Airborne hydrogen cyanide measurements using a chemical ionisation mass spectrometer for the plume identification of biomass burning forest fires.

Le Breton et al., Authors' response to reviewer's comments

We would like to thank the referees for their thoughtful and helpful comments and will give detailed responses were appropriate.

Referee 1

The reviewer questions the validity of the 10 sigma approach. We are using a standard analytical definition of the limit of quantification, as defined by ICH-Q2B (1996), 10 sigma can be used to define a significant change above the ambient background conditions. This technique was implemented on the data attained from the CIMS during the BORTAS campaign. It was found that decreasing the number of standard deviations above background to 6 showed no significant change in the R^2 correlation to CO and gradient of this relationship, as represented in table 1. Decreasing the sigma value from 10 to 6 incrementally increased the number of data points used for the calculations without affecting the correlating relationship.

The flights during BORTAS were operated low in the boundary layer and extent up to 8000 metres. Biomass Burning (BB) influenced plumes were detected throughout this range of altitudes and ranged from 1 to 11 days old when the photochemical age is calculated. The R^2 correlation coefficient of 0.86 would surely not have survived this range of conditions and possible mixing if influences from fossil fuel (FF) plumes from North America were present. The ambiguity of this mixing was observed by Singh et al., (2012) as an increase in the HCN:CO mixing ratio was observed. The change is gradient observed in figure 5 is a result of data from flight B621. Back trajectories of this flight confirm the plume intercepted originates from BB**,** although the C_2H_2 data also follows the same structure that HCN, CO and black carbon exhibit.

The reviewer asks for more details of the instrumental set up. As we outlined in the original manuscript a thorough description had already been published in the more appropriate journal for a description of experimental set up, namely Atmospheric Measurement Techniques (Le Breton *et al.*, 2012). We have now included details of the the HCN standard used, which was a BW Technolgies HCN calibration cylinder was diluted from 10 ppm mix with an accuracy of +/- 10%.

The ionisation scheme presented there confirms no clustering, fragmentation and interference for measurements of formic acid. HCN measurements do not suffer from these issues. HCN is detected at mass 154 as an adduct with I^-. The "stickyness" of species such as formic acid will only affect measurements for the mass itself and our results have shown that even for so called sticky gases inlet losses in the current CIMS set up are not an issue. Although formic acid data is available from CIMS measurements during BORTAS, the current manuscript focuses on a new method of the identification of BB plumes using HCN.

The reviewer also has a few specific questions about the current CIMS set up

P5654 Under our current operating conditions, the local electric field divided by the gas number density (E/N) was 180 Townsend ($Td = 10^{-17}$ V cm^2) and under these operating conditions N is always = 1. The adduct forms with I^-.

P5655, L20 The inlet was actually heated to 50^0C and not 40^0C like previously stated. Formic acid is the most stable mass the Manchester CIMS currently studied. In flight calibrations are currently performed for formic acid and extensive lab tests have enabled relative calibrations of other species during the flight to be calculated. The relative calibration to formic acid allows the sensitivity of the CIMS to HCN to be validated and monitored during a flight.

P5656 The sensitivity of the CIMS to formic acid is dependent on the ion counts at amu 145, $I^-.H_2O$, if the number of counts falls below a threshold of 100 000 ion counts s^{-1}. The instrumental electronic tuning for the instrument can be changed for specific instrumental use. The formic acid paper was in the tuning which made the mass for formic acid independent of mass 145. The CIMS during the BORTAS campaign was operating under different conditions and therefore further tests were undertaken to confirm the dependency of formic acid sensitivity under these conditions on mass 145 and it was found that mass 154 ($HCN.I^-$) was independent of mass 145. The text has been amended to account properly for the formic acid relative calibration. The following text has also been added to inform the reader that HCN is dependent of water cluster counts

The HCN sensitivity was found to be independent of water cluster counts. The ion count signal throughout the flights were normalised to the formic acid sensitivity which was determined by calibrations pre, post and during the flight.

