



**Airborne HCN
measurements from
biomass burning**

M. Le Breton et al.

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

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Abstract

A Chemical Ionisation Mass Spectrometer (CIMS) was developed for measuring hydrogen cyanide (HCN) from biomass burning events in Canada using I^- reagent ions on board the FAAM BAe-146 research aircraft during the BORTAS campaign in 2011. The ionisation scheme enabled highly sensitive measurements at 1 Hz frequency through biomass burning plumes in the troposphere.

A strong correlation between the HCN, carbon monoxide (CO) and acetonitrile (CH_3CN) was observed, indicating the potential of HCN as a biomass burning (BB) marker. A plume was defined as being 6 standard deviations above background for the flights. This method was compared with a number of alternative plume defining techniques employing CO and CH_3CN measurements. The 6 sigma technique produced the highest R^2 values for correlations with CO. A Normalised Excess Mixing Ratio (NEMR) of 3.76 ± 0.022 pptv ppbv $^{-1}$ was calculated which is within the range quoted in previous research (Hornbrook et al., 2011). The global tropospheric model STOCHEM-CRI incorporated both the observed ratio and extreme ratios derived from other studies to generate global emission totals of HCN via biomass burning. Using the ratio derived from this work the emission total for HCN from BB was $0.92 \text{ Tg(N) yr}^{-1}$.

1 Introduction

Biomass burning (BB) is considered to be a major source of trace gases in the atmosphere (Li et al., 2000, 2003, 2009; Shim et al., 2007) and at levels significant enough to perturb regional and global atmospheric chemistry and composition (Levine, 2000). For example, large boreal forest fires in Russia from 2002–2003 were responsible for global growth rates of many trace gases including carbon dioxide and methane (Kasischke et al., 2005; Yurganov et al., 2005; Simpson et al., 2006). Fires in boreal regions are estimated to account for 9 % of global fire carbon emissions (Van derWerf et al., 2010) and their occurrences are predicted to increase by 30 % by 2030, with

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a 74–118 % increase in area burned by 2100 (Flannigan et al., 2005). The area burned in Canada has increased since 1970 as a result of rising surface temperatures (Gillett et al., 2004; Kasischke and Turtesky, 2006) resulting in an expected doubling of CO₂ equivalent greenhouse gas emissions from Canadian fires (Amiro et al., 2009). Long-range transport of the emissions is enabled in the troposphere and lower stratosphere via convection and pyroconvection (Fromm et al., 2000; Jost et al., 2004; Val Martin et al., 2010). This enables fires to not only impact local and regional air quality (Colarco et al., 2004; Morris et al., 2006), but also contribute to climate change (Damoah et al., 2004; Vivchar et al., 2010; Tilmes et al., 2011).

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). HCN has previously been observed from field biomass fires (Hurst et al., 1994a,b; Goode et al., 2000; Yokelson et al., 2007b; Crouse et al., 2009) and using laboratory biomass combustion systems (Lobert et al., 1991; Holzinger et al., 1999; Christian et al., 2004; Becidan et al., 2007). Column measurements of HCN were measured from the International Scientific Station of the Jungfrauoch (ISSJ) by solar infrared (IR) spectroscopy in 1998 during an intense period of biomass burning in the tropics (Rinsland et al., 2000). Singh et al. (2003) observed a HCN contribution from automobiles and from aircraft over the United States, although sources from automobile exhaust and industrial processes are thought to be negligible in comparison with BB (Lobert et al., 1991; Bange and Williams., 2000; Holzinger et al., 2001). A field experiment also indicated no detectable emissions of HCN from domestic biofuels (Bertschi et al., 2003). Thermodynamic calculations carried out by Boldi (1993) predict that an air parcel associated with lightning strikes could have a chemical composition such that the HCN/CO ratio would be around 10⁻⁴. Stribling and Miller (1987) showed that simulated lightning in a laboratory could produce HCN on planets such as Jupiter, strengthening the case that lightning-produced HCN has been observed on this planet (e.g. Podolak and Barnum, 1988). There have been examples where HCN has been observed in lightning

perturbed air in the Earth's troposphere (Singh et al., 2007; Liang et al., 2007), making lightning a possible additional source of HCN, although how much is still to be determined.

HCN is lost in the troposphere via the reaction with the hydroxyl radical (OH), creating a lifetime of a few years, although the reaction with singlet oxygen (O^1D) is suggested to be important in the lower stratosphere. Uptake into the ocean is currently thought to be the dominant sink with an inferred global HCN biomass burning source of 1.4–2.9 Tg(N)yr⁻¹ and an oceanic saturation ratio of 0.83 (Li et al., 2000). This oceanic loss produces a lifetime of 2–5 months (Li et al., 2000, 2003; Singh et al., 2003). Although HCN may play an insignificant role in atmospheric chemistry (Cicerone and Zellner, 1983), it is thought to be an important source of nitrogen in remote oceanic environments (Li et al., 2000). HCN is currently thought to be a useful tracer of BB as a consequence of its limited sources and sufficiently long atmospheric lifetime (Lobert et al., 1990; Holzinger et al., 1999).

