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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "New emission factors for Australian vegetation fires measured using open-path Fourier transform infrared spectroscopy – Part 1: methods and Australian temperate forest fires" *by* C. Paton-Walsh et al.

Anonymous Referee #3

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This is a good paper, the data is useful, and it should be published. However the presentation can be improved in my view. Currently about 29 pages (including 6 tables) are devoted to methods, error, fire description, and some speculation about things outside the scope of this experiment. Then the discussion about the representativeness, novelty, uses, etc of the final results is only three pages. For instance, the authors recommend that their data should replace data currently used for Australian forest fires when some users might prefer to include this new data weighted into in an evolving literature average. Or some may prefer to use the data for modeling "small hazard reduction burns." I offer more thoughts on discussion items in the detailed comments below. My thought would be to shift the balance by reducing the first 29 pages (delete some stuff and move some stuff to supplement) and then flesh out the discussion by examining the work in a larger context.

In my view, the detailed description of the spectral analyses is too long. Much of it has been in the literature before and most could only be followed by a few specialized readers and may be better in a specialized AMT paper, supplement, or appendix. I leave this to the authors and editor to decide. For a general audience it would be of more widespread interest to describe the overall challenges, trade-offs, and innovations associated with the measurement configuration in 1-3 paragraphs written in not overly technical fashion. By way of explanation, most scientists do spectroscopy when the optical path is all at a single easily-measured temperature and pressure. A smaller subset do atmospheric total column spectroscopy when slowly-changing a-priori profiles for concentration and temperature can be assigned to a system modeled as a "stack of layers." In the present work, the fire essentially produces "layers" of potentially very different, unknown temperature and concentration that are rapidly changing in position, extent, and content. Each packet of emissions has a different, unknown vertical velocity that may be needed to properly calculate a flux of emissions. There may be rising, hot CO2 and falling, cold CO in the same measurement path? This challenge may be highest if one targets flaming emissions that normally account for most of the emissions with an optical path in/near the flames. If one targets more cooled/mixed emissions with the measurement path to minimize the (unmeasured?) variability along the optical path, it seems to come at the cost of relying on the complex fire-side meteorology to drive representative emissions sideways to the optical path rather than in "the normal" upward direction. Thus, the measurement geometry seems to present non-trivial challenges based on first-principles alone. Despite the lengthy technical section, I did not feel like these basic concerns were completely dismissed. The authors do cite Smith et al who evidently explored the effect of assuming an incorrect single temperature for the whole optical path, but maybe the major source of uncertainty is temperature variation along the optical path: potentially from 300-1100+ C? It was not specifically stated that the study of Smith et al. addressed all the issues that might be encountered with this measurement geometry. Having offered these concerns, it is important to state that in my view the authors are perhaps more qualified than anyone else to deal with these challenges and enact innovative solutions. Further, a very important point is that the authors obtained results within the envelope of previous work and so maybe I've overestimated the problems. In any case, it would be of widespread interest to summarize how these challenges are addressed in a manner accessible to a wide audience and how they impact true overall uncertainty for the individual fires sampled.

At the next level up, a discussion item is essentially: fire to fire variability vs individual fire uncertainty. In airborne studies of well-mixed samples, the uncertainty in individual fire EF is almost always smaller than the uncertainty in the study-average EF. In this work, the uncertainty in the study mean is sometimes smaller than the uncertainty in the individual fire value, but in general the study standard deviation is larger reducing the need for discussion of error in individual fires and making the possibility of systematic bias more of a concern to address. Real variability, possible bias, and measurement representativeness are important for modelers using emission factors at any scale. Sample size (this study is a rather small sample of five fires) is an important aspect of assessing those issues, but is not yet discussed. An additional discussion item, perhaps the single most important issue, involves going from uncertainty in these measurements to representativeness for regional modeling when the majority of biomass burned in Australian forest fires is consumed in very large, intense, uncontrolled fires as opposed to the small planned fires the authors current approach is designed for. The authors have done a great job of comparing in the limited fashion possible to emission ratios in major Australian wildfires that were measured using their solar-tracking FTIR system when smoke was transported over the group's lab. The good comparison for fires burning on different scales should be pointed out more clearly even though the result may not be as good in future comparisons of fire emissions at different intensity

scales. The authors already compare to airborne forest fire measurements, from the rest of the world, which is also good, but they point out the possibility of regional differences. Given the small sample size in their study and the large natural variability observed in all work, it may still be TBD if regional differences or if other factors (fuel moisture, season, etc) drive EF variability. Some papers that explore "non-geographic" or "non-vegetation" sources of variability include:

van Leeuwen, T. T., et al.: Dynamic biomass burning emission factors and their impact on atmospheric CO mixing ratios, JGR, 2013.

