Interactive comment on "ACE-FTS measurements of trace species in the characterization of biomass burning plumes" by K. A. Tereszchuk et al.

Anonymous Referee #1

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The authors have measured high quality trace gas ratios in some aged biomass burning (BB) plumes. The analysis, on a large scale, might be of great value in building a climatology of the characteristics of various aged BB plumes in the free troposphere (FT). Even though most BB smoke is confined to the planetary boundary layer, much more knowledge of the impacts and aging of BB smoke in the free troposphere is needed. The authors can likely identify the rough geographic origin of their fires and thus plume ages within plus or minus a day or so for their FT samples. With fairly high uncertainty, the authors could show how normalized excess mixing ratios in smoke plumes evolve as a function of age, which is useful for testing photochemical models as well as documenting the impact of BB on the free troposphere. The observation of N2O5 in smoke plumes may be unique and is certainly very interesting. N2O5 would likely be a signature of night-time smoke processing of smoke emitted at night (due to the short lifetime of NO2 during the day), which is a largely unexplored topic. However, the authors need to acknowledge the uncertainty in ground-level fire location (and thus age) associated with the fact that fires are often not detected as hotspots and they inject smoke at a variety of initial altitudes. In particular, the MODIS hotspots are easily available with daily resolution (even overpass resolution) and it is important to include them for possible source identification. To illustrate the problem of undersampling by active fire detection, the climatological cloud cover for July in western Canada is about 50% (Stubenrauch et al., 2011) meaning many fires would go undetected by active fire detection and sources would be mis-located when relying on hotspots. This general comment is particularly relevant to Figure 1 where the back trajectory does not go near any actual hot-spots.
Stubenrauch, C.J., Cros, S., Guignard, A., & Lamquin, N. (2010). A 6-year global cloud climatology from the Atmospheric InfraRed Sounder AIRS and a statistical analysis in synergy with CALIPSO and CloudSat. Atmospheric Chemistry Physics, 10, 7197- 7214.

The HYSPLIT trajectory model is used to help give a general indication of the movement of air masses over a given period of time to assist in determining the source of biomass burning emissions. HYPLIT backtrajectories have been used concertedly with AATSR and MODIS hotspots with great success in the BORTAS-A and BORTAS-B campaigns (http://www.geos.ed.ac.uk/research/eochem/bortas/) to confirm the locations of Boreal fire emissions and were used to corroborate IASI CO near real time data and and GEOS-5 CO model forecasts that were employed during the campaign for flight planning purposes. Determining a ground-level fire location is not as problematic an issue as you have painted it out to be. Focus is not placed on individual, sporadic hot spots from small fires which would have negligible emissions that would be difficult to detect remotely. The locations of individual hot spots is trivial. The measurements made in this work are from the outflows of substantial biomass burning events, where continued burning occurs in the same geographical region over an extended period time; dozens of hots spots within the same geographic location. e.g. Like the Boreal fires in Western Ontario that were measured during the BORTAS flight campaign (July 2011), the Russian forest/peat fires (July/August 2010) and the Boreal fires in Saskatchewan/NWT depicted by the fire spots in Figure 1, which represents a burning event that lasted nearly two weeks. Measurements of the emissions from these events are the basis of this work. There is no mis-location particularly when you can physically see the burn area using the MODIS imager data. Hot spots from both AATSR and MODIS, IASI CO and MODIS imager data are all used concertedly to confirm source location. Animations are create using the morning and evening passes of IASI to observe plume movements over the period of time leading up to the time of the ACE measurement to determine where plume outflows are originating from and if the the is convergence from different sources.

With respect to NO_2 and N_2O_5, I agree that a more detailed investigation needs to be done. Once I have completely processed the ACE-FTS database, I will focus on investigating the differences in the measurements made for the sunrise and sunset occultations to study the day- and nighttime chemistry within the plumes.

A few other sources of uncertainty need to be better acknowledged:

1) In general, but especially in areas of intricate and rapid land-use change, such as the Amazon, it's not possible to confidently assign a single fire to a single ecosystem. For instance, a random fire in the Amazon could be a deforestation fire, an understory fire, a crop residue fire on a soybean plantation, or a pasture fire. There is no reliable way to be certain from space in many cases, especially when the exact location is not known. Even when a specific hotspot is assigned a land cover using a very recent land cover map this is probably only meaningful when averaged over a large number of hotspots.

I agree that some fires may consist of a combination different ecosystems. Your example of the different types of biomass burned in the Amazon is a valid point, which is why the MODIS hot spots and imager data are used to visualize the burn area and elucidate what is being burned and where to abate any ambiguity in the source of the biomass burning outflow.