Carbon monoxide (CO), acetonitrile (CH₃CN) and HCN are all currently used as a BB tracer, but a standard approach has not been well defined. Thresholds of CO are used, but CO has many other strong sources (e.g. industrial activity), there can be difficulties in filtering out plumes which do not originate from BB. Recent studies implementing these various methods of identifying a BB plume have resulted in an uncertainty in the ratio of HCN to CO (Simpson et al., 2011; Vay et al., 2011; Hornbrook et al., 2011; Yokelson et al., 2009; Sinha et al., 2003; Andreae and Merlet., 2001). Using measurements of HCN and CO, BB plumes can be uniquely identified and emission factors can be calculated.

Previous atmospheric measurements of HCN have been made using IR spectroscopy (Coffey et al., 1981; Zhao et al., 2002; Kleinböhl et al., 2006; Rinsland et al., 2007; Li et al., 2000). In situ measurements were first made in the stratosphere using NI-CIMS (Negative Ion-Chemical Ionisation Mass Spectrometry) (Schneider et al., 1997). Tropospheric measurements were then made by long-path Fourier transform IR (FTIR) spectroscopy within BB plumes (Goode et al., 2000; Yokelson et al., 2007), with

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5 a GC system, using a reduction gas detector (RGD) (Singh et al., 2003), by NI-CIMS using CF_3O^- as the reagent ion (Crouse et al., 2006, 2009; Yokelson et al., 2007), and by PTR-MS (Proton Transfer-Mass Spectrometry) (Knighton et al., 2009). Crouse et al. (2006) have shown that CIMS can be used to detect HCN selectively in the lower atmosphere, with a low detection limit and at a high frequency. Hornbrook et al. (2011) recently reported HCN to CO ratios from BB plumes using HCN measurements from a chemical ionisation mass spectrometer.

10 The overall goal of the “quantifying the impact of BOREal forest fires on Tropospheric oxidants using Aircraft and Satellites (BORTAS)” campaign was to investigate the connection between the composition and the distribution of biomass burning outflow, ozone production and loss within the outflow, and the resulting perturbation to oxidant chemistry in the troposphere (Palmer et al., 2013). Airborne measurements were taken on-board the BAe-146 large Atmospheric Research Aircraft (ARA) over Eastern Canada between the 12 July and 3 August 2011. The evolution and composition of these BB plumes were studied using the airborne instruments, ground instruments and satellite. In order to study the characteristics of these plumes, an accurate method of plume identification is required. The rapid time response of CIMS utilizing the I^- ionisation scheme (Le Breton et al., 2012) is deployed here for HCN measurements. The main aim of this work is to develop a statistical methodology to define BB plumes using HCN measurements and chemical enhancements within the plume which can then determine their emission factors with respect to CO and VOC's.

2 Experimental

2.1 CIMS

25 A Chemical Ionisation Mass Spectrometer (CIMS) was used for real-time detection of HCN. The CIMS instrument employed here was built by the Georgia Institute of Technology as previously described by Nowak et al. (2007) and has been previously

described for formic acid measurements (Le Breton et al., 2012). Subsequently various adjustments have been made to the inlet and these are described in the following section. The schematic in Fig. 1 shows the set up used and operating conditions of the CIMS on board the airborne platform FAAM BAe-146 research aircraft.

The inlet consisted of 3/8" OD diameter PFA tubing of length 580 mm which was heated to 40 °C to reduce surface losses. An orifice of diameter 0.9 mm was positioned at the front of the inlet to restrict the flow to 5.8 SLM. The pressure in the ionisation region was maintained at 19 Torr (133.322 Pa) throughout the flight by controlling the flow of nitrogen into the ionisation region using a mass flow meter.

2.2 Ionisation scheme

The ion-molecule chemistry using iodide ions (I^-) for trace gas detection has been described by Slusher et al. (2004) and was utilised here to detect HCN. A gas mixture of methyl iodide, CH_3I , and H_2O in N_2 is used to obtain reagent ions I^- and water clusters $I^- \cdot (H_2O)_n$, of which the latter is important for the ionisation of HCN, forming the adduct observed in the mass spectrum (Fig. 2). HCN was ionised by I^- via an adduct reaction,



which enabled HCN to be detected selectively at $m/z = 154$.

2.3 HCN calibrations, sensitivity and LOD

HCN was calibrated relative to that of formic acid which was measured and calibrated in-flight throughout the campaign. The response of HCN relative to formic acid was determined from laboratory calibrations performed with lab air with an RH ~ 55 % and dry air by passing the lab air through a drierite dryer. Known concentrations of HCN and HCOOH were flowed into the CIMS under these conditions and sensitivities for both gases were calculated. An average sensitivity ratio of 33 : 1 was observed. The

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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 to altitude. The average sensitivity ($\pm 1\sigma$) for each flight was determined by taking the normalized sensitivity and multiplying by the reagent ion count rate to account for reagent ion variability from flight to flight. The average sensitivity for HCN was 4 ± 0.9 Hz pptv⁻¹ for 1 MHz of reagent ion signal. The 0.8 Hz data were then averaged over 3 s for the analysis here.

