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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Airborne hydrogen cyanide measurements using a chemical ionisation mass spectrometer for the plume identification of biomass burning forest fires" *by* M. Le Breton et al.

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Airborne HCN measurements by Le Breton et al.

Biomass burning (BB) is a major, but poorly characterized source of trace gases and particles to the global atmosphere and HCN is mostly emitted by BB (although in variable amounts) making it of significant value as a tracer/marker for understanding this important source. The authors obtained an I- chemical ionization mass spectrometer

that was set up for measurements of HCN and possibly other species. They deployed it in airborne measurements over eastern North America and the North Atlantic in both aged plumes (1-11 days old) and background air in an experiment designed to measure the effect of boreal BB outflow on tropospheric oxidants over the North Atlantic. The main focus of the paper is the best way to use HCN data to identify when the aircraft was in a BB plume. They test several methods and decide that the best indicator of a BB plume is when HCN is 6 standard deviations above the flight-average background. The authors state this has advantages over other options, especially for detecting very dilute plumes. A good HCN instrument has potential to contribute significantly to the field of atmospheric chemistry and the data obtained are of great interest to the community. However, the paper requires extensive, major revisions before it can be accepted. There is a large amount of information that is normally included in papers of this type that is missing and must be added. There is also a large amount of space devoted to topics that their measurements were not well-suited to address. The latter should be eliminated or redone in a more relevant manner.

I've, spent too much time on this review to make sure it is educational rather than just listing problems. I don't have the additional time to consolidate, polish etc, so I apologize that it is repetitious.

General comments:

The author's conclusion that HCN's presence above a "6-sigma threshold" defined by the flight-average background seems a bit arbitrary as they only tested 6-sigma and 10-sigma for reasons that I did not see explained. One expects that both false positives and errors of omission would be sigmoidal functions versus the number of sigmas with no sharp threshold. The authors appear to have tested two values of sigma and some other plume-id criteria used in the literature and then they present indirect evidence that "6-sigma" was the best of the options tested. Regardless of whether their criterion is perfect it is useful for detecting BB-influenced plumes. However, even though a plume with HCN more than 6-sigma above background will likely be BB-influenced, it may be

a mixed plume from several sources and may not be a “pure” BB plume. In particular, downwind of eastern North America where one-fourth of the population of the continent lives, there is high potential for mixing with urban fossil fuel (FF) emissions. Thus, if they wish to discuss pure BB outflow, BB/FF mixing needs to be conclusively ruled out by using an FF tracer (perhaps one measured by others on the same aircraft). Otherwise, the discussion needs to be recast to acknowledge this important issue. Note, this is the problem Crounse et al. (2009) faced downwind of the Mexico City metro area where FF and BB emissions mix. Crounse et al used the different HCN/CO and C2H2/CO ratios characteristic of FF and BB to determine the contributions of each source. C2H2 was measured by Lewis et al on the BORTAS aircraft used in this study. No true source ratios were measured in BORTAS, but some are available in the literature for boreal fires. In any case, the authors should use other species measured in BORTAS to attempt to probe the extent of non-biomass burning influence on the data reported here. They should also use and present back trajectory analysis to investigate: 1) possible BB/FF mixing, and 2) the type of biomass fuel burned if possible.

The most likely effect of BB/FF mixing would be a reduction in the HCN/CO ratio. On the other hand, Singh et al., (2012) observed slightly higher HCN/CO ER in mixed BB/FF plumes than in “pure” BB plumes. They attributed that to a poorly characterized urban source of HCN, which is certainly a possibility, but perhaps unlikely as mixing is an averaging process rather than an additive one. Thus, their finding could also be a coincidence (given the high natural variability in HCN emissions and small sample size) or a result of higher fuel N in fires near urban areas. The latter could be caused by higher N content in vegetation near cities for natural reasons, or due to fertilization effecting crop residue that is burned, or deposition of urban NOx as seen in several studies noted in Yokelson et al., (2011).