As the reviewer requested, we have now included a much more thorough description of the other possible sources of HCN. The variation in NEMRs cited by Akagi *et al*. (2011, 2013) has also been acknowledged. The range of different HCN:CO ratios have been reported in an updated in table 2 and as can b seen there is broad agreement between the studies. The use of C_2H_2 as a marker for FF and mixing comes with uncertainties which negate its use. Firstly C_2H_2 is produced in BB and FF and therefore does not separate the plumes as it cannot solely be used as a marker to distinguish either plume (Parker *et al*., 2011). This paper also suggests the photochemical decay of the CV that C_2H_2 exhibits with CO, deeming it difficult to extrapolate information of mixing from an air mass. The back trajectories have been presented in the BORTAS overview paper by Palmer *et al.,* (2013) paper and the low variation of the NEMR with altitude reported in the work here suggest mixing of the plumes detected BORTAS-B is negligible. The BORTAS over view paper by Palmer *et al.,* (2013) includes all the information required regarding flight tracks, dates, times, locations and back trajectories. Fire activity areas and ground station locations are also presented here. We do not feel that given this is a special issue of ACPD that it is needed to replicate descriptions, however, a plot has been included to represent the flight tracks for the data in this paper and altitudes at which the aircraft operated during the flight.

The reviewer has some concerns about the modeling aspects of the current work. We appreciate the time and effort that the referee has invested in this review and hope that our replies are interpreted in the good spirit in which they are written. First, there are of course a range of measured biomass burning ratios for HCN:CO and other species in the literature and nowhere in the paper do we state that any of these are incorrect. There are myriad reasons why there will be different ratios, e.g. vegetation type, temperature of the burn and many more reasons that the referee is far better placed to comment on than us. However, it is instructive to integrate a mature global chemistry and transport model, that has endured extensive testing of its dynamical (advection, convection etc.), chemical (gas-phase kinetics and photolysis) and physical loss processes (dry and wet deposition) using these extreme values to determine what HCN global field is produced. We do discover that the lowest reported ratios produce a global HCN field that is much lower than available field measurements and the highest produces a global field that appears too high when compared with a range of field observations from surface stations and airborne campaigns. Does this mean that the lowest and highest values are wrong, definitely not but it provides a starting point to determine the budget for HCN and when more measurements become available we will be able to improve the model analysis. Why have we adopted the approach of using one ratio and not using vegetation specific ratios? There are two reasons for this; first, we hope that this will make the integrations more useful to the general atmospheric community (see text) and second, it allows us to look at the impact of different emission ratios and different deposition velocities in a more straightforward manner. Of course we will integrate the model with the ratio we have determined in this study as one of the collection of integrations but as we are at pains to say, we are not doing this to prove that this ratio is the correct one but to see what impact this ratio would have on a global field. What the model results show us is that the global ratios (whether different ratios are used in different regions or one ratio used throughout) that produce fields that are in keeping with current measurements do lie between 0.4 and 12.6. However, we also alert the community that we do not just need biomass burning ratios from as wide a distribution of burning types as possible but that the loss process appears to be dominated by ocean loss and that this deposition velocity must be characterized more fully in order to reduce the uncertainty of the budget. The referee is quite correct that there is a further uncertainty associated with the CO biomass burning total and that more details in the model description and further additional comments about uncertainty are warranted in the discussion of the model results and this has been added.

Now, why such an analysis is a problem to the referee is a puzzle? Surely the referee would like to know this information in addition to the biomass burning ratio returned? We want these model integrations to be easily interpreted and by stating that we are using a universal ratio and showing results from a range of these ratios does provide a back drop for the community to view and use these data easily. There are caveats, it is a model after all, but we believe that these data add to and not detract from the paper. Therefore, we have kept this section in.

Regional model analysis is being prepared with a view to looking at all gases sampled during BORTAS, where inter-comparison on a regional basis can be tackled using a wide dataset. The point about sampling 10% of the biomass burning region would be valid if we were stating that this is the one and only ratio that it is correct, something we are not saying. We are trying to perform an analysis that we believe adds value to the study of the HCN budget. In addition, the CO distribution on which our HCN emissions are based is segregated on biomass type and has different emission factors depending on these types.

We are not trying to model each ecosystem where biomass burning may occur with a specific value but imagining what would happen if all systems when burned produced a specific ratio. The fact of the matter is that the lifetime of HCN is sufficient for it to become quite well mixed in the troposphere and that the background levels that are measured will reflect a more weighted 'average' ratio. We are well aware that one ratio is not appropriate for each ecosystem. We disagree with the referee that there is value in this approach.