2.4 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,b; Utembe et al., 2009, 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 h (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-min time step. Formation of secondary organic aerosol (SOA) was derived from the oxidation of aromatic hydrocarbons, monoterpenes and isoprene (Utembe et al., 2009, 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

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being distributed evenly between the convective cloud top height and the surface. The emissions are scaled so that the global total NO_x emission from lightning is 5 Tg (N) yr^{-1} . The NO_x 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 $0.85 \text{ Tg(N) yr}^{-1}$.

2.5 HCN

Using the biomass burning emission ratios derived in this work for $\text{HCN}:\text{CO}$ (3.76×10^{-3}) the total emission of HCN via biomass burning introduced into the model was $0.92 \text{ Tg(N) yr}^{-1}$. HCN is removed by reaction with OH ($k = 1.2 \times 10^{-13} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and deposited to the ocean at a rate of $3.4 \times 10^{-15} \text{ g(N) cm}^{-2} \text{ s}^{-1}$. The model derived lifetime for HCN is then ca. 3 months, consistent with other studies. Further simulations were carried out using more extreme ratios derived from other studies, e.g. 0.43×10^{-3} which yields a total emission of $0.11 \text{ Tg(N) yr}^{-1}$ and 12.6×10^{-3} which yields a total emission of $3.13 \text{ Tg(N) yr}^{-1}$. In addition to these three integrations, a second set of three, using the three HCN BB emission ratios relative to CO were performed with a lower deposition velocity (halved) leading to an overall lifetime of ca. 6 months.

2.6 Aircraft measurements

In addition to HCN data, observations of CO and CH_3CN are also used in the analysis. CO data are reported at 1 Hz using a fast fluorescence CO analyser with an uncertainty of $\pm 5\%$ (Gerbig et al., 1999). CH_3CN was measured by proton-transfer-reaction mass spectrometry (PTR-MS) (see Murphy et al., 2010 for experimental details). During the BORTAS flights the PTR-MS measured selected VOCs (volatile organic compounds) with a cycle time of around 15 s. CH_3CN , was measured at a m/z value of 42, which corresponds to the CH_3CNH^+ ion.

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2.7 Biomass burning plume identification

HCN is a known BB tracer (Lobert et al., 1990) and CH₃CN is also an indicator of BB emissions which is not significantly enhanced in areas of anthropogenic activity (de Gouw et al., 2003, 2006). These tracers and CO are regularly used to identify BB plumes but a consistent method has not yet been established. Variation in background levels can make it difficult to define exactly when a plume is encountered without the aid of trace gas measurements which are not characteristic of BB fires. Hornbrook et al. (2011) defined a BB plume as having a CO mixing ratio above 175 ppbv, a CH₃CN mixing ratio of > 200 pptv and an HCN mixing ratio of > 400 pptv. Detection of BB plumes occurred when background levels of these species were low. When the background concentrations are low, the plumes selected are generally picked by enhancement above background, but this is an inaccurate method. Vay et al. (2011) limited the HCN mixing ratio to above 500 pptv, CO to above 160 ppbv and CH₃CN to above 225 pptv, but again will experience similar issues with background concentrations. Simpson et al. (2011) states that the plume locations are defined by maximum CO concentrations. Holzinger et al. (2005) define a plume as CH₃CN concentrations increasing three standard deviations above neighbouring points.

Here we evaluate a statistical approach to plume identification by assuming that the limit of quantification of a plume is ten times that of the standard deviation above the variation in the background (ICH-Q2B, 2009). The lifetime of HCN is long enough to allow plumes to be identified weeks away from the date of the fire. Dilution during this period will lower the concentrations but there will still be a strong characteristic enhancement above the background levels. The long range transport and evolution of BB plumes can be evaluated using this method as the plume is not identified by a general enhancement for any air mass.

In order to define the plume, the median background concentration for each flight was calculated and the 6th and 10th standard deviation above this value were set as the two alternative lower limits of the plume. This was utilised to create a HCN to CO

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Normalized Excess Mixing Ratio (NEMR) as shown in Table 1. The difference between the slopes produced by the 6 and 10 sigma approach are within 2 sigma error and have similar R^2 values 0.72 and 0.67, respectively. The 6 sigma method reports a higher R^2 and utilises more data points in the calculation; therefore the 6 sigma approach is used for the analysis of flights B621, B622, B624, B626 and B628 as shown in Fig. 3. The HCN to CO ratios derived from the BORTAS flights are similar to those reported in the literature (Table 2). In order to assess the accuracy of this method, other possible approaches to BB plume identification were implemented using this data set. HCN, CO and CH_3CN have all been used in previous work (Vay et al., 2011; Hornbrook et al., 2011) to identify BB plumes. We have used 7 methods to define a plume; (1) 6 sigma above the HCN background (2) 6 sigma above the CO background (3) 6 sigma above the CH_3CN background (4) above 100 ppb of CO (5) above 300 ppt of HCN (6) above 175 ppt of CH_3CN and 100 of ppb CO (7) above 200 ppb of CO. The HCN to CO NEMRs for each of the methods with the corresponding errors and R^2 value are shown in Table 3 and the percentage of data calculated to be in a plume is shown in Table 4.