Another general problem is that both the description of the instrument and the presentation of the results are inadequate. Hopefully the other referees will cover potential technical issues regarding clustering, fragmentation losses, interference, etc. A major

concern though is that smoke contains hundreds of known, unknown, reactive, and “sticky” species (Yokelson et al 2013). The potential for interference is high. The role of formic acid, which is difficult to measure needs to be better described as discussed in detail below. The formic acid data should be shown in the paper along with any other species monitored. Finally, some commercial HCN standards are not of high-quality. Using two independent IR reference spectra we found that one commercial standard was off by a factor of 2, which we speculated could be due to inadequate stabilization.

The paper needs to include standard information such as flight tracks; dates, times, locations (lat, long, alt) of samples; back trajectories from the samples, etc. All this is standard stuff that goes in papers introducing airborne measurements with a new instrument/species. The authors should also show vertical profiles for HCN in background air for several reasons discussed more below.

The authors have over-simplified the interpretation and application of the normalized excess mixing ratios (NEMRs) they observed. The NEMRs could be accurate without necessarily representing initial emissions from fires in at least two ways. In the highly-diluted plumes they observed, various mixing scenarios (e.g. with FF or with changing background air) could erase the original signature ratios emitted by sources. Assuming that they operated within the free troposphere (missing critical information), the authors should present some quick calculations of the effect of a smoke plume diluting first in the boundary layer (BL) and then in the free troposphere (FT) using their measured HCN/CO value for each layer. They should also consider the possible effect of FF/BB mixing on their NEMRs. They should note that their higher HCN values shown in Figure 5 confirm a significantly higher HCN/CO ratio than their study average ratios. Regardless of the outcome of the partial mixing analysis suggested above, the non-linear results in Figure 5 coupled with the long lifetime of HCN suggests that mixing effects strongly modified the observed ratios.

The authors are comparing results from their mission to airborne initial emissions studies where excess CO values ranged up to 30,000 ppb with HCN in the hundreds of ppb.

Other studies measuring HCN/CO in laboratories had concentrations 10X that (see 4 ppm HCN in Lobert et al., 1991). In the authors samples max CO is on the order of 1000 ppb with HCN getting up to 4 ppb. Certainly this is adequate to ensure good S:N, but the plumes they sampled have diluted by a factor of up to 1000 with background air. So again, simple algebra with realistic assumptions about possible changes in the background HCN/CO ratios or BB/FF mixing shows that it is quite possible that the original NEMR would not survive.

Also, other studies have measured many smoke samples with HCN/CO ratios similar to or below what the authors report. But they also measured many HCN/CO ratios that were higher. It's the study-average for the other work (using GC-TID, GC-RGD, FTIR column, FTIR in-situ, and the Caltech CIMS) that are all higher, but that was of course for samples the authors did not measure. For comparing data, it is important that the literature standard reporting method is to show the mean and the standard deviation of the mean. The authors have chosen a different method to calculate their uncertainties that is somehow causing them to underestimate their coefficient of variation (CV) by several orders of magnitude. Note that a large CV (on the order of 50%) is a hallmark signature for all BB emissions except CO2, which is to be expected for an uncontrolled activity in diverse environments. In fact, CVs are normally even higher for emissions that contain N or S or Cl due to highly variable fuel chemistry. When the authors compute realistic CVs their measurements overlap better with other work.

The value of the global modeling exercise is highly questionable. The authors select HCN/CO values for fire initial emissions that are already shown to be extremes in the literature and then use a global model run to "discover" that the ratios are extremes. If they retain a modeling component (against my advice) they should compare to their mission-wide measured values or input the HCN/CO values already recommended in the literature for specific fire types and run with those. However, given all the uncertainties in the amount of global BB-CO (factor of 2, Wiedinmyer et al., (2011)), high uncertainty in the vertical mixing between the FT and BL, the fact that the atmosphere

is very undersampled in the remote regions where BB dominates, etc, a global model run probably can't provide any constraining insights or interpretive power regarding the authors current measurements. In general, a global model run really doesn't have a place in a paper that introduces a new instrument and that has so far measured only in an environment that accounts for $<$10% of global BB. A finer scale regional model that is compared to all flight-measured HCN values would be a much better choice.