The modeling text in the paper has been amended to read

STOCHEM-CRI modelling

The STOCHEM-CRI global chemistry-transport model has been described in detail in several recent papers (Archibald *et al.*, 2010; Cooke *et al.*, 2010a; Cooke *et al.*, 2010b; Utembe *et al.*, 2009; Utembe *et al*., 2011) and will only be briefly described here. STOCHEM-CRI is a global three-dimensional model, which uses a Lagrangian approach to advect 50,000 air parcels using a fourth-order Runge-Kutta scheme with advection time steps of 3 hours (Collins *et al*., 1997). The transport and radiation models are driven by archived meteorological data, generated by the Met. Office numerical weather prediction models as analysis fields with a resolution of 1.25° longitude and 0.83° latitude and on 12 vertical levels extending to 100 hPa (Derwent *et al*., 2008). The CRI (Common Representative Intermediates) chemical mechanism (CRIv2-R5; Jenkin *et al*., 2008; Watson *et al*., 2008; Utembe *et al*., 2009) has been incorporated into STOCHEM. CRIv2-R5 emits methane and 22 non-methane hydrocarbons. Each air parcel contains the concentrations of 219 species involved in 618 photolytic, gas-phase and heterogeneous chemical reactions, using a 5-minute time step. Formation of secondary organic aerosol (SOA) was derived from the oxidation of aromatic hydrocarbons, monoterpenes and isoprene (Utembe *et al*., 2009; Utembe *et al*., 2011). Surface emissions for CO, NO_x and non methane hydrocarbons (NMHC), distributed over five emission types (anthropogenic, biomass burning, vegetation, ocean and soil) are taken from the POET (Precursors of Ozone and their Effects in the Troposphere) inventory (Granier *et al*., 2005). The distributions for lightning emissions are parameterized based on the work of Price and Rind (1992) with the emissions being distributed evenly between the convective cloud top height and the surface. The emissions are scaled so that the global total NOx emission from lightning is 5 Tg (N) yr^{-1}. The NOx emissions from civil and military aircraft are taken from NASA inventories for 1992 [Penner *et al*., 1999]. The implementation of the emissions from aircraft is the same as for lightning with an annual total of 0.85 Tg(N) yr^{-1}.

The model dynamical scheme and depositional schemes has been tested extensively through comparisons with ^{222}Rn and other models (e.g. Stevenson et al, 1998) and was part of a major model inter-comparison study of the CO budget using 26 global chemistry transport models (Shindell et al., 2006). This inter-comparison showed that model transport schemes compared favourably with measurements and other models. The model Stratosphere-Troposphere exchange (Collins et al., 2003) and its ability to transport pollutants over range of scales effectively (e.g., Derwent et al., 2004) has also been demonstrated. In addition, convection within the model has been extensively tested and validated (e.g. Collins et al., 1999; Collins et al., 2002). Therefore, in terms of transport and depositional loss (loss via OH for HCN is slow), the model is more than adequate for the intended study.

The biomass burning emissions for HCN are distributed as that of biomass burning emissions for CO with a single ratio used. The distribution is taken from the POET database and although there are several other distributions, we have not integrated using other methods so that we can make a direct comparison with other model integrations by us. However, we do provide an analysis of uncertainty in the discussion section of this paper.

Model results

The purpose of the model integrations were to inspect the global HCN levels generated using the extreme HCN biomass ratios (relative to CO) reported in the literature and the value determined in this study, using two ocean deposition velocities that lead to HCN lifetimes of *ca.* 3 months and *ca.* 6 months. It should be noted that the variation in emission ratio reported in the literature is not in question here, there are myriad reasons for the variation in terms of vegetation type, temperature of the burn etc. It is also noted that the limited available field measurements make comparison and constraint of the model somewhat limited. However, as we hope to show, the model results are instructive. The model results are in line with basic expectations, i.e. as the emission ratio increases the global HCN level increases and when the deposition velocity is decreased the global HCN for all three integrations also increases. Model results are presented in figure 7, which shows yearly averaged latitude-altitude profiles, given the overall uncertainties it is not justified to present more detailed seasonal results. We have deliberately used one HCN/CO ratio to distribute HCN emissions in these model runs to simplify them, we are not trying to reproduce any field data but we can compare with measurements and of course compare between the integrations performed in a straight forward manner. If we assume the lower deposition velocity leading to a lifetime of about 6 months we observe that an emission ratio of 0.4 x 10^{-3} leads to a global yearly averaged HCN level of 10-20 ppt, an emission ratio of 12.6 x 10^{-3} leads to a global yearly averaged HCN level of 300-600 ppt and an emission ratio of 3.7 x 10^{-3} leads to a global yearly averaged HCN level of 80-180 ppt. In each case the highest levels are observed over the tropical regions, obviously driven by high biomass burning, with little variation in vertical structure, reflecting the surface deposition process dominating loss and leading to a sink in the Southern Hemisphere in the model.

