measurements and they were likely accurate to ±20% (Burling et al., 2011).

Background: The uncertainty associated with our airborne determination of PM2.5 based on light-scattering can be partially assessed from the standard deviation of the mean conversion factor measured when we compared nephelometer data to gravimetric filter sampling in smoke from a selection of wildland fuels prior to the airborne campaign: (208800 ± 11900 (2σ) μg sm 2), which would imply ~6% uncertainty at the 95% confidence level. A more conservative approach considers the different conversion factor derived from an independent airborne sampling comparison between the same model nephelometer and gravimetric filter sampling in smoke from an Alaskan wildfire: Nance et al., (1993) obtained a conversion factor of 250000, which is 16.5% larger than our factor. Finally, Trent et al., (2000) found that the Nance et al conversion factor reproduced gravimetric particle mass measurements for a variety of wildland fuels burned in lab fires within ±12%. Additionally, in a comparison on one of the field fires in this study (Akagi et al., 2012a), the sum of organic aerosol, chloride, ammonium, nitrate, sulfate, and black carbon measured on the aircraft by an aerosol mass spectrometer (AMS) and single particle soot photometer (SP2) was reported to be about 80% of the PM2.5 inferred from the light-scattering, but the PM2.5 also contained metals not measureable by the AMS or SP2. A note of caution is that much different conversion factors between scattering and gravimetric-mass (e.g. ~500000) have been measured for cooking fires that produced high black carbon emissions as discussed by Christian et al. (2010) so the conversion factor we used for wildland fuels should not be applied unthinkingly to all global biomass burning. Considering all the available data, we feel that an error estimate of 20% is reasonable and should be included in the revised text.

R1.2. Page 21541, line 4ff: There appears to be a discrepancy between what is said in the text and what is actually in Table 1. The text states that two techniques of converting lab to field EF are given in the table. But the table actually shows the lab data, the results of the MCE method of transformation, and the ratio of the lab/field averages. This is quite confusing to the reader.

A1.2. (We assume the Referee meant to say the table shows the field data.) The lab/field averages that are shown in Table 1 are actually the basis of how the simple,

second method of transformation is developed, but this needed to be stated a lot more clearly in the text. To accomplish this we added text at page 21541, line 4 as follows:

Old text: "In Table 1 we show the results of treating our current lab and field EF with both approaches previously used to "transform" lab EF to field EF. CO and . . ."

New text: "In Table 1 we show the results of treating our current lab and field EF with both approaches previously used to "transform" lab EF to field EF. Specifically, columns 5, 6, 11, and 12 show the predictions of the lab MCE-based equation adjacent to how those predictions compare to the field data for the pine and semi-arid ecosystems, respectively. Columns 7 and 13 show the lab/field EF ratios for the two ecosystems. The inverse of the average ratio for each ecosystem is the simple correction factor in the approach employed by Yokelson et al., (2008). CO and . . ."

Then on page 21542, L2-4: We added the following change: Old text: "As a result, we suggest that dividing the lab EFs for smoldering compounds by 0.37 (or multiplying by 2.7) is the preferred way to predict the EFs expected in the field for semiarid shrubland fires."

New text: "As a result, we suggest that dividing the lab EFs for smoldering compounds by 0.37 (see the bottom of column 13) or, equivalently, multiplying by 2.7 is the preferred way to predict the EFs expected in the field for semiarid shrubland fires."

R1.3. Page 21546, line 6ff: The authors state that the present emission estimates and those by Akagi et al are much larger than "widely used previous estimates". It would be of interest to know what these estimates are and have the references stated. Koppmann et al. (2005) and Andreae and Merlet (2001) come to mind.

A1.3. There is a complex back story here and including all the details may be beyond the scope of this paper. Andreae and Merlet (2001) provided a global estimate of non-methane hydrocarbons (NMHC) from biomass burning of 100 Tg/yr, which is about 4-7 times lower than the estimate of total non-methane organic compounds (NMOC) of

Akagi et al., 2011. The discrepancy arises because the Andreae and Merlet estimate was explicitly for hydrocarbons only and did not include oxygenated volatile organic compounds (OVOC). When one incorporates the data provided by Andreae and Merlet for OVOC, an estimate for NMOC a little below that of Akagi et al is obtained. Allowing for unidentified species would make the estimates even closer. Unfortunately, the real NMOC estimate implied by the Andreae and Merlet 2001 data appears to have gone un-noticed by many users who mistook the NMHC estimate as the equivalent of an NMOC estimate. This is all discussed in Akagi et al. (2011). In summary: it's important to point out that this work shows that NMOC from biomass burning have been underestimated in global models, but we don't want to interrupt the flow of this section or reference Andreae and Merlet when the problem lies with a misinterpretation of their work rather than any shortcoming of their work. In addition, the details are in the provided reference. Thus, we plan the following simple change at P21546, L7:

Old text: "The global NMOC estimate of Akagi et al. (2011) was 4–7 times larger than widely used previous estimates, but it is strongly supported by this work suggesting that global model runs with much larger NMOC emissions per unit mass of biomass burned are needed."