The boreal forest is a huge ecosystem that is close to a lot of people and the sensitive Arctic. Oxidants over the North Atlantic play an important role in processing pollutants both from fires and much of the developed world. High quality field measurements were made that deserve focused attention! The data interpretation frequently discussed initial emissions (which were not measured) and global modeling. This "mission creep" detracts from the excellent work that was done.

The authors should cite the most recent HCN BB measurements throughout the paper. Updates to the published version of Andreae and Merlet (2001) are available by contacting the first author. The two values in the published 2001 version are from off-line matrix isolation FTIR studies by Hurst et al., (1994). Akagi et al. (2011) have an updated review of HCN emission factors, the text has special section on HCN, and updated supplemental tables should be posted soon. Meanwhile, Akagi et al. (2013) present additional, very recent HCN results and compare them to previous results. All three papers and the original literature cited make it clear that BB HCN/CO ratios have a high fuel dependence ranging from below detection for pure wood in cooking fires (to date) to 3% or greater for some peat samples. There are other papers that don't present field-measured EFHCN broken out by fire type, but nonetheless provide extremely useful HCN/CO ratios for BB whose values should be cited including: (1) Rinsland et al., (1999) HCN/CO at Mauna Loa of 0.00982 by column FTIR. (2) Lobert et al., (1991) HCN/CO for lab fires that averaged 0.0113 and ranged from 0.0005 to 0.058 (more than two orders of magnitude) by GC-TID. (3) Singh et al., (2010; 2012) HCN/CO ranging from 0.001 – 0.011 for fires in CA and Canada (the high end mostly

in Canada) by GC-RGD and measured at CO up to 2500 ppb.

Specific comments in page number, line(s): format.

P5651, L13: The coefficient of variation is wrong.

P5651, L17: It makes no sense to apply the boreal value to the whole planet when data exists for other ecosystems where most of the burning occurs.

P5651, L25: Boreal forest fires are only ∼9% of global BB according to author's source, which reinforces my comment above.

P5652: Good review of other possible sources.

P5653, L8: Other global models get up to 3 times the HCN source they do with their model. If a modeling component is retained in the paper, which I don't recommend, then the reasons for these large differences should be discussed/evaluated.

P5653, L20: Rephrase to acknowledge natural variability especially in fires.

5653, L22-3: There is a big difference between identifying a BB-influenced plume and measuring emission factors.

5654, L19-21: It is worthwhile to develop a method to detect dilute BB-influenced plumes, but assuming you can measure initial emissions from far-field is harder to defend.

5655, eqn 1: "n" is a variable so how does one get a single mass out of that? HCN+I would be 154 by itself so should the third dot be a + sign? Or are they just not describing a subsequent collisional drying step?

5655, L20: "calibrated relative to that of" means what? I don't understand why formic acid is the best internal standard since it is sticky and difficult to work with. Is 40C warm enough for the inlet? Veres et al., (2010) use 70C and also noted interference for formic acid with their ion chemistry. I skimmed thru the formic acid paper referenced,

but its exact role in quantifying HCN is still not clear, nor is any formic acid data shown in this paper even though it is a very interesting BB emission (Akagi et al., 2012).

5656: Reading quickly it seemed to say formic acid was sensitive to altitude, but the formic acid paper did not seem to mention that.

5656, L15-16: Is the model vertical mixing and vertical resolution adequate to accomplish anything relevant to this paper?

5656: A lot of irrelevant info is given on the model, but not the model year or how the BB-CO emissions are calculated, which is critical. On line 26 it is implied that the fire emissions come from POET and no uncertainty or temporal resolution is given. There are other BB-CO estimates available: GFED3, FLAMBE, FINN, but they are all highly uncertain and some factor of uncertainty needs to be assigned here; I suggest a realistic factor of two.