There is no attempt here to reproduce field measurements, but it is instructive to compare field data with the model. We have concentrated on lower and mid tropospheric measurements and note that there are measurements in the upper troposphere and lower stratosphere. Liang *et al*., (2007) observed HCN using aircraft during INTEX-A (July-August 2004). This field campaign ranged across the USA and Canada and took in measurements in both the Pacific and Atlantic Oceans. Although very high levels were detected in biomass burning plumes (1090 ± 850 ppt), the background levels observed were 290 ± 70 ppt. In their comparison, Liang *et al*., (2007) reported levels in Asian plumes of 420 ± 60 ppt compared with 270 ± 80 ppt returned by Jacob *et al*. (2003) during Trace-P. Notholt *et al*., (2000), conducted vertical column measurements of HCN and other gases between 57^{o} N to 45^{o} S across the central Atlantic. HCN was detectable between 30^{o} N and 30^{o} S, with column amounts retrieved between 0-12 km. The HCN column amounts ranged from 100-220 ppt, with the maximum occurring just south of the equator (10-15^{o} S). Singh *et al* (2003) report HCN levels of around 250 ± 150 pptv for HCN in February to April and Ambrose *et al* (2012) and Rinsland *et al* (2007) report mean mixing ratios of 360 ppt and 220 ppt respectively, while Knighton *et al* (2009) report a concentration ranging from 100-600 ppt and a mean background of 200 ppt. Therefore, based on the available measurements discussed thus far we would conclude that yearly averaged levels of HCN vary between approximately 100-450 ppt in the lower to mid troposphere. In the upper troposphere lightning may well contribute an additional non-negligible source and this region will be impacted by continental scale plumes, evidenced by a variety of measurements (e.g. Liang *et al*., 2007; Singh *et al*., 2007; Park *et al*., 2008; Randel *et al*., 2010; Wiegele *et al*., 2012). These plumes will contain a mixture of potential sources of HCN, of which biomass burning may well be the most predominant. It is also recognised that emission ratios will vary for different types of biomass burning, depending on vegetation type, temperature of burn etc. and no one ratio will be representative of the global emission. However, inspection of the model integrations suggests that the extreme ratios returned from field measurements are indeed extreme values: Adopting a uniform ratio of 0.4 x 10^{-3} returns a globally averaged HCN that is far too low, irrespective of whether the lifetime is 3 or 6 months. Similarly, adopting a ratio of 12.6 x 10^{-3} produces HCN levels that have been observed but are somewhat higher than expected for a yearly average, given the background measurements made. Using the ratio derived in this study as a global value produces HCN levels that are reasonable, compared with available field measurements, but are an underestimate. An underestimate is completely consistent with the fact that more influential biomass burning regions have returned a higher HCN:CO ratio. The satellite derived measurements of Wiegle *et al.*, (2012), although restricted in altitude to above 5 km, suggest strongly that biomass burning (particularly that located in the southern hemisphere) is a dominant source and lends confidence to the present broad brush model comparisons with measurements. Vegetation has also been suggested as a non-negligible source of HCN (e.g. Fall *et al.*, 2001) and vertical profile data from the Jungfraujoch station in Switzerland (Rinsland *et al.*, 2000) suggests that, in addition to biomass burning, there may well be a significant direct emission from vegetation.