2) The statements about differences and similarities between regions have high uncertainty when based on only a few data points and the number of plumes from each region needs to be clarified throughout.

I will expand upon this section.

3) In Figure 3 (upper panel) the slope is believable as a C_2H_6/CO ER since only BB plumes were selected based on HCN. However, in the background plot in Figure 3 there are some CO and C_2H_6 values that are higher than many of those in the BB plume. One might initially guess the background values would be near the backgrounds implied by the intercept in the upper panel. Are these high values in the "background" indicating industrial plumes and that the background samples are more correctly labeled "non-BB samples"?

This is a good point. I will label them as "non-BB samples" or refer to them as "off-plume" measurements throughout the manuscript.

4) The statements about differences and similarities need to be expressed in some sort of quantitative language. The statistical analysis is weak with statements like "upon inspection it is apparent" – when I actually see no correlation at all. Some sort of quantification is expected in a scientific paper. For instance saying: " the ratio of X/Y in plume group 1 is 0.5 plus or minus 0.3" and in plume group 2 it is 1.5 +- 0.2, not just "1 obviously differs from 2." Or a claim that two groups of data have unique signatures can be supported by principle component analysis, etc.

I will elaborate more on the quantitative aspects of the comparative analysis in the manuscript.

5) Please give the units for the standard deviations prominently. It's most common to express standard deviations in the same units as the mean. Thus throughout this paper the standard deviations appear to be huge, which is incorrect and in any case they need to be defined prominently.

I will add the units for the stdev.

6) I am doubtful about the long-range outlook for measuring age-dependent emission factors from space. There are at least four serious problems with this concept. First, the degree of photochemical processing can vary greatly for the same processing time. Second, since species

lifetimes vary greatly, it is not clear what sort of age or "equivalent OH-age" increments would be needed and how they would be implemented in models. Third, a fire located on the upwind or downwind side of the grid box in a large scale model would produce a plume with very different ages as it enters the next grid box. Fourth, ACE is only sensitive to the emissions that are lofted to the free troposphere by flaming combustion or deep convection, which has associated scavenging. Most fire emissions globally stay in the boundary layer so they would be overlooked. The authors work is valuable, but primarily for documenting impacts on the FT rather than as model input of a GCM that has to represent all layers of the atmosphere.

We are not looking to derive age-dependent emission factors; we are looking to generate sets of age-dependent emission ratios, which can be used as constraints for modeling work, such as that being conducted for the BORTAS project which seeks to investigate not only processes in the free troposphere, which the ACE data will help elucidate, but chemical processes below and above the boundary layer as satellite data is being used in conjunction with aircraft and ground measurements to provide a more complete picture of the chemistry occurring in biomass burning emissions. At no point was it ever suggested that from ACE data alone, can we get complete information of the chemistry of plume emissions and aging, rather it should be used as complimentary information.

7) The basic atmospheric chemistry needs to be recognized. NO2 is an initial fire emission that can photolyze to make O3 or react with OH to make HNO3. The HNO3 is thought to react quickly with NH3 to make ammonium nitrate. At night NO2 + O3 can make NO3 and NO2 plus NO3 can make N2O5, which can hydrolyze to make HNO3. If PAN or alkyl-nitrates form in the plume then if the plume warms they can decompose and release some NO2 in the aged plume, though not nearly as much as is released in the fire originally. O3 can be consumed by a variety of reactions on smoke plumes. I don't understand the statements about negative correlations indicating that a species is a secondary product. It seems clear from the data presented in Table 2 that O3, HNO3, and NO2 are all lost as the plume ages – so they are not secondary products.
I.E. if ΔCO is positive by definition in a BB plume, then a negative value of ΔX normally means it is present at a mixing ratio lower than in the nearby background air so it has been destroyed by plume chemistry.

I will append the additional information, but until we have our PAN retrieval and the retrievals of additional pyrogenic VOC and OVOC species which is currently being conducted, it would be premature to go into a more detailed discussion of the chemistry taking place in the plumes.

I don't understand how an increase in the concentration of O3, HNO3 and NO2 can be considered a loss? It is ΔCO that is the negative, CO concentrations diminish with age from dilution, chemical processes, etc.. and O3, HNO3 and NO2 increase relative to their concentrations found in fresh plumes.

Some specific comments:

P16613, last paragraph, this is too long to discuss hypothetical future work.

I will abbreviate the paragraph

P16615, L5, "highly successful" not needed. L11, Akagi et al final ACP version is now published.