5657, L9: The HCN annual global production that is obtained from the authors HCN/CO ratio implies that about 472 Tg CO are produced by open burning in POET. FINN gives 332-409 Tg/y (2005-2010) and estimates that these values are uncertain by a factor of 2. GFED3 is lower than FINN. Does the POET CO total include biofuels? If so an HCN/CO close to zero for that part of the CO would be recommended (Akagi et al., 2011).

5658,

L10-11: What does it mean that "plumes were detected when background levels were low"? Weren't they detected when plume levels were high?

L12: It is stated that a method is inaccurate, but no reference is provided. The real world is fuzzy; there is no perfect definition of a plume. A more restrictive definition will miss more plumes, a less restrictive one will have more false positives, and there is a gray area in the middle that can't be eliminated by picking a magic number of stdevs.

5658, L19: Should rephrase since you would not drink water that contained a poison

at only five or nine times the standard deviation. Any S:N above 1 is “meaningful.”

5658, L23: There can be a strong enhancement, but the source NEMR may not be preserved after mixing. Use your measured or literature typical BL and FT values for HCN and CO and investigate.

5658, L25: Defining a single flight-average background is often inadequate if the flight sampled several layers (e.g. BL, FT) with different background levels. For a flight average background you have the complication that you have to define plumes to define the background by omission so it’s circular. Then the background may not be constant. Most people use enhancements above the local background. After this lengthy discussion you only tested 6 and 10 stdevs, why not test 3-11 etc?

Table 1: The averaging is wrong. 2.9+/- 1.5 is correct way to report the tabulated data including B622 or 3.5 +/- 1.0 without B622. The tabulated values assume only one plume per flight, which may not be the case.

5659, L7: Table 2: “Andrea” spelled wrong and that value is from Hurst MI-FTIR anyway. Please give year of reference. For the same boreal ecosystem the author’s mean is below the mean minus one stdev from other studies using two independent techniques, but not lower by 2 stdevs. HCN/CO from BORTAS do not really agree well with literature, they are at low end. That does not mean they are wrong it just means they are at low end of a large range from $\sim$0.0005 - $\sim$0.06. Again, the authors have reported the uncertainty in their mean incorrectly.

5659, general: The authors discuss different methods of id-ing plumes at length, but it’s also important that you need two tracers to identify pure plumes in regions where the mixing of plumes from different sources is common. Further, if they wanted ER or EF for global model input it would have been more straightforward to fly to a fire and measure them there.

5660,

L22: Aging is not a likely cause of a low HCN value within 11 days given the long lifetime of HCN.

L23 Mixing (or natural variability) is a more likely cause of low HCN/CO. There is no way of knowing if all the plumes were mixed to some extent downwind of eastern NA megacities. There is an impressive body of auxiliary data from BORTAS though and hopefully some tracers for other sources were measured.

5660 L24: Change “The previously reported in previous work” to “The NEMRs reported in previous work”

5661, L7: Andreae and Merlet were quoting Hurst et al who (from memory) measured at least partially in Australian savannas – not forests. Akagi et al., (2013) has a relevant, updated discussion of HCN/CO ratios from forests.

5661, L16-17: No-one disputes that HCN is emitted mostly by fires, but it is in variable quantities. The 6-sigma method sounds good for id-ing plumes influenced by fires, but not pure BB plumes unless some other tracer is added.

5662: Highly uncertain assumptions about vertical mixing, interhemispheric mixing, and the amount of fire are limiting factors here. Why not try to reproduce the authors own field measurements in well mixed background air with a higher resolution regional model?