It is clear that the depositional velocity adopted for HCN is crucial in any budget analysis, and for the ones used in this study increasing the lifetime of HCN from *ca.* 3 months to 6 months increases model HCN levels by a factor of ~ 1.4, irrespective of the emission ratio used. In this integration the CO biomass burning total used is ~ 500 Tg yr^{-1}, there are a range of estimates for this total summarized in table 5.

Table 5. Estimated CO emission totals from biomass burning in Tg yr^{-1}. * Totals reported follow the analysis of Stroppiana *et al*. (2010).

Total (Tg yr^{-1})	**Source**	**Reference**
720	Inventory	Andreae and Merlet (2001)
1422	VGT inventory	Liousse *et al*. (2010) *
548	ATSR inventory	Mieville *et al*. (2010) *
770	MODIS inventory	Chin *et al*. (2002) *
365	GFED3 inventory	Van der Werf *et al*. (2010)*
594	MOPITT inventory	Pétron *et al.* (2004)
270	Model derived	Taylor *et al*. (1996)
507	Model comparison	Shindell *et al*. (2006)
494	POET inventory	Granier *et al*. (2005)
332-409	FINN Inventory	Wiedinmyer et al., (2011)

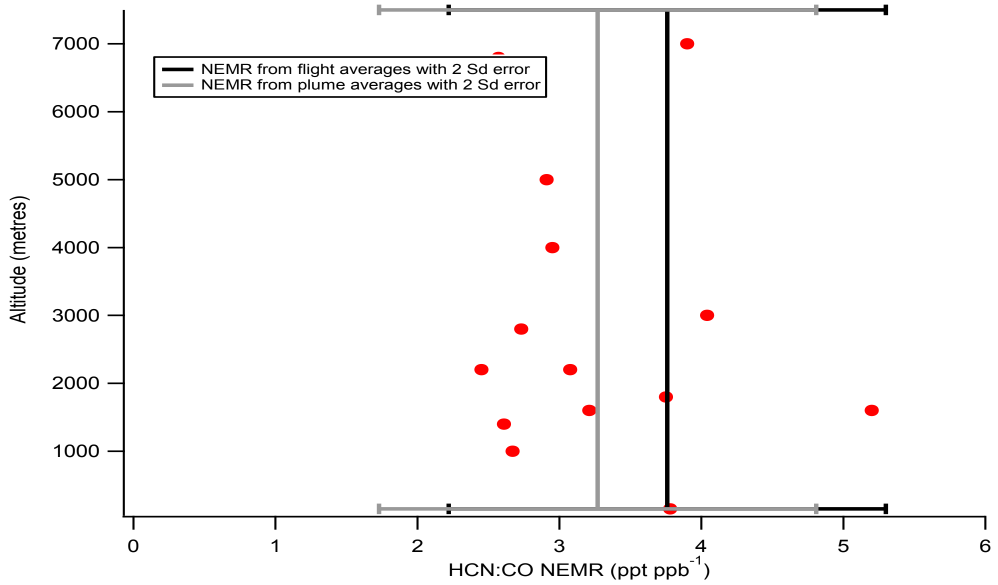
There is a wide range of estimates, but the majority lie between 750 Tg yr^{-1} and 350 Tg yr^{-1} and therefore to a first approximation the model estimated HCN levels will vary by a factor of 1.5 based on the CO emission uncertainty alone. HCN:CO biomass burning emission ratios will vary with type of burn and vegetation where It is noted that this ratio will vary with vegetation type and that using one ratio is not physically correct. However, the range reported has allowed us to investigate in a simple way the impact of these ratios on atmospheric levels.

In summary, model integrations suggest that the extreme ratios reported in the literature generate too little or too much HCN and really are extreme values. Using the ratios reported in this study to drive the model emissions produces HCN levels that are an underestimate compared with a range of field measurements which are consistent with the fact that higher ratios are seen in tropical biomass burning events for example. However, the model integrations highlight that depositional loss is very important to determining HCN atmospheric background levels and that further work is required to constrain this loss process. In addition, more atmospheric measurements are welcome, particularly vertical column and transects.

The NEMR error has been recalculated so it reads 3.76 ± 0.149 pptv $ppbv^{-1}$. We have also carried out a plume by plume analysis of the NEMR. If all plumes are selected separately and the NEMR and error is calculated for each, the average value for these lies with 1 standard deviation of the stated current NEMR in the paper, as shown in the table below.

