

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-245

Anonymous Referee #2

Referee comment on "Reconciling the total carbon budget for boreal forest wildfire emissions using airborne observations" by Katherine Hayden et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-245-RC2>, 2022

This paper uses airborne measurements of 250 compounds from 15 instruments to analyze the total carbon budget from a boreal forest wildfire that was sampled on June 25, 2018. The results were also used to derive emission factors (EFs) and compare with satellite observations and modelled emissions.

Analyzing and presenting such a large suite of measurements is challenging and I appreciate the work the authors have done. However there are still a large number of issues to address, including rigorous uncertainty analysis. Several results are given to 0.1% or to 5 sig figs without error bars. The AWAS measurement uncertainty is 40%, but AWAS EFs don't have error bars. Some EFs differ from the literature by 40x or more, which needs much more discussion. HONO and the butanes seem to have a measurement issue, and isoprene could have furan interference. Intercomparisons for compounds measured by multiple instruments should be presented.

Another issue is that EFs for I/SVOCs were done without background subtractions, which are a fundamental part of the calculation. If there aren't suitable background values, the calculations shouldn't be presented as EFs. This also impacts the 7.4% I/SVOC contribution presented in the abstract. Specific comments are given below.

L25: Here and throughout, please use error bars. What is the uncertainty on 46.2%? With >200 compounds and multiple instruments, the uncertainties are sure to be considerable.

L26: If I understand well, $46.2 + 7.4 + 46.4\% = 100\%$, so it's confusing to say 46.2% ... 'of which' 7.4% are I/SVOCs. Please clarify.

L112-114: The GEM measurements are described using the same sentence here and in the SI. The manuscript is already long and the SI should supplement the main paper, not repeat it. Same comment on L114-116, L118-120, etc. Please check the rest of the Methods and SI for this.

L143: In order to compare PM_1 from this study with $PM_{2.5}$ EFs from other studies, the aerosol mass between 1 and 2.5 μm was estimated to be 10% (SI L170-173). What is the uncertainty in this estimate? In Table A1, does this mean that the PM_1 EF from the literature is actually $PM_{2.5}$? (I see later on L442 that it does.) This should at very least be clearly stated in the caption, but I'm wondering what the value is of forcing this intercomparison.

L168: How many AWAS samples were taken in Screen 1, which was used to determine emissions? How many plume samples and how many background? I'm guessing the sample size was small. How does this impact uncertainty in the emission calculations?

L170: Please further discuss losses (photochemistry, deposition) in the 42 mins (SP) and 72 mins (NP) from emission to sampling. Even if they're the some of the freshest emissions, losses over this time (and the uncertainty it introduces) should be discussed, especially for the most reactive species.

L179: Please add detection limits to Table S1, and plume and background concentrations to Table A1, so we can see their values and how they compare. What percent of background data were below detection and how was this handled for the background subtraction?

L194: Please quantify 'well above', 'co-varied well' and 'majority of measurements.' At this point we still don't know what the 250 compounds are (Table A1 isn't mentioned until L342).

L326: Later on L342 we learn that there are no I/SVOC background values for background subtractions, which ERs also require (Eq. 1). So what was done for the ER calculations in Table S7?

L342: This doesn't make sense. The EF requires background-subtracted mixing ratios (L201). So how then were the I/SVOC EFs calculated? It's not possible to avoid the issue of background then present and discuss EFs anyways.

L358: This section will need to be reworked. If I/SVOC EFs can't be properly calculated, then TC partitioning based on derived EFs is also affected (Fig. 6, Fig. S8). From Figure 6,

I/SVOCs contribute 7.4%, but this isn't known to 0.1%. On L360, the EF is given to 5 sig figs without an error bar. On L364 the 46.2% hinges on the 7.4% for I/SVOCs, which has uncertainty.

L373: Uncertainty needs to be treated holistically in this paper. If some compounds are uncertain to a factor of 2, it's not realistic to present percentages to 0.1%. Each uncertainty needs to be quantified and carried through.

L409: In Fig. S11, I was surprised by some of the differences between the NP (older) and SP (younger). Long-lived acetylene is in the SP top 25 but not the NP. Reactive isoprene is in the NP top 25 but not the SP. The NP isoprene value (0.6 g/kg) is high compared to boreal forest fire literature (0.07-0.15; Andreae, 2019, Akagi et al., 2011), which could be possible furan interference (e.g., Santos et al., 2018, <https://doi.org/10.5194/acp-18-12715-2018>). Please discuss these issues.

L430: Akagi et al. (2011) and Andreae (2019) also present PM results from boreal forest wildfires. Please state which specific particle species results are the first here.