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 O_3 formation rates in some South Carolina biomass burning plumes, Atmos. Chem. Phys., 13, 1141-1165, doi:10.5194/acp-13-1141-2013, 2013.

http://www.atmos-chem-phys.net/13/89/2013/acp-13-89-2013.html

Some of the speculation that is beyond the scope of this study could be minimized throughout. For example, the authors discuss airborne vs ground-based measurements. While I think such a discussion doesn't need to be in this paper, I reluctantly offer some thoughts that may have been overlooked in the author's discussion mostly to illustrate that the issues may be more complex than recognized in the discussion paper. Ground-based measurements can only sample at the edges of a fire whereas airborne platforms can sample over the whole fire (which is often inhomogeneous with different fuels in the interior). Aircraft can sample the explosive blow-ups that may account for most of the fuel consumption. In particular, the airborne observer has the perfect view of the whole fire and can usually command the aircraft to all parts – including the most active parts. The ground-based observer is confined to fire-lines that are normally constructed well away from the heaviest fuel accumulations to make control easier and they cannot see most of any moderately-sized fire because of intervening smoke and vegetation. If the ground-based observer does see other important areas, they may be unable to move the pre-ordained fixed path. In Akagi et al. (2014) the fire was ignited on the perimeter and burned towards the interior and away from the immobile ground-based measurement path. Thus the aircraft was still sampling weakly-lofted, mostly-smoldering emissions from the interior of the unit after the ground-based measurements had ceased. Ground-based measurements can only be used for prescribed fires, can't be used to search for fires, and can't probe plume evolution in the described configuration. Both airborne and ground-based have some sensitivity to both flaming and smoldering. The ground deployment gets some flaming if/when fortuitous wind gusts direct smoke sideways instead of up. Airborne deployments get some smoldering because the intense convection column entrains smoldering emissions and even debris from the site. On real fires a moving flame front will often persist throughout most of the fires occurrence rather than as a brief initial burst at a point. Airborne sampling favors smoke from high fuel consumption rates, while ground-based sampling favors smoke from low fuel consumption rates, thus airborne sampling may often be inherently more representative of whole fire emissions. An exception would be fires with little or no flaming combustion. Ground-based sampling would be inherently more representative of fires that burn almost entirely by smoldering, where some subset of peatland fires may fall in the category. Lab fires are the only way to capture all the smoke and they usually produce the highest flaming to smoldering ratio of all three main deployment platforms, but this is probably an artifact related to dryness and lack of wind which makes burning wetter fuels harder and may elevate MCE. See discussion in link above. Speculating about "thermal mass," large metal blocks used in "green buildings," is not tested and may be irrelevant.

Specific comments.

The paper could be re-focused to some extent so here I just list possible errors and offer ideas on potential revisions.

P4328, L14: "given" to "measured locally"

P4328, L17-20: Include realistic uncertainties in the EF.

P4329, L27: "are large uncertainties" to "is large natural variability" to minimize implication of measurement error?

P4330, L10 and 15: Actual large-scale fires in the field don't really burn in flaming and smoldering stages that often. It's more that there is a site-specific, potentially dynamic mix of flaming and smoldering combustion. Most other comments on how to sample fires are contained in general comments above. E.g. smoldering emissions are also lofted by convection, flaming may be long-lasting (for days); not "rapid." L25: Re: "very limited temporal coverage" - flaming is not just an "initial" phenomenon on real fires, where the flames can constantly move into new fuels.

P4331, L4: What ground-based geometry works when the flame lengths are 50-200 feet as is common on Australian forest fires?

L8: Akagi et al. (2013) cited but not in references.

L4334, L15: Eqn 5 is not actually needed to get EF since that is already covered by eqns 1 and 2. I don't think it is ever made clear if there is a need for eqn 5. Just getting a full set of ER to CO2 or CO by the sum or plot method and then converting to EF is simplest. The idea to use ER times EF of a reference species just seems to add extra work and error since the ER are included in the EF of reference species. Perhaps what the authors are getting at is the ER plots minimize effect of low S:N for some species?

P4335. L8: "Itdecreases"

P4336, L6: "often" only applies to lab work, for ground-based it is "on rare occasions" and in the air "never" – see also comments on Fig 4 at end.

P4336, L21-25: How could Wooster et al get fire-averaged EF that resembled those at high MCE, but a medium fire-average MCE of 0.91?