Flight	Plume	NEMR	Error
B624	1	2.45	0.22
	2	3.076	0.21
	3	2.73	0.24
b626	1	3.78	0.24
	2	2.57	0.27
	3	2.61	0.22
	4	3.21	0.20
b628	1	2.67	0.27
	2	4.04	0.25
	3	2.91	0.24
	4	2.95	0.23
	5	3.9	0.23
b621	1	3.75	0.250
	2	5.2	0.27
b622	1	1.26	0.250
	2	0.67	0.21
	3	1.2	0.21
	4	1.72	0.25
Total Average (exlcuding B622)		**3.27**	**0.24**
sd of NEMR		0.77	

Below is plot of the individual plume NEMR as a function of altitude



Again, as can be seen with error all NEMRs agree.

The reviewer also, asks about the influence of mixing, there is no doubt that rapid mixing will erode any initial emission ratio. However, buoyant plumes such as those generated by intense biomass burning will retain their plume integrity over large distances > 100 km (e.g. Freitas et al., 2011, Journal of Advances in Modeling Earth Systems, 2011, 3, DOI:10.1029/2011) and within the plume tracer ratios can be preserved for some time, before mixing alters that ratio.

The reviewer also includes a list of points that needs to be addressed. The responses to points that have not already been addressed are as follows.

P5652 The review of HCN sources reads as follows

BB is considered to be the major source of HCN in the atmosphere (Li *et al*., 2000, 2003, 2009; Liang *et al*., 2007; Shim *et al*., 2007) via the pyrolysis of N-containing species within the fuel (Johnson and Kang, 1971; Glarborg *et al*., 2003). Cooking fire emissions of HCN have also been observed in Mexico and Africa (Christian *et al.,* 2010), although concentrations fell below FTIR detection limits.) Singh *et* al. (2003) observed enhancements of HCN in China which correlated with CH_3Cl indicating a source from hard coal burning for cooking. It must also be noted that biofuel is widely used in China (Streets *et al.,* 2003) although data from Africa suggest emissions of nitriles are negligible (Bertschi *et al*., 2003; Yokelson *et al*., 2003). HCN is also known to be emitted from motor exhausts, but is though to be at negligible levels (Li *et al*., 2003; Lobert *et al*., 1991).

P5653, L20 The text has been amended to read

Recent studies implementing these various methods of identifying a BB plume have resulted in an uncertainty in the ratio of HCN to CO due to the variability observed in fires and potential mixing from other sources.

P5653, L22-23 The text has been amended to read

Using measurements of HCN and CO, BB plumes can be uniquely identified; enabling emission factors can be calculated from aircraft measurements.

P5658, L10-11 Hornbrook *et al*., (2100) states “Because background mixing ratios of CH_3CN, HCN and CO are not constant throughout the regions covered during ARCTAS, plume identification was done using the 1-min merge and TOGA merge data files and hand-identifying time periods with elevated fire tracer mixing ratios ranging from one minute up to 2 h in duration. Generally, “elevated” refers to CH_3CN mixing ratios >200 pptv, HCN mixing ratios >400 pptv, and CO mixing ratios >175 pptv, but in regions with lower background mixing ratios, long-range BB plumes with lower threshold mixing ratios were also sometimes identifiable above the background.”

The sentence in the text has been removed and merged with the comment below to now read

When the background concentrations are low, the plumes selected are generally picked by enhancement above background. This method is likely to cause inaccuracies there is no definite point at which “plume data” can be determined.

5658, L19 The text has been amended to read

Here we evaluate a statistical approach to plume identification by assuming that the threshold limit to define “in plume” data is ten times that of the standard deviation above the variation in the background (ICH-Q2B, 2009).

P5658, L25 We tested 6, 7, 8, 9 and 10 standard deviations above background and found no difference, within experimental error, between their R^2 and gradient. Thus, using a standard deviation above 6 was deemed to be unnecessary as this will only reduce the number of data points.

The text has been amended to read

In order to define the plume, the median background concentration for each flight was calculated. 10 standard deviations was initially implemented as the threshold for “plume data”. It was found that decreasing the number of standard deviations incrementally by 1 made no significant change in the NEMR, i.e. the NEMR was within error the same, and R^2 until 6 sigma.