5662, L11: The use of a single HCN/CO ratio for all fires on the planet does not make sense as measurements from around the world confirm this ratio varies widely. For the two largest types of open burning I believe Akagi et al., (2011) recommend $\sim$ 9 (in the author’s ppt/ppb units) for savannas and $\sim$6 for tropical forest for an average of $\sim$7.5, which might be the best guess if you are constrained to use a single number. By extrapolation, it seems like those recommended values would agree with Liang’s global background pretty well.

5662, L23: Did Liang et al report HCN/CO?

5663, L21-23: Again, there are measured ratios for different ecosystems in Akagi et al., 2011. If you are going to bother with a model run – use the recommended values.

5663, L25: Looking only above 5 km has limited value as a constraint because smoke is nearly all emitted in the BL and so poorly understood vertical mixing is an important control on what is seen at higher levels.

5664, L5-7 and conclusions: The plumes sampled were directly downwind of one-fourth the population of the North American continent and thus the HCN/CO ratios could have been altered by BB/FF mixing.

L15: Accuracy would be determined by some other test not the attributes listed here.

L16: "burning plumes" should be "BB-influenced plumes"

L17: The authors HCN mixing ratios are at the low end of what has been reported in BB plumes.

L23: "biomass burning" $>$ "BB-influenced"

L24: Wrong CV.

L25: "Andrea" misspelled.

L26: One doesn't show accuracy by falling within a large range established by other work. Accuracy is normally supported by use of a certified calibration standard or intercomparison.

5665, L1: Surely they don't mean only their NEMR is accurate. If global modeling is retained best to replace "The accurate NEMR" with "Our-study average NEMR"

5665: Last sentence clumsy construction and bad grammar.

Tab 3: CVs wrong.

Fig 2: Now HCN calibration is hinted at, but there is no discussion in the text.

Fig 3: Flight B622 appears to have sampled 4-5 plumes with very different HCN/CO ratios. B621 probably sampled two different plumes.

Fig 5. A quick glance at the data shows that the vast majority of really elevated HCN points are are clustered only about halfway out along the CO axis. This is the classic signature of a compound whose ER to CO diminishes after emission due to mixing or photochemical losses. One can easily see that the fresher or purer samples would return a slope of about 3500-4000(ppt)/700(ppb) or 5-5.7 ppt/ppb, which would likely overlap (within uncertainty) the study means of other measurements of boreal forest fires (Simpson, Hornbrook).

My instinct was to reject this paper, not because I think the data is wrong, but because 1) the paper does not adequately focus on the work that was done, 2) inadequate proofreading, and 3) requests for major revisions are often ignored. However, I would like to see the development and use of this instrument pursued and the current data set published. Thus, I summarize my suggestions for the content of a majorly-revised paper that would a good description of the author's important work:

1. Describe the instrument adequately. In particular: which m/z are monitored in flight,? calibration,? do they use two stabilized standards,? clustering,? fragments,? the role of formic acid and any formic acid measurement issues. Show the formic acid data. Any aging trends in formic acid noted (see Akagi et al., 2012)?

2. Show some vertical profiles in background air and compare to other published profiles. Is there a gradient between BL and FT? Is there a gradient above surface of ocean that can be used to estimate the HCN sink?

3. Show examples of data from a plume passage. Show a map of where plumes were encountered. Give altitudes of samples and run some back trajectories to see if you can id possible BB/FF mixing or what was burning in the fires.

4. Compare the measured NEMRs to fire ERs, but with proper caveat that BORTAS

was not designed to measure ERs and that the NEMRs could be different because of mixing. Explicitly estimate the possible effect of mixing of BL and FT air on the NEMRs. Calculate the uncertainty in mean ERs properly.

5. Address my comment on Fig. 5 and use some of the auxiliary data from BORTAS to investigate the possibility of BB/FF mixing.

6. Drop the global modeling or re-do it with ecosystem specific recommendations from Akagi et al., (2011). Or use a model with a domain that matches the study area well.

7. As a general principal, stick to the science that was addressed by the scope of the experimental design and avoid excess speculative, superficial interpretation.

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