L434: How fresh were the plumes in Liu et al. (2017)? Could different plume aging between the two studies also play a role?

L434, 439: Different boreal versus temperate forest fuels are used to help explain EF differences, but their vegetation types can also be similar (L421). Please state the major vegetation species for Permar et al. (2021) and Liu et al. (2017) so their fuels can be compared with this study.

L444: The paper still needs to present the sample duration used for EF calculations. From Fig. 3 (Screen 1), it looks like up to 20 minutes of in-plume sampling (10 mins each for NP and SP) over 1 hour of flight time. Please discuss sample size/duration as a potential limitation or source of uncertainty.

L451: Here and elsewhere, ensure that the average and its uncertainty match after the decimal place. So 0.31 ± 0.028 should be 0.31 ± 0.03 . In Table A1 the BC error isn't right (0.11 ± 0.0098). And so on.

L458: What would explain HONO differing by a factor of 41 (!) from Andreae (2019)? Could it be a measurement issue? HONO EFs across all vegetation types range from about 0.2-1.2 (Akagi et al., 2011; Andreae, 2019), so the EF reported here (0.01, Table A1) is far off and unlikely to be explained by limited studies (L459).

L458: What would explain NO_x being lower by a factor of 15? Also check if 15x is an error (Table A1): 1.2 (Andreae) divided by 0.12 (this study) = 10x not 15x? The SO_2 EF is 0.22 (Andreae) and 0.17 (this study) so better agreement than 4.7x? Please check all calculations.

L469: Something is wrong with the butanes in the top 25. The EF of n-butane should be 2-3 higher than isobutane (Akagi et al., 2011; Andreae, 2019), yet only isobutane is in the top 25 (Fig. 8). The isobutane EF (0.47) is about 10x higher than the boreal literature (0.042-0.052), also suggesting a measurement issue.

L472: In Table A1, why are temperate forest EFs (Permar et al.) being used for the butanes, rather than boreal forest EFs (Akagi et al., Andreae)? (0.042-0.052 for isobutane, 0.11-0.12 for n-butane). Is the same value for both (0.12) in Table A1 a typo?

L516: What might explain the much higher EF for pyruvic acid compared to the literature (37x)? How were measurement issues ruled out? When there are such huge discrepancies, it doesn't make sense to then cite acids as 10.3% of NMOGs (since the errors aren't as small as 0.1%).

L518: As well as HONO, isocyanic acid is also much lower than the literature. There is also a factor of 4 difference between the two isocyanic acid instruments in this study (Table A1). Please present and discuss instrument intercomparisons.

L579: Again, what would explain lower EFs in this study for so many compounds, including lower by up to 49-57x? These are huge differences. Please discuss, and also check your calculations.

L587: Throughout avoid qualitative wording ('much lower', 'slightly higher', 'slightly different'). Use percent differences. ALK5 is so very far off in Fig. S12 (70x?) - what caused this?

L593: 'more representative' - this study has large differences from the literature, and a number of results point to possible measurement issues. These need to be resolved before drawing this conclusion.

L617: Please provide more detail for the mass balance calculation. What parameters were used and how were the error bars were derived?

L631: The UTC time isn't intuitive in Fig. 10. Use local time instead (or as well) to clearly indicate when local morning/evening is. Include some local time conversions in the text.

L647: Please avoid 'very similar' and 'well within the uncertainties.' Provide error bars for both emission rates. Is there a typo? The two values are 10x different.

L648: Avoid using 'ER' (which is emission ratio, L405) for 'emission rate.' On L648 and L649, do not use 'ratio' if you mean emission rate. On L651, add error bars and do not cite to 5 sig figs.

Figure 1 doesn't indicate scale or orientation. Please include axis labels, a distance scale, and North direction. Is the 'large arrow' missing? Please label the five screens, especially since Screen 5 isn't shown in Fig. 2.

SI L92: A measurement uncertainty of 40% for AWAS grab samples (Table S1) is incredibly high for this type of measurement. What's contributing to this? If it's this high, how does it impact the EFs based on AWAS? (which so far don't have error bars in Fig. 8 and Table A1)

SI L375-377 (Table S7): It doesn't make sense to talk about EFs in a table that presents ERs. Do you actually mean ERs here? Using concentrated plume values to 'approximate' an ER (or EF) isn't OK. Without a background subtraction the ER can't be presented as an ER.

ADDITIONAL COMMENTS. Lots of details to address. Please proof the paper carefully.

L20, L80: Because boreal forest fires have been studied, change 'a lack of' to 'limited'

L54: Wording is very similar to L18.