P5659, Table 2 has been amended to acknowledge the correct paper

P5659 The consistency of the ER calculated in plumes ranging from 1 to 11 days old implies the ability for ER to be calculated close to the plumes and potentially at a distance if conditions are suited. This is an extension on how this new instrument technique can be applied to furthering our knowledge of development with biomass burning plumes with age.

P5660, L24 The text has been amended to read

The NEMRs reported in previous work

P5661, L7 The text has been amended to read

Using the NEMR`s calculated by Hurst *et* al., 2001, Hornbrook *et al.* (2011) report the low ratio of 0.43 pptv ppbv^{-1} originating from African Savannas, tropical forests and extratropical forests

P5661, L16-17 The text has been amended to read

The 6 sigma HCN method of identifying BB plumes has shown the veracity of HCN as a BB influenced plume marker.

P5664, L5-7 and conclusions: Although the ratios could have been altered due to BB/FF mixing, the high correlation to CO shows consistency to the other research referenced.

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

The text has been amended to read

“high precision”

L16 this has been changed to “BB-influenced plumes”

L26 The end of this sentence has been removed and now reads “The NEMR (relative to CO) calculated using this plume identification method was 3.76 ±0.02 pptvppbv which is in the range of previously reported values (Andrea et al., 2001; Sinha et al., 2003; Yokelson et al., 2009; Hornbrook et al., 2011)

P5665, L1 The text has been amended to read

The study-average NEMR

5665 The text has been amended to read

These first results of HCN measurements by CIMS using I^- chemistry shows the capability of CIMS to attain high frequency HCN measurements in the lower atmosphere with a high sensitivity and low limit of detection.

Referee 2. The reviewer has a few points that need to be addressed

1 The LOD for HCN at 3 seconds is 5 pptv. Laboratory tests determined the instrumental background for HCN by flowing N_2 through the inlet. The CIMS inlet has been designed to cope with “sticky” gases such as formic and nitric acid. The laboratory tests showed that HCN has an e-folding time of 8 seconds. The instrumental background signal was determined by shutting the inlet and flowing N_2 through the instrument. Day to day backgrounds were determined

2 The Flight tracks are presented in the BORTAS overview paper, Palmer *et al*. (2013). The following brief section has been included to inform the reader of the flight locations and altitudes and also to direct the reader to the Palmer *et al*., 2013 overview paper which reports all flight tracks, fire active areas and ground stations. The following section and graph have been included.

The BORTAS –B campaign was conducted between 12 July and 3 August 2011 based in Halifax, Canada. CIMS data from 5 flights during this campaign are presented here. The Palmer *et al.,* (2013) presents an overview of the campaign with full descriptions of the operating area, all flights and fire activity maps. Figure 3 below shows the flight paths and altitude of the aircraft for the data presented here.