New text: "The global NMOC estimate of Akagi et al. (2011) was 4–7 times larger than some previous estimates of organic trace gas emissions from fires that ignored oxygenated organic compounds and unidentified species, but it is strongly supported by this work suggesting that global model runs with much larger NMOC emissions per unit mass of biomass burned are needed."

R1.4. Page 21547, line 15ff: The EC/TC ratios seem indeed high. Given that there are numerous publications that show the possibility of huge errors in EC measurements in biomass smoke aerosol (as much as a factor of ten!), a thorough discussion of the potential measurement bias is required.

A1.4. High errors for EC on filter samples of smoke have indeed been seen using

the thermal method especially when high K+ is also present. The main issue with the thermal optical method we used is artifact EC produced by charring of OC. This can introduce a large error in EC mostly when EC is much smaller than OC as is usually the case with biomass burning. However, it is a less serious issue when EC/OC is very high as for these fires. Thus, we are confident that the high EC/TC is due to the higher-than-normal MCE as already stated in the text. In addition, the cited paper describing the EC/OC measurements is now submitted to JGR and will soon be available with all the details and a discussion of errors showing that they are small.

Anonymous Referee #2

R2.1. General Comments: This discussion paper gathers a large data set of biomass burning studies, in the laboratory and at the field with prescribed burnings, and calculates from those studies emission factors (EF) for a large number of identified and tentatively identified or unidentified compounds, for controlled field fires. The authors, with basis on comparison of various burning and environmental parameters, translate the results from controlled laboratory experiments to the estimation of EFs for hundreds of organic compounds (mostly in the gaseous phase) in real field fires, using measured campaigns of prescribed burning as testing experiments to adapt laboratory estimated values to external field emissions. The manuscript provides a very large data set, mostly of it already published in previous papers, and by using state of the art mass spectrometers, capable of identifying, tentatively identifying or through detection of unknowns, are able of demonstrating that there is an enormous amount of organic compounds, most of them previously (or still) unknown, that are emitted from field fires. These compounds being oxygenated, semivolatile, etc., presumably have an important role in photochemical and gas to particle conversion processes in the regional and global atmosphere impacted by transport from emission sources. The authors discuss and show that emission rates and composition are highly dependent, not only from the fuel type, but also from burning conditions. Therefore they have to adapt estimated EFs from laboratory experiments to field conditions by using the results from prescribed fire campaigns as calibration examples. However it is necessary to account for the fact that prescribed fires are always done in periods of the year (season) and weather conditions that, although permitting the progress of burning, are impeditive of uncontrolled fire behaviour. Therefore I have doubts that emission factors adapted to prescribed fire conditions are representative of wild fire emissions. Of course that the authors always refer to emission factors estimation for prescribed fires, not wild fires; but then I would like to have in the paper a discussion about the representativeness of prescribed fire emissions by comparison with wild fires and, or, the importance of prescribed fires as sources of pollutants in the regional/global atmosphere.

A2.1. We agree that both the applicability and the context of this work should be very clear. Thus, we plan the following improvements at various locations in the paper:

1) P21522, L10: Insert sentence before "The" – "Small, unregulated anthropogenic fires in the tropics account for most of the global biomass burning while prescribed fires account for more fuel consumption than wildfires in the southeast US and wildfires consume more fuel than prescribed fires in the western US and globally in boreal ecosystems (Wiedinmyer et al., 2011)."

2) P21542, L8: The Sect. 3.3 title is too broad. Change from "Biomass burning emission factors for temperate ecosystems" to "Emission factors for prescribed fires in temperate ecosystems"

3) P21542, L10-12: Change: " ... for field fires in pine forest understory, semiarid shrubland, coniferous canopy fuels, and organic soils." To " ... for prescribed fires in pine forest understory and semiarid shrubland and fires in coniferous canopy fuels and organic soils."

4) See also our addition to the conclusions detailed in our reply to the last Referee comment below.

In addition, note that through-out the paper we digress from our results to describe

how wildfires may be different. E.g. (i) our inclusion of RSC results in the figures; (ii) P21544, L23-25 where we note that higher NMOC/PM2.5 may be applicable for wildfires; (iii) P21549, L20 where we point out higher fuel consumption on wildfires; etc.

R2.2. The paper is somehow too long with some repetitions and, with some effort, it could be pruned and made more linear and easy to read. Some of the discussions (see for example section 3.6) direct the reader to Tables in the annexed section, in order to fully understand the paper presentation. In my opinion this is not correct; supplementary material should only be provided as complementary information for other uses.