L58, L61, L597, L608, L611: Please provide references.

L69: Should 'and ratios' be deleted here?

L94-95: Please use different wording in the abstract, introduction and conclusions.

L104: Is 'intervals' the correct word here? Do you mean time resolution?

L104: Typo: change to 'measurement methods.'

L130 and SI L92 give AWAS fill times of 20-30 sec, but SI L96 states approximately 15 sec (30 sec max). Which is it?

L132 says that AWAS measured <C10 hydrocarbons, but SI L229 says <C9. Which is it? (from Table A1 it seems to be \leq C10)

L169: Typo: 'depositional'

L172, L194: What's the basis for these statements? Is it just based on absence of upwind cities and industries?

L203: TC was already defined on L115.

L239: Quantify 'low NO_x levels.' Fig. S2 shows up to 5 ppbv in the plumes, which is much higher than background.

L258: If OA is 276 $\mu\text{g}/\text{m}^3$, please change the scale in Fig. 3 so the data don't go off-scale.

L263: How do you get 85%? The reduced compounds in Fig. 4 sum to 79.4% (oxidized are 20.6%).

L281: Hydrocarbons (defined on L279) sum to $27.2 + 19.3 + 3.1 = 49.6\%$ (Fig. 5). How do you get 52.8%?

L282: Please reference Fig. 5 here. The text goes back and forth between Fig. S6 and Fig. 5.

L313: The text here is qualitative. Please include concentrations and error bars.

L326: Table S7 lists C11 CH compounds with an ER of 0. Is this a typo?

L333: The CH compounds peak at C18-C23 in Table S7, not C20-C25.

L342: Here and on L1410 change 'Table A1' to 'Table 1.' On L1412 delete 'Table S7'

L364: Here and throughout, define all error bars and how they were derived.

L392: Grammar: change 'SVOCs to VOCs categories' to 'SVOC to VOC categories'

L405: Define EFs and ERs earlier, not here.

L415: L152 states that Jack pine, not lodgepole pine, is a dominant fuel in this study.

L429: Quantify 'generally similar' (within what %?)

L442: Too many sig figs

L456: Quantify 'very close.' In Table A1, the CO₂ EF has too many sig figs.

L458: The text uses HONO but Table A1 uses HNO₂. Use one notation for easier cross-referencing.

L458: Add HONO to Table S1 (to show its measurement uncertainty).

L464: Quantify 'fairly well', 'do not vary widely'. On L550 quantify 'fairly good'

L481: The value of 57% may change depending on what you find for isobutane.

L482: Typo: 'lower lower'

L531, 543: Please discuss how possible interference from furan was checked or ruled out.

L565: It looks like you could add 'NMOG' to 'CO and CH₄' since it's also comparable in Fig. 9d.

L601: Typo: change 'CFFEPs' to 'CFFEPS'

L614: 'corresponds with' doesn't make sense ... how can 0.29 MW/ha correspond with >0.4 MW/ha?

L642: The text states 23:00 UTC but Fig. 10 indicates 21:00 UTC (L1402). Is 23:00 correct? If so why aren't the data from 21:00-23:00 shown in Fig. 10?

L643: Do you mean 'emission factor' rather than 'emission ratio' here?

L648: Typo: change '2000' to '20:00'

L650: Please state the date and time that the fire 'went out'

L654: Add error bars (which will give the actual upper limits) and do not use 5 sig figs.

L666: Typo: change 'I/SIVOCs' to 'I/SVOCs'

L1418: Why are both letters and numbers used for superscripts? Just use one. Delete the extra bracket.

Figure 2: The distance scale is faint and only includes one label (16.9 km). Please increase the font size in the CO legend.

Figure 9: This Figure is very busy. Can the labeling be simplified?

SI L17: Begin the SI numbering at 1.0 rather than 2.0 (otherwise it seems cut-and-pasted)

SI L99: Please quantify 'as soon as possible.' Hours? Days?

SI L126: Does this mean two cartridge samples were used for emission calculations?

SI L217: Change 'ethyl benzene' to 'ethylbenzene'

Table S1: Replace 'Canister grab samples' with 'AWAS.' Change 'Grab' to a range in seconds.

Table S2: Capitalize 'c4h4o2' in the third column (also in Fig. S11)

Table S6: Use subscripts for C₈H₁₆, C₉H₂₀, C₁₀H₁₄, C₁₀H₂₂. Check the manuscript for this.

Table S7: Add error bars to the ERs.

Table S9: Some molecular weights have as many as 10 significant figures (IVOC, 227.3333333)

Figure S12: Label the units on each axis with what's plotted ('Hayden et al.' is not an axis label)