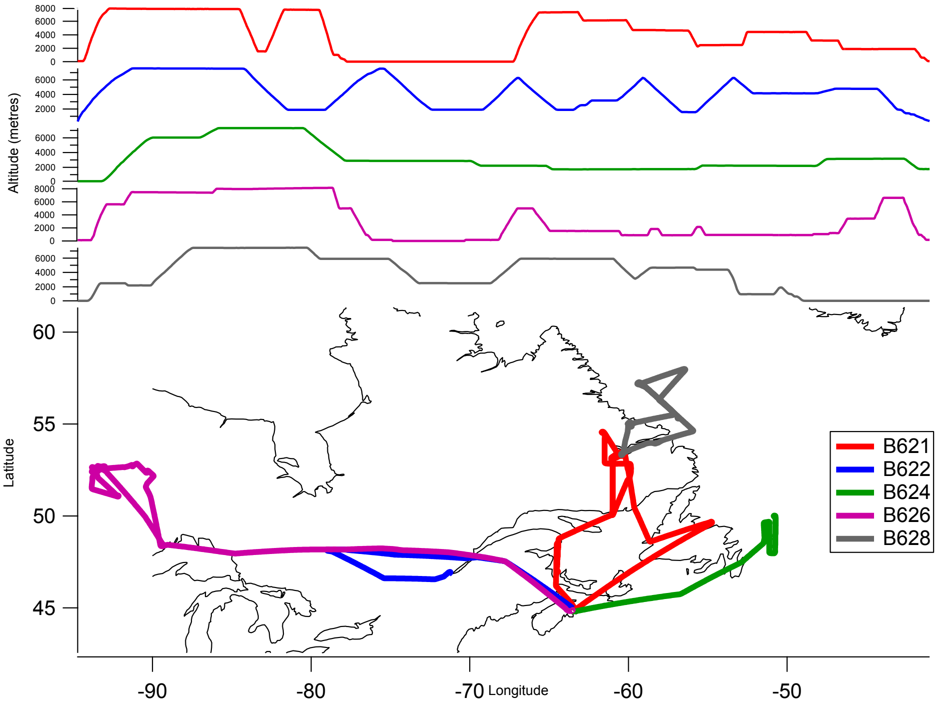


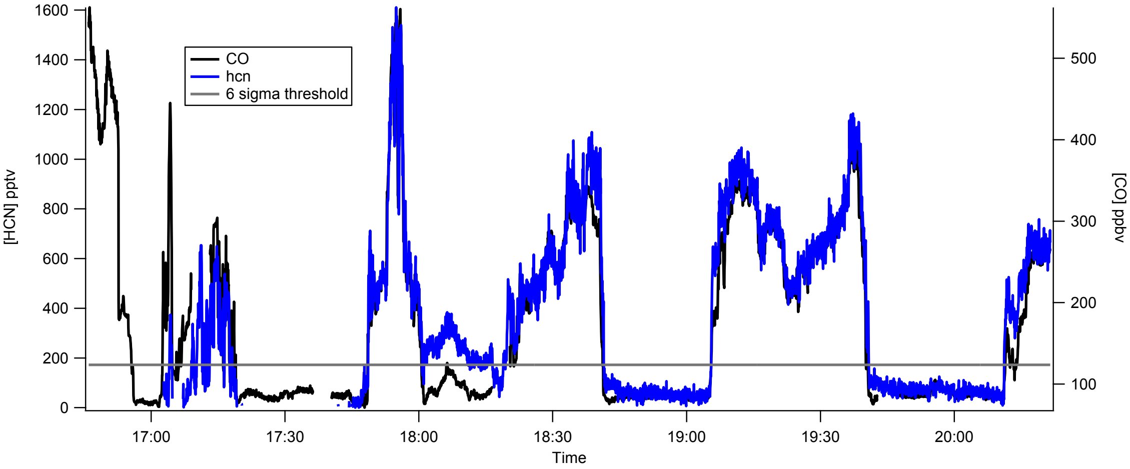
Figure 3. The flight tracks from BORTAS –B from the CIMS data is presented here

We have also include two altitude profiles and the section has been included that now reads.

Figure 6 displays an altitudinal profile performed in clean air from flight B622. An average concentration of 45 pptv is observed to remain fairly constant up to an altitude of 6000 metres. The concentration then rises at 6000 metres to a maximum of 111 pptv at 7000 metres. Figure 7 represents the whole data set from flight B622 exhibiting stratification between atmospheric layers. There is clear evidence of distinct BB plumes as a function of altitude, providing further evidence of the preservation of distinct BB plumes.

3. The plumes measured during BORTAS were from distance (up to 11 days old) and next to the source, flight B626. The R^2 of figure 8 shows that varying the plume age, altitude at which it is intercepted and source does not greatly affect the ER. The 6 sigma method is able to help distinguish between the regions of strong anthropogenic sources of CO as only a small amount of HCN may arise from this activity, therefore not crossing the 6 sigma threshold. The modeled section has been amended and text has been added to discuss the issues with deriving a HCN budget from the NEMR presented here. This text is presented above in response to the first referee's comments.

4. The reviewer has a question about how our method selects data in plume. Table 1 has been amended to show the background, 1 sigma and 6 sigma on each flight that we feel addresses the point raised by the referee. The following graph is typical of how the 6 sigma method picks the "in plume" data. However, we do not feel that this would aid the reader above and beyond the extra information given in Table 1.


CO
hcn
6 sigma threshold
[HCN] pptv
0
200
400
600
800
1000
1200
1400
1600
[CO] ppbv
100
200
300
400
500
17:00
17:30
18:00
18:30
19:00
19:30
20:00
Time