Will change accordingly.

P16616, L4-5, if BB plumes were observed above the tropopause this would be worth discussing!

There is no mention of BB plumes being observed above the tropopause, in fact, it is specified in the experimental section that all data measured above the tropopause is filtered out!

L19, fires are usually more readily observed during the day.

Agreed.

P16619, L13, words like “rainforest” or “jungle” should be replaced with the appropriate term such as “tropical evergreen forest.” Also on page 16620, L4, there may be a reference to Amazon savanna?

Will change accordingly.

P16619, bottom, here and throughout it should be made clear what the uncertainties in the mean are as a percent or fraction of the mean!

Will clarify.

P16620-16623: revise plume aging conclusions per general comments.

Will adapt conclusions to reflect the general comments.

P16623, last line, one example of assumptions about the land cover in the Amazon that may not be correct, and “Rainforest” not usually capitalized within a sentence.

Will change accordingly.

P16624, L15-16, see comments below about comparisons. Also, smoke differs in composition between lofted and unlofted emissions, but also by fuel N and S content, which can be quite variable. See Burling et al. (2011). Burling, I. R., Yokelson, R. J., Akagi, S. K., Urbanski, S. P., Wold, C. E., Griffith, D. W. T., Johnson, T. J., Reardon, J., and Weise, D. R.: Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States, Atmos. Chem. Phys. Discuss.,
11, 18677-18727, doi:10.5194/acpd-11-18677-2011, 2011.

Will make note of this in the manuscript.

Table 1:

Show “n” for each geographic region and the land cover type if known? (which illustrates a main point) The Amazon and Congo have quite similar ER for stable species except for CH4. Both are areas of tropical rain forest that are however, experiencing rapid development. Is the stdev the stdev of the mean emission ratio? If so they seem highly unconstrained? The authors own data, upon my casual inspection, seems to disprove the idea of characteristic emission ratios for the fires as they have grouped them. E.G. they are not identical, but neither do they appear to differ much at the one-standard deviation level.

I will include “n” for each of the regions. The stdev is the stdev of the mean emission ratio. For some molecules, they are quite high. In the future, stricter filtering of the data will probably be required to improve these values. The fires are grouped in accordance to R value. Characterization and differentiability to be determined by high R values not the emission ratios. Why should the emission ratios be identical for different types of biomass being burned? One would expect the opposite, i.e. that the differing chemical compositions of the biomass being burned from each ecosystem would generate unique molecular VMR values for plumes at a given age. This is why the correlation coefficients are used for characterization purposes, because R values are not directly dependent on VMRs, but emission ratios on the other hand are.

Table 3:
Instead of showing raw concentrations, it would be much more useful and instructive to show ratios to CO on an excess basis: $\Delta X/\Delta CO$ by subtracting the values of "X" and CO in a background from a nearby retrieval in very clean air. This would enable the reader to determine the trends in photochemistry by normalizing for dilution!

I will change the table accordingly.

Table 4:
The comparisons may be tricky. In some cases, Akagi et al. (2011) present ecosystem averages based on both lofted smoke sampled from aircraft and unlofted smoke sampled from the ground. In particular, for the Boreal forest fires, their supplementary tables break out individual averages for the airborne and ground-based measurements. The airborne average in the supplementary tables would be expected to be more comparable to the ACE retrievals in the FT. The Akagi et al airborne average has the advantage of being based on a number of vetted studies carried out over the years. (The overall average in Akagi et al may better reflect the total fire emissions that need to be considered in some applications.) The authors could also add a column to compare to the Simpson et al. (2011) Boreal forest fire data, which is an airborne average from western Canada collected in July 2008: the same month as the ACE retrievals! If the authors don't compare to Simpson et al, they should remove it from the reference list.

I realize that comparisons between the ACE data to the emission factors derived by Akagi et al. can only provide general insight on the comparability of the in-situ ground measurements to those of made remotely via satellite. Particularly since the EFs presented by Akagi et al. are derived from biomass burning emissions measure at the time of combustion and are being compared to remote measurements of plumes which have aged. I agree that the airborne averages would be expected to be more comparable to the ACE-FTS data. I will use the supplementary data to determine if there is any substantial difference in the comparison of the EFs and possibly improve upon the current comparison of the ACE data and the ground-based measurements which are already in very good agreement.
I will remove the citation to Simpson et al. from the references, as I would rather wait until we have the retrievals for additional pyrogenic VOC and OVOC molecules so that we can elaborate more on plume chemistry and make direct comparisons with the results of other projects and campaigns.