P4337, L7: The EF from the summation method is indeed better than the time average

EF, but it ignores potentially higher vertical velocity of emissions during flaming. In the field, the flaming emissions (and entrained smoldering emissions) may “surge” into the atmosphere at 10 m/s while any un-entrained smoldering emission may linger at ground level or only rise weakly. Thus the same mixing ratio can represent different production of products. The fix for this in lab studies is to use a constant entrainment flow that is much larger than the fire-driven flow so that the summation method is rigorous, but this is not feasible in field.

P4339, L13: does unmodulated radiation cause a baseline (zero) offset? If so, this can impact retreivals.

P4339, L16-18: This doesn’t sound realistic. How is the ~1100 C temperature of flames accounted for when sampling “thru flames” or is there a filtering process by which this data can actually be rejected without impacting representativeness? Related question re P4341, L13: How would you know “true amounts” along a complex open path other than in well-mixed, independently-measured background air?

P4339, L23: 7 seconds for a 1.0 cm-1 scan sounds like a slow mirror speed and there can be effects of concentrations changing during the scan.

Sect 3.2: presents an overly long discussion of error that may largely omit what might be the largest source of error; temperature?

Sect 3.3, specifically P4341, L2 – P4342, L2: These spectral “windows” (i.e. wavelength regions) could be helpful starting points for other novice workers, but I would disagree with recommending these spectral windows for “any other users.” The best windows depend on RH, resolution, path length, concentration range, what interferences are present (it varies), instrument function, etc. and each study must optimize for their conditions to ensure good results. One way to test open-path systems is by using cal gases and permeation tubes with closed cell systems at similar path/concentrations and with an identical instrument function, etc as in Akagi et al (2013). Examples of deviating from the authors “recommended” windows follow. In Brazil, at H2O mixing ratios

of 2-3% and with a 100 m path, the region above 3500 cm-1 can have too much water absorption for some detectors. Akagi et al., 2013 found excellent agreement with a suite of directly-introduced NIST-traceable CO/CO2 standards that covered the range of field observations when using a spectral window from 2040 to 2100 cm-1. That window keyed on the CO2 feature at 2077 cm-1, which is outside the CO2 region in Table 1. The alternate region has lower H2O interference and it out-performed the region in Table 1 in the Akagi et al tests for their specific application. It appears the N2O retrievals may not have been challenged with calibration gases yet and Griffith et al. (1991) detected no significant N2O enhancements in smoke with a longer path. The window from 920-1000 cm-1 also contains CO2 hotbands which can be prominent in smoke spectra though maybe not important in this work. There are other species sometimes analyzed for not in the author’s windows. A useful QC check is that when a species appears in more than one window it should ideally have the same value in all windows. For instance, the CO2 in the C2H2 window should agree with the CO2 in the “main window” (first and last windows in authors table). This ensures that the interference is fit properly. Of course this requirement can be relaxed if the interfering peaks are very small compared to the target analyte. It’s also sometimes more accurate to average multiple windows. For many reasons such as these cited above, I believe a lengthy discussion of windows is of limited value to the general readership and should be condensed to less than 5% of its current length. For research applications, it’s important that each practitioner optimize for their specific application and not simply accept a prescription.

Section 4. This could be too much information on the fires if the rest of the paper is not shortened. It could be described in a paragraph or put in a supplement. Or OK to keep all this detail if the preceding material is condensed.

Section 5.1. Now we are 22 pages into the paper and again presenting detailed methods as results. Eqns 7 and 8 apparently explicitly repeat earlier equations, which were already a bit much in my view. Sect 5.1-5.3 place a burden on the reader when most just want the mean, a realistic estimate of the uncertainty in simple tabular form, and then some interpretation.

P4350, L14-15: If most of the absorbing gas is in a small region of elevated temperature, then does it matter what the average temperature is? L26. I don't see a discussion of S:N:R, which is a common element of uncertainty. It's not 100% clear that all the known and unknown uncertainties are easily estimated, but even 20-30% uncertainty in many trace gases and more for some is very useful and if this is realistic for this experiment it could be communicated as a short, useful estimate rather than a lengthy, complex, and potentially over-optimistic discussion.

P4351: The uncertainty in fuel carbon is estimated at 0.5 +/- 0.05, which is probably a 2-sigma uncertainty in view of published carbon analyses for forest fuels. Meanwhile, maybe the other uncertainties are one-sigma? Best to adopt and specify same "number of sigma" throughout. Also 10% may be high, but regardless the uncertainty in EFCO2 is also 10%, which may be optimistic given the many difficult sources of error. L19: Reason to switch from sum method here? It was never clear to me why the authors don't just get their best estimate of how the carbon is partitioned and then put that in the carbon mass balance method; once. L27: "reson"

P4352: L26-27: Temperature affects density, but may also impact the relative line strength of different gases differently (via the Boltzmann factor), or different parts of the path may have different gases and different temperatures, so temperature errors may not completely cancel in ratios.