A2.2. We agree paper is long and have attempted to control the length by moving some material that is previously published or very extensive to the supplement. Moving it back to the main paper might be convenient for the reader, but would also substantially lengthen the paper. Unfortunately, there really is no way to include all the relevant info from the 20 or so related papers and some data is easier to use/browse as a downloadable spreadsheet than it is as huge journal table. Also, most of the Referee comments specify errors of omission. Thus, without specific pruning suggestions we prefer not to guess at further material that we could cut without negative effects.

R2.3. Specific comments: Page 21524, line 10 – Substitute "for modeling; we employ" with "for modeling, we employ"

A2.3. Thank you, we changed the semi-colon to a comma

R2.4. Page 21525, line 8 – Akagi et al.(2012b) is a paper in preparation- what does that mean? Is it already submitted?

A2.4. We will update the text to reflect that this paper is now available on ACPD: http://www.atmos-chem-phys-discuss.net/12/25255/2012/acpd-12-25255-2012.html Also we will update the references as shown:

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and variable O3 formation rates in some South Carolina biomass burning plumes, Atmos. Chem. Phys. Discuss., 12, 25255-25328, doi:10.5194/acpd-12-25255-2012, 2012.

R2.5. Page 21528, lines 10-11 – Hosseini et al. (2012)- another paper in "preparation"

A2.5. We will update "in preparation" to "submitted" Hosseini, S., Urbanski, S., Dixit, P., Li, Q., Burling, I., Yokelson, R., Johnson, T., Shrivastava, M. K., Jung, H., Weise, D., Miller, W., and Cocker III, D.: Laboratory characterization of PM emissions from combustion of wildland biomass fuels, submitted to J. Geophys. Res., 2012JD018904, 2012.

R2.6. Page 21531 and following, Section 2.2 - Data reduction approach - The section deals mostly with emission factors and or emission ratios for CH3OH and HCOOH and there is an important discussion in relation to CH3OH; but there is no discussion in relation to HCOOH! In this section it is also discussed the conversion of signals for unknown compounds detected into total VOC mass ; using of a simple total VOC analyzer based of FID detection could not help in the job?

A2.6. The HCOOH comparison is excellent as already shown in detail in Veres et al., (2010a). In the interests of saving space we do not repeat the comparison in this paper and just provide the reference. Total VOC analyzers have a poorly characterized response to substituted hydrocarbons (e.g. organics with N or O) and thus the uncertainty in total VOC would be similar to that from the full mass scan, while also not providing any details on the mass and probable properties of the detected total VOC. Older papers that deployed TNMHC analyzers have consistently reported sums similar to the sums from our full mass scans, but again without the useful partitioning by mass. Nonetheless, we have recently co-deployed a THC analyzer with a PTR-TOF-MS and

will report on the comparison in future papers.

R2.7. Page 21534, equation 1 – too many significant digits?

A2.7. Rounding off the intercept so that both "coefficients" in equation 1 have three significant figures (0.0824 and 1.38) changes the predicted number of carbon atoms (after rounding off "n" to the nearest whole number) for just one MM, which is MM35 and we report no data for MM35. Thus, we have dropped one digit in the intercept and the r-squared value. We trust it is clear that the equation is only meant to produce a reasonable estimate.

R2.8. Page 2154, lines 6-136 - HCN is introduced as a flaming compound but from the discussion comes out as a smouldering compound – please rephrase.

A2.8. P21540, L7-12:

Old text: HCN is important as a biomass burning tracer and in some studies is associated with both flaming and smoldering combustion (Akagi et al., 2011). In this study HCN was strongly associated with smoldering combustion in both the lab and field in both ecosystems as shown by its increasing EF at lower MCE (bottom row Fig. 3).

New text: HCN is an important biomass burning tracer that was associated with smoldering combustion or both smoldering and flaming combustion in past studies (Akagi et al., 2011). In this study HCN was strongly associated with smoldering combustion in both the lab and field for both ecosystems as shown by its increasing EF at lower MCE (bottom row Fig. 3).

R2.9. Subtitle of Fig 2 and 3 – describe RSC (Residual Smoldering Combustion); in the text, page 21540, some discussion could be introduced about the quite different EF values for RSC in Figures 2 and 3

A2.9. This comment revealed to us that we had not described RSC in the text, which should be done for context/boundary-conditions even though it is not a focus of the study. This is addressed in several locations:

1) A search for first use of RSC finds it on page 21529, line 22. The existing text was: " . . .we were able to use ground-based FTIR to measure a suite of gases emitted by residual smoldering combustion (RSC) (Burling et al., 2011). This aspect of the study has high general importance because RSC can account for much or most of the fuel consumption by some wildfires . . .."