The 6 sigma HCN method produced the highest average R^2 of 0.76. The methods using CO as a threshold exhibited low correlations on flight B628, as a result of a peak in CO during low level sections of the flight, as shown in Fig. 4. This can be attributed to non-BB sources of CO enhancing the CO levels where no HCN sources were present, as CO is known to have other natural and anthropogenic sources (Logan et al., 1981). This highlights a potential problem when using CO as a marker, as other measurements are required in order to determine the source. B622 had low CO concentrations but did show structure which was reciprocated by the HCN measurements. The CH_3CN data was too close to the detection limit during flight B628 to be able to determine a 6 sigma above background. The 200 ppb CO threshold approach removed all of these data from this flight, which would suggest that none of the flight encountered a BB plume. The method previously used by Hornbrook et al. (2011) produced an R^2 of 0.30 for this flight as a result of the low CO and CH_3CN concentrations, whereas the 6 sigma HCN approach produced an R^2 of 0.69. Using CO as a BB marker is limited

due to the variability in sources of CO. This method can be used for relatively fresh and unmixed plumes, whereas aged plumes may suffer from enhancements of CO from other sources.

The methods using CH₃CN data did produce a high R^2 on many flights, as shown in Table 3. However, the Limit of Detection (LOD) of the PTRMS to CH₃CN during BORTAS was a factor of 2.5 worse than the LOD of the CIMS towards HCN. As a result when sampling aged, hence dilute, plumes the S/N ratio is not significant enough to identify a plume, as exemplified by flight B628. Furthermore, as the PTRMS was used to detect a range of compounds during each flight, the time response was slower than that of the CIMS system. As a result, the CH₃CN data has a time average from 9 to 20 s, depending on the number of target gases that were being measured. With this particular sampling protocol it is difficult to measure accurately plumes close to the source as the lower measurement frequency may struggle to pickup small plumes as a result of the speed of the aircraft. Nevertheless, CH₃CN can be used to accurately detect a BB plume, under most conditions, as exemplified by flight B626.

2.8 Emission ratios

The 6 sigma technique is used here to calculate the emission ratio of HCN from 4 flights during the BORTAS campaign 2011. Figure 5 shows all the data points which are used to calculate the mean NEMR; 3.76 ± 0.02 pptv ppbv⁻¹. The NEMR was calculated using the equation

$$\text{NEMR} = \frac{\Delta[X]_{\text{plume}} - [X]_{\text{background}}}{[\text{CO}]_{\text{plume}} - [\text{CO}]_{\text{background}}} \quad (2)$$

The data from flight B622 were omitted from this calculation due to the possible ageing and mixing of the plume. The NEMRs calculated during BORTAS are similar to those found in previous work, as seen in Table 2. The previously reported in previous work vary from 0.43–12.8 pptv ppbv⁻¹. The NEMRs calculated here for HCN from Canadian

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BB plumes is lower than that found by Simpson et al. (2011), $8.2 \text{ pptv}^{-1} \text{ ppb}^{-1}$. Hornbrook does highlight the observed variation in the ratios, and offers a possible explanation for the difference between these NEMRs, but this variation is not seen from flight to flight during the BORTAS campaign, which measured both fresh plumes and aged plumes. Californian fire emission ratios during ARCTAS-CARB were significantly lower than the Canadian and Asian fires (Hornbrook et al., 2011), ranging from 2.4 ± 0.9 to $8.8 \pm 3.8 \text{ pptv ppbv}^{-1}$, respectively. Andreae and Merlet (2001) reported very low ratios (0.43 to $1.5 \text{ pptv ppbv}^{-1}$) in densely forested regions while Yokelson et al. (2007b) reported a ratio in the Mexico City region of $12 \pm 7 \text{ pptv ppbv}^{-1}$. The increase in these ratios may be attributed to the high NO_x levels found around Mexico City. Although emissions of HCN from motor vehicles are not believed to be important on a global scale, localised emissions may become significant (Crouse et al., 2009). Boreal forests are the primary source of fires in Canada, whereas Californian fires may be as a result of varying fuels, such as coniferous forests and grass and shrubs (Hornbrook et al., 2011).

The 6 sigma HCN method of identifying BB plumes has shown the veracity of HCN as a BB marker. In addition, this method performed better than the others over the BORTAS campaign, as indicated by the statistics presented. Also, the 6 sigma HCN method showed the ability to define BB plumes accurately in air masses which had a low HCN background, enabling the identification of BB plumes in air masses distant from sources that were not constrained by a set threshold concentration. For example, a plume may have dispersed over large distances, lowering the concentration below the limit that defines a plume using previous methods. Nonetheless, this 6 sigma technique is still able to identify these plumes, as they are defined relative to the background. This 6 sigma method also has the same ability to determine VOC to CO ratios with the percentage of data at a high time resolution (3 s). This method is therefore used to determine a HCN to CO ratio for models to calculate a global HCN budget.

