



Long-term high frequency measurements of ethane, benzene and methyl chloride at Ragged Point, Barbados: Identification of long-range transport events

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Abstract

Here we present high frequency long-term observations of ethane, benzene and methyl chloride from the AGAGE Ragged Point, Barbados, monitoring station made using a custom built GC-MS system. Our analysis focuses on the first three years of data (2005–2007) and on the interpretation of periodic episodes of high concentrations of these compounds. We focus specifically on an exemplar episode during September 2007 to assess if these measurements are impacted by long-range transport of biomass burning and biogenic emissions. We use the Lagrangian Particle Dispersion model, NAME, run forwards and backwards in time to identify transport of air masses from the North East of Brazil during these events. To assess whether biomass burning was the cause we used hot spots detected using the MODIS instrument to act as point sources for simulating the release of biomass burning plumes. Excellent agreement for the arrival time of the simulated biomass burning plumes and the observations of enhancements in the trace gases indicates that biomass burning strongly influenced these measurements. These modelling data were then used to determine the emissions required to match the observations and compared with bottom up estimates based on burnt area and literature emission factors. Good agreement was found between the two techniques highlight the important role of biomass burning. The modelling constrained by *in situ* observations suggests that the emission factors were representative of their known upper limits, with the *in situ* data suggesting slightly greater emissions of ethane than the literature emission factors account for. Further analysis was performed concluding only a small role for biogenic emissions of methyl chloride from South America impacting measurements at Ragged Point.

These results highlight the importance of long-term high frequency measurements of NMHC and ODS and highlight how these data can be used to determine sources of emissions 1000's km away.

1. Introduction

Long-term trace gas measurement programs have provided invaluable data to further our understanding of the composition and chemistry of the atmosphere; for example the oxidizing capacity of the troposphere (Montzka et al., 2011a; Prinn et al., 2005). Atmospheric science crucially relies on the exploitation of high quality long-term *in situ* and remote measurements. Programs like the Advanced Global Atmospheric Gases Experiment (AGAGE) and the National Oceanic and Atmospheric Administration's Global Monitoring Division (NOAA GMD) are at the forefront of these efforts. The AGAGE network consists of 11 dedicated

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research stations spread throughout the globe making high frequency (~hourly) atmospheric measurements of a range of Ozone Depleting Substances (ODS), controlled under the Montreal protocol, and Greenhouse Gases (GHG), controlled under the Kyoto protocol. These measurements have, for example, provided hard evidence for the phase out of CFCs and the rise of their replacements (Derwent et al., 2007).

In this paper we present long-term high frequency measurements of ethane, benzene and methyl chloride made as part of the long-term AGAGE monitoring program at Ragged Point, Barbados (RPB) and investigate periodic observations of high levels of these compounds. Our aim is to assess whether biomass burning and biogenic emissions are the cause of these episodic perturbations (above background) witnessed in the measurement record. Our paper is split into the following sections: In the following section we discuss in more detail the measurement record at Ragged Point. In section three we then describe the set up of the NAME (Numerical Atmospheric Modelling Environment) model, which was applied in this analysis. Section four and five discuss the analysis of air history associated with the observations we focus on and the simulation of biomass burning plumes we perform with NAME. In section six we discuss the results of emission estimate calculations, whilst section seven and eight are dedicated to the discussion of the results and conclusions of the study.

2. Long term measurements at Ragged Point, Barbados

Continuous measurements of a range of ODS and GHG have been made at the AGAGE atmospheric research station at Ragged Point, Barbados (13° N, 59° W, 42 m above sea level – from here on referred to as RPB), since 1978. In the analysis of long-term measurements, stations like RPB are often used as they are classified as “clean air” sites. That is to say, that they are situated in remote regions, which should give a representative account for the background atmosphere (not directly impacted by local emissions). The use of these types of stations is critical, as biases from non-linear local chemistry, and very local emissions can, to a large extent, be omitted. However, even remote stations may be influenced by transport of pollution over very large distances and from very different sources (anthropogenic, biomass burning, and/or biogenic emissions).

Since 2005 an extended range of more than 40 species have been measured using the ‘Medusa’ Gas Chromatography-Mass Spectrometer (GC-MS) (Miller et al., 2008) at all AGAGE sites (<https://agage.mit.edu/data/agage-data>). The Medusa was developed specifically to monitor ambient mixing ratios of both the Montreal and Kyoto Protocol gases (Miller et al., 2008) and has numerous publications related to these species (O’Doherty et al., 2014; Saikawa et al., 2012; Vollmer et al., 2011, 2015). However, the Medusa system has also shown itself to be capable of extending the measurement suite at all AGAGE stations to include, amongst other compounds, a number of non-methane hydrocarbons (NMHC) (Mühle et al., 2007; Yates et al., 2010; Grant et al., 2011; Derwent et al., 2012). The extension to measure NMHCs is important, as there are very few high frequency long-term observations of these compounds. At the heart of the Medusa is a Polycold “Cryotiger” cold head which maintains a temperature of -175°C, even with a substantial heat load, using a simple single-stage compressor with a proprietary mixed-gas refrigerant. This cold end conductively cools multiple traps to ~ -165°C. By using standoffs of limited thermal conductivity to connect the traps to the cold head, each trap can be independently resistively heated to any temperature from -165°C to +200°C, while the cold head remains at low temperature. The use of two traps filled with HayeSep D adsorbent and with wide programmable temperature ranges permits the desired analytes from 2-liter air samples to be effectively separated from more-abundant gases that would otherwise interfere with chromatographic separation or mass spectrometric detection, such as N₂, O₂, Ar, H₂O, CO₂, CH₄, Kr and Xe. Importantly, the dual traps also permit the analytes to be purified of interfering compounds by fractional distillation and re-focusing from the larger first-stage trap (T1) onto a smaller trap (T2) at very low temperatures, so that the resulting injections to the Agilent 6890/5973 GC-MS are sharp and reproducible. Methyl chloride was detected using the MS in selected ion monitoring mode (SIM) with a target ion, CH₃³⁷Cl⁺ (m/z 52), and qualifier ion CH₃³⁵Cl⁺ (m/z 50). Ethane was detected using a target ion, CH₃C⁺ (m/z 27) and a qualifier ion CH₂C⁺ (m/z 26). Benzene was detected using only a target ion, C₆H₆⁺ (m/z 78). The ratios of the target ion/qualifier ions were monitored to ensure that potential interferences from co-eluting species did not affect the analysis. Measurement precision was determined as one standard deviation (1σ) of the ratio of each standard response to the average of the closest-in-time preceding and subsequent standard responses. The typically daily precision for each standard was calculated as 0.5% for methyl chloride and ethane; and 0.8% for benzene, this value was used to estimate the precision of each in situ measurement.

The Medusa calibration method is identical between its traditional suite of gases and the NMHC’s; ambient air mixing ratios are calculated via ratio to bracketing whole-air quaternary standards. These quaternary standards are themselves calibrated via propagation of the primary scale hosted at Scripps Institution of Oceanography (SIO). Methyl chloride is calibrated on SIO-05 via a gravimetric method of primary standard production (Prinn et al., 2000). As yet the ethane and benzene do not have SIO gravimetric primary standards. Ethane is calibrated on the scale maintained at the National Center for Atmospheric Research (NCAR) and the University of Miami, Rosenstiel School of Marine and Atmospheric Science (RSMAS)