P4353, L21-26: Maybe not useful, but worth checking is the CH4/H2O window keyed on the CH4 q-branch at 1306 cm-1.

P4353, L28: Again, is assuming a single temperature relevant?

P4354 and Fig 6: NH3/CO lower for low MCE is counterintuitive since NH3 is a smoldering compound. Might be fuel N and also worth checking if it is an artifact of not

having CO2 in the NH3 window.

P4355, L13: NH3 decreasing with aging is well-known and seen in Goode et al. (2000) and Akagi et al. (2012).

Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmos. Chem. Phys., 12, 1397-1421, doi:10.5194/acp-12-1397-2012, 2012.

P4355, L18: Has the 2005 value been corrected for the large change in HCOOH cross-section in HITRAN? Factor of $\sim$2.

P4355, L21-22: The Goode et al value should be adjusted to reflect the change in HCOOH cross-section since that paper was published as explained in Akagi et al., (2011). The Goode et al. (2000), Akagi et al. (2012), Yokelson et al. (2009), and others all show HCOOH/CO increasing with aging as measured by FTIR or CIMS and this is by now a well-known phenomenon.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys., 9, 5785-5812, doi:10.5194/acp-9-5785-2009, 2009.

P4356, L3-4: The original HCOOH data in Andreae and Merlet 2001 is about a factor two too high due to the old incorrect HITRAN cross-section. The corrected values are in Akagi et al. (2011).

P4356, L6: The citation to Akagi et al 2013 should be to Akagi et al 2014. Also Burling et al., 2011 (ACP) report a range of study-average EFHCOOH of from 0.11- 0.57 in the same nominal ecosystem so a similar average but high variability illustrating the importance of a large sample size.

P4356, L16: Rapid drop in C2H4/CO also seen in Akagi et al. (2012).

P4357: L5-7: I agree that the variability in fuel carbon (at one-sigma) is less than assumed, but it is not clear how a comparison of standard deviations would suggest that. It seems the authors get about the same EFCO2 every time because they assume the same %C every time and the CO2/CT is not varying a lot. CO2/CT not varying is also essentially why the MCE are all similar. But if CO2/CT was the same and the real fuel carbon was unknowingly only 25% you would get same EF.

P4357, L11-15: Not sure how you conclude the sample is representative from the uncertainties? That is often assessed by looking at sample size ("n") rather than standard deviation of mean. A low range of MCE for different geometries doesn't prove representativeness if the real MCE's varied. It's interesting that the MCE from all "fire-side deployments of FTIR" from 1991 thru 2014 have almost the same MCE near 0.9 On the other hand, airborne, lab, and tower-based (e.g. Ward et al. 1992 JGR) measurements always show a large range of MCE. I'm not sure what that means, but perhaps worth discussing? Again, capturing some flaming and some smoldering is not necessarily the same as capturing the right relative amounts.

P4358, 8-9: I think these data are valuable to use as is, or averaged with other available data, which may make more sense for some users. The choice could depend on several factors: such as model specificity or whether one choses to believe five data points represent real differences in Australia or just another data set to add to the pile and maybe shift the overall average. For instance, Akagi et al. (2013) report very different EF results than Burling et al. (2011) in the same nominal ecosystem using the same measurement approach, but one in spring and one in fall. If the authors repeat this experiment in other Australian temperate forests and get similar values, then more meaningful evidence for a regional difference is starting to accumulate. In any case, it's not apparent what the logic is here: the logic unintendedly comes across as "since

we don't understand this we recommend you use it." I think the intent was to say the variability doesn't correlate with something like MCE. Normally fire EF correlate with MCE, but in this small study the MCE are essentially all the same so there is no way to isolate any MCE dependence. Finally, a lot of important gases are missing from this data set so literature values from elsewhere still need to be used for those.

P4359, L10-16: It's great to recommend using this data, but I caution against recommending that the exact methodology be used in other future work. Future workers may find that different spectral windows or different analysis methods work better for their data.

P4360, L3-5: Most of the paper is about uncertainties, but they are dropped at the end of the text Standard scientific practice for many reasons is to include the uncertainties for any recommended values.

References: randomly noticed that Yokelson et al 1999a and b appear to be same paper?

Fig 4: Circular CO versus CO2 plots like this are the norm for lab fires and it is just a time series starting with post-ignition flaming progressing up the low leg and then returning to origin via the high leg during smoldering. This indicates the ground-based system measured the history at a location, whereas airborne data in fresh smoke above small hazard reduction burns is normally a series of similar well-mixed samples with gradually increasing CO/CO2 ratios

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