3 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. 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 Fig. 6, which shows yearly averaged latitude-altitude profiles. If we assume the lower deposition velocity leading to a lifetime of about 6 months we observe that an emission ratio of 0.4×10^{-3} leads to a global yearly averaged HCN level of 10–20 ppt, an emission ratio of 12.6×10^{-3} leads to a global yearly averaged HCN level of 300–600 ppt and an emission ratio of 3.7×10^{-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° N to 45° S across the central Atlantic. HCN was detectable between 30° N and 30° S, with column amounts retrieved between

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0–12 km. The HCN column amounts ranged from 100–220 ppt, with the maximum occurring just south of the equator (10–15° 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: a ratio of 0.4×10^{-3} returns a globally averaged HCN that is far too low, irrespective of whether the lifetime is 3 or 6 months. Similarly, a ratio of 12.6×10^{-3} produces HCN levels that have been observed but are somewhat higher than expected for a yearly average, given the background measurements made. There is no suggestion that the ratio derived in this study is the one that should be used for global model studies, but it does produce HCN levels that are reasonable, compared with available field measurements, if a little on the low side. The satellite derived measurements of Wiegler 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

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to biomass burning there may well be a significant direct emission from vegetation. Therefore, the tendency to underpredict lower and mid tropospheric HCN levels using the ratio derived in this study may also point to a strong vegetation source. 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. The values reported in this study produce HCN levels that are consistent with field measurements but are on the low side.

4 Conclusions

A CIMS instrument was developed for the airborne measurement of HCN in the lower atmosphere using methyl iodide as the ionisation reagent gas. HCN measurements were successfully attained over Canada in July and August 2011, during the BORTAS-B 2012 campaign onboard the FAAM BAe-146 aircraft. The high sensitivity (4 ± 0.9 ion counts s^{-1} pptv $^{-1}$), low limit of detection (5 pptv) and selectivity of the data acquired and presented here with a time resolution of 3 s illustrates the ability of this instrument to measure HCN accurately; it is, therefore, a highly sophisticated instrument for detecting burning plumes. The mixing ratios measured through the biomass burning plumes ranged from sub 0.1–3.7 ppb covering the range of previously reported atmospheric levels (Singh et al., 2003, 2012; Knighton et al., 2009) and were strongly correlated with CO and CH₃CN, strengthening the ability of HCN to be a unique marker for biomass burning.

The 6 sigma methodology implemented and tested here for plume definition has been shown to produce the strongest correlation with CO, indicating that it is potentially an excellent method for defining biomass burning plumes. The NEMR (relative to CO) calculated using this plume identification method was 3.76 ± 0.02 pptv ppbv $^{-1}$ 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) indicating the accuracy of the HCN

measurements. The accurate NEMR was then used to estimate the total emission of HCN via biomass burning, which was calculated to be $0.91 \text{ Tg(N) yr}^{-1}$.

These first results from CIMS for HCN measurements using I^- chemistry suggest that the instrument is capable to measure HCN in the lower atmosphere with a high sensitivity, low limit of detection and high time resolution. The data produced also shows the accuracy at which HCN measurements can define biomass burning plumes and the reliability of this method.

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Table 1. HCN : CO NEMRs (in pptv ppbv⁻¹) for 5 flights during BORTAS campaign in plumes determined by 6 or 10 sigma above background and R^2 of correlations. NEMR units are ppt ppb⁻¹.

| Flight | 6 sigma slope | 10 sigma slope | 6 sigma R^2 | 10 sigma R^2 |
|----------------------|-----------------|-----------------|---------------|----------------|
| B621 | 4.7 ± 0.05 | 4.68 ± 0.05 | 0.83 | 0.83 |
| B622 | 0.66 ± 0.02 | 0.66 ± 0.02 | 0.46 | 0.46 |
| B624 | 2.68 ± 0.03 | 2.68 ± 0.03 | 0.82 | 0.79 |
| B626 | 2.72 ± 0.09 | 2.82 ± 0.06 | 0.81 | 0.83 |
| B628 | 3.68 ± 0.05 | 3.3 ± 0.08 | 0.69 | 0.45 |
| average | 2.89 ± 0.05 | 2.83 ± 0.05 | 0.72 | 0.67 |
| Average without B622 | 3.45 ± 0.06 | 3.37 ± 0.06 | 0.79 | 0.73 |

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Table 2. HCN : CO NEMRs as quoted in literature and the calculated NEMR for HCN from data collected throughout the BORTAS campaign, excluding flight B622. NEMR ratio units are ppt ppb⁻¹.

| Andrea | Sinha | Yokelson | Simpson | Hornbrook | This work |
|------------------|------------|-----------------|---------------|-----------------|-------------------|
| 0.43 ± 0.15 (Sv) | 9 ± 3 (Sv) | 12.8 ± 9.5 (MC) | 8.2 ± 2 (Can) | 8.8 ± 3.8 (As) | 3.76 ± 0.02 (Can) |
| 1.5 (TF) | 6 ± 2 (W) | 6.6 ± 4.8 (Yu) | | 2.4 ± 0.9 (CA) | |
| 1.4(TF) | 9 ± 5 (G) | 7 ± 5.9 (TF) | | 7.7 ± 3.2 (Can) | |