We will expand that a bit as follows:

" . . .we were able to use ground-based FTIR to measure a suite of gases emitted by residual smoldering combustion (RSC) (Burling et al., 2011). RSC can be loosely defined as combustion producing emissions that are not lofted by flame-induced convection. RSC emissions have high general importance because they can account for much or most of the ground-level air quality impacts and fuel consumption by some wildfires . . .."

2) Then on page 21540, lines 14-17: we eliminate the second definition of RSC and explain why the emissions are different:

Old: "The plots for the pine-understory fuels in Figs. 2 and 3 also show the residual smoldering combustion (RSC) EF measured from the ground (Burling et al., 2011) for context and because of the potential high contribution of RSC to wildfire emissions that we noted earlier."

New: "The plots for the pine-understory fuels in Figs. 2 and 3 also show the RSC EF measured from the ground (Burling et al., 2011) for context and because of the potential high contribution of RSC to air quality impacts and wildfire emissions that we noted earlier. The RSC measurements are of individual smoldering fuel elements rather than a blended convection column and thus do not normally fit the pattern established by airborne measurements (Akagi et al., 2012b)."

3) In the caption for Fig. 2: We append the sentence: "The "Grd" (green symbols) indicate data for residual smoldering combustion provided for context (see text)."

R2.10. Page 21542, line 22- there is no reference for Veres et al., (2011)

A2.10. Thank you, this was actually the wrong reference and should have been "Roberts et al., (2010)" since their Figure 8 shows HNCO as a flaming compound.

P21542, L22: change "Veres et al., (2011)" to "Roberts et al., (2010)"

R2.11. Page 21543, lines 24-26 – Coherence in the presentation of numbers (as digits or with letters)

A2.11. P21543, L25: change "$\sim$9" to "about nine"

R2.12. Page 21547, lines 26-28 – There are some other published results concerning OC and EC, at least for south Europe (see for example Alves C.A., Gonçalves C., Pio C.A., Mirante F., Caseiro A., Tarelho L., Freitas M.C., Viegas D.X. (2010) Smoke emissions from biomass burning in a Mediterranean shrubland. Atmospheric Environment. 44, 3024-3033. http://dx.doi.org/10.1016/j.atmosenv.2010.05.010)

A2.12. A major goal of this paper is to present a lab/field comparison that is narrowly focused on our specific measurement sites, but also to place that comparison in a broader context. Thus, our use of the word "similar" was not precise enough and we modify the text to reflect that as shown below. In addition, the reference suggested by the Referee contains results (EC/TC of 0.0033 at an MCE of 0.99) that differ widely from other literature results and are somewhat relevant since the Mediterranean shrubland ecosystem is related to our chaparral fuel type. They serve as an example of variability in reported biomass burning emissions that we now cite in the conclusions to recognize the broader context.

1) P21547, L27: Old text "To our knowledge, the only published peer-reviewed field study of emissions from similar fuels that reports aerosol OC and EC or black carbon (BC) is Akagi et al. (2012a)."

New text "Akagi et al. (2012a) made field measurements of aerosol OC and EC or black carbon (BC) from one of the same semiarid shrubland fuel types we sampled in the lab as part of the series of studies synthesized in this paper."

2) P21552, L23, add "(e.g. Alves et al. 2010) or for wildfires" after "other areas"

Authors note: We made some small voluntary changes to improve the paper listed next:

1) P21523, L7-8: "Veres et al., 2010" should be "Veres et al., 2010a"

2) P21523, L10 "is" should be "are"

3) P21530, L4 change "," to ";" after "foliage"

4) P21537, L23: change "study" to "studies"

5) P21538, L11: add "trace gas" before "emissions" as emissions of metals in PM are often highly fuel dependent.

6) P21538, L24 add "trace gas" before "EF" for same reason s above

7) We take several steps to recognize and cross reference to a paper in progress from this series of studies that should be posted on ACPD by the time this paper is finalized:

P21546, L25-26: Old text: "Following that approach a more comprehensive assessment is now possible using the data we present in Table 2."

New text: "Following that approach a more comprehensive assessment of firefighter exposure is now available based on the data we present in Table 2 coupled with measurements of CO on the perimeter of South Carolina prescribed fires (Akagi et al. 2012c)."

We add the following to the reference list:

Akagi, S. K., Burling, I. R., Johnson, T. J., Cameron, M., Griffith, D. W. T., Mendoza. A., Weise, D. R., Reardon, J., Maitland, J., and Yokelson, R. J.: Field measurements of trace gases emitted by prescribed fires in southeastern US pine forests using an open-path FTIR system, in preparation, Atmospheric Chemistry and Physics Discussions,

2012c.

And on P21547, L9-10: to recognize that the assessment has been done, but not perhaps overstate its significance: change "the data in Table 2 could contribute significantly to such an effort." To "the data in Table 2 contributes to such an effort."

8) We have adopted a more consistent and conventional nomenclature for the compound names in a new Table 2.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 21517, 2012.