Sv: African savannas, TF: tropical forests, W: savanna woodland, G: savanna grassland, MC: Mexico city region, Yu: Yucatan, As: Asian, CA: California, Can: Canada

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Table 3. The HCN : CO NEMRs (in pptv ppbv⁻¹) with R^2 of slope for 5 flights during BORTAS campaign calculated using varying methods previously described in literature.

| | 6 sigma HCN | | 6 sigma CO | | 6 sigma of CH ₃ CN, HCN : CO | | 100 ppb CO | | 300 ppt HCN | | 175 ppt CH ₃ CN and 100 ppb CO | | 200 ppb CO | |
|---------|--------------|-------|--------------|-------|--|-------|--------------|-------|--------------|-------|--|-------|--------------|-------|
| | Slope | R^2 | Slope | R^2 | Slope | R^2 | Slope | R^2 | Slope | R^2 | Slope | R^2 | Slope | R^2 |
| B621 | 4.70 ± 0.042 | .83 | 4.92 ± 0.038 | 0.83 | 4.75 ± 0.11 | 0.83 | 4.81 ± 0.035 | 0.85 | 5.03 ± 0.06 | 0.82 | 5.11 ± 0.049 | 0.84 | 5.81 ± 0.087 | 0.83 |
| B622 | 0.46 ± 0.016 | 0.66 | 0.74 ± 0.010 | 0.62 | 0.85 ± 0.021 | 0.74 | 0.73 ± 0.011 | 0.59 | 0.40 ± 0.030 | 0.25 | 0.78 ± 0.013 | 0.61 | 0.69 ± 0.017 | 0.45 |
| B624 | 2.68 ± 0.029 | 0.82 | 2.91 ± 0.037 | 0.76 | 3.24 ± 0.072 | 0.85 | 2.93 ± 0.418 | 0.72 | 2.72 ± 0.035 | 0.76 | 2.98 ± 0.047 | 0.70 | 3.13 ± 0.064 | 0.64 |
| B626 | 2.72 ± 0.094 | 0.81 | 2.85 ± 0.074 | 0.83 | 2.83 ± 0.109 | 0.96 | 2.94 ± 0.050 | 0.83 | 2.97 ± 0.069 | 0.83 | 3.00 ± 0.134 | 0.81 | 2.64 ± 0.254 | 0.74 |
| B628 | 3.68 ± 0.050 | 0.69 | 6.77 ± 0.10 | 0.60 | 0 | 0 | 6.21 ± 0.17 | 0.42 | 0.74 ± 0.11 | 0.24 | 4.66 ± 0.270 | 0.30 | 0 | 0 |
| average | 2.85 ± 0.047 | 0.76 | 3.64 ± 0.052 | 0.73 | 2.33 ± 0.062 | 0.68 | 3.52 ± 0.062 | 0.68 | 2.37 ± 0.061 | 0.58 | 3.31 ± 0.103 | 0.65 | 2.45 ± 0.084 | 0.53 |

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Table 4. Percentage of data determined to be within a plume from the BORTAS flights using varying possible plume identification methods.

| % data in plume flight | 6 sigma HCN | 6 sigma CO | 6 sigma CH ₃ CN | 100 ppb CO | 300 ppt HCN | 175 ppt CH ₃ Cn and 100 ppb CO | 200 ppb CO |
|------------------------|-------------|------------|----------------------------|------------|-------------|---|------------|
| B621 | 25.05 | 38.60 | 22.35 | 43.28 | 16.65 | 39.00 | 11.00 |
| B622 | 46.80 | 83.47 | 62.51 | 73.40 | 12.31 | 51.00 | 49.00 |
| B624 | 58.25 | 64.92 | 55.23 | 61.07 | 49.42 | 49.00 | 37.00 |
| B626 | 13.71 | 22.12 | 13.89 | 48.23 | 24.22 | 8.00 | 3.00 |
| B626 | 46.49 | 63.65 | 0 | 48.52 | 2.52 | 12.00 | 0.00 |
| average | 38.06 | 54.44 | 30.80 | 54.90 | 21.02 | 31.80 | 20.00 |

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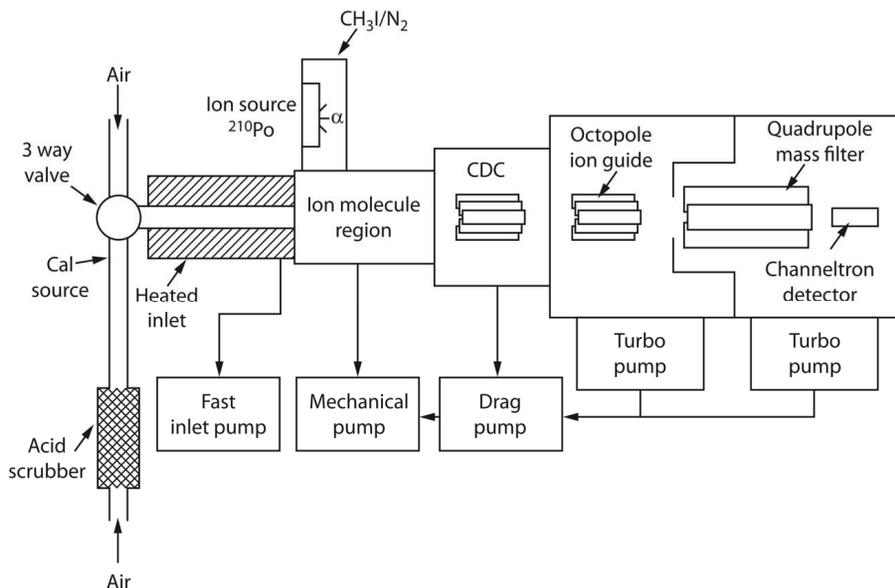


Fig. 1. Schematic of chemical ionisation mass spectrometer (CIMS) used in this study. Arrows indicate direction of gas flow. Dimensions are not to scale.

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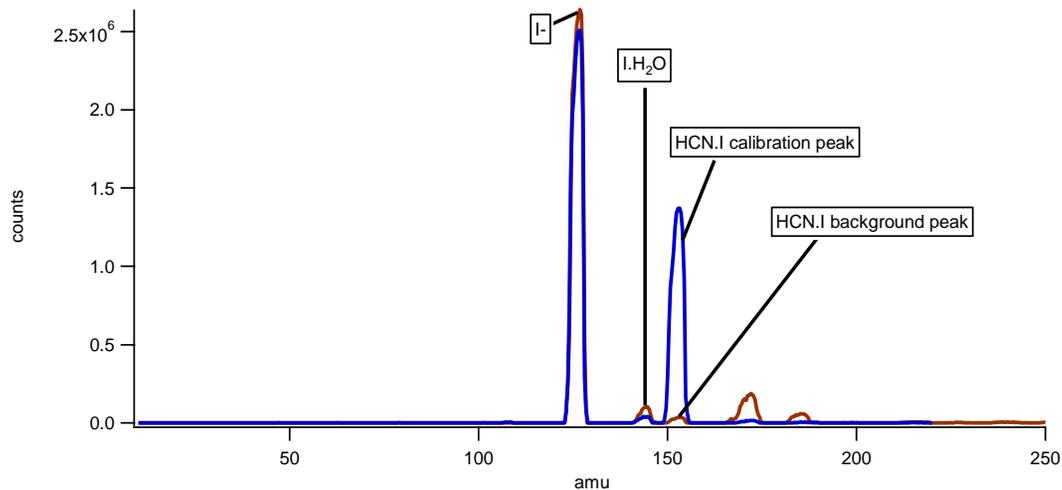


Fig. 2. Mass scan from the CIMS during background (red line) and encountering a HCN calibration peak at mass 154 (blue line).

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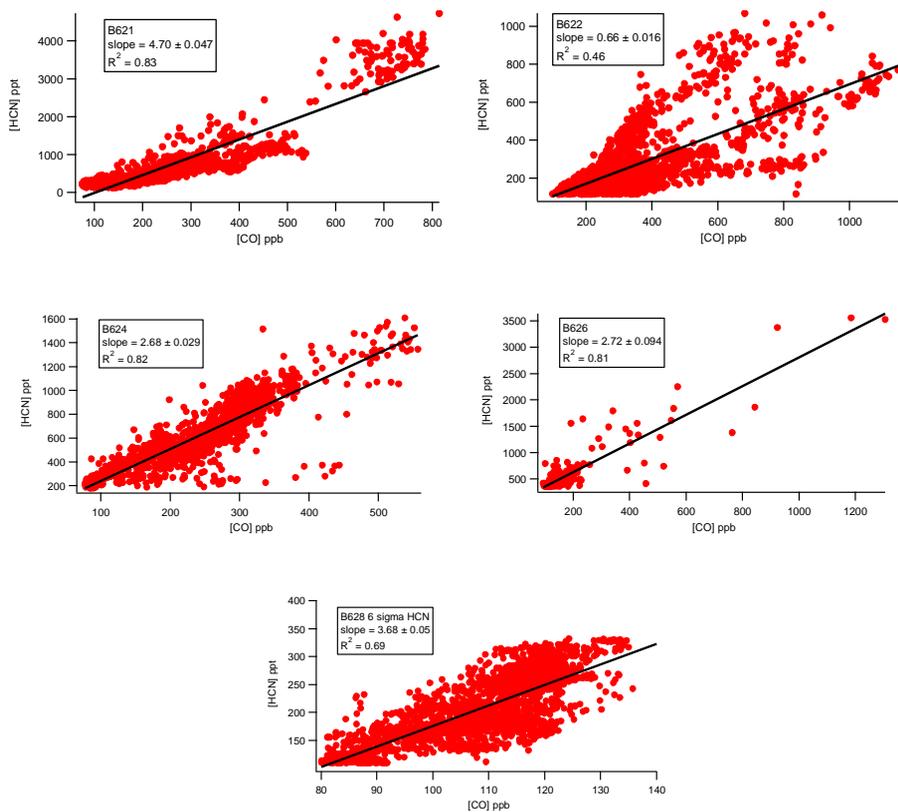


Fig. 3. HCN : CO correlations in plume determined by the 6 sigma HCN approach for 5 flights during the BORTAS campaign.

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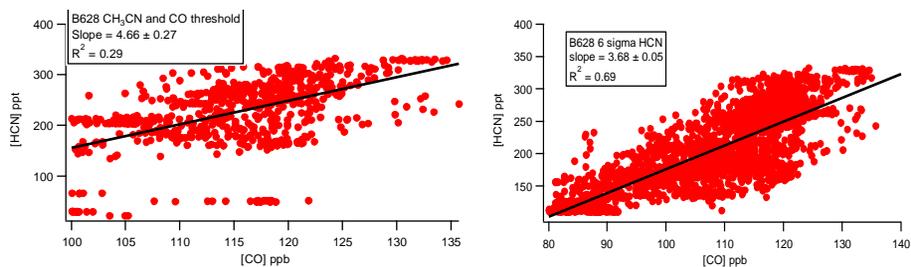


Fig. 4. In plume HCN : CO ratio from flight B628 using the 6 sigma HCN approach and the 175 ppt CH₃CN and 100 ppb CO thresholds.

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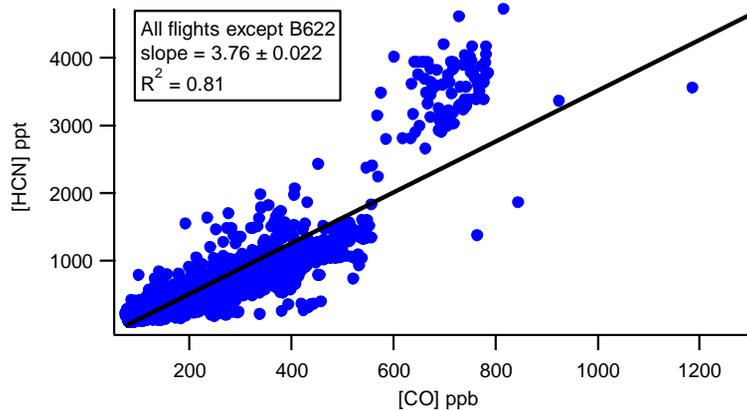


Fig. 5. HCN : CO correlations within BB plumes from the BORTAS campaign as determined using the 6 sigma HCN approach. Flight B622 data has been excluded due to the possible two separate slopes observed.

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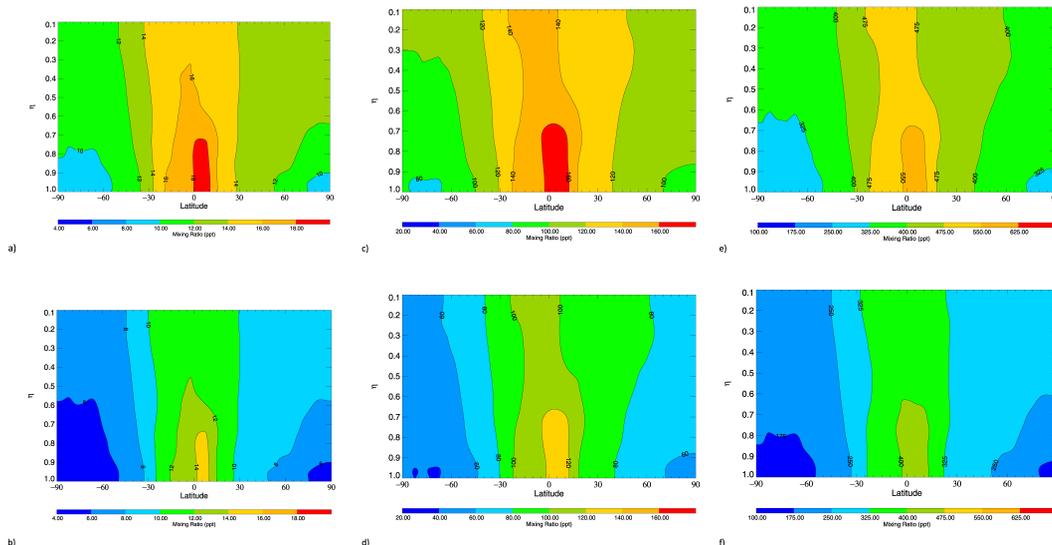


Fig. 6. Year average HCN derived from model integrations with two ocean deposition velocities leading to a lifetime of 3 months and 6 months. **(a)** Emission ratio (HCN : CO) of 4×10^{-4} ppb ppb^{-1} and a lifetime with respect to deposition of 3 months. **(b)** Emission ratio of 4×10^{-4} and a lifetime with respect to deposition of 6 months. **(c)** Emission ratio of 3.7×10^{-3} and a lifetime with respect to deposition of 3 months. **(d)** Emission ratio of 3.7×10^{-3} and a lifetime with respect to deposition of 6 months. **(e)** Emission ratio of 12×10^{-3} and a lifetime with respect to deposition of 3 months. **(f)** Emission ratio of 12×10^{-3} and a lifetime with respect to deposition of 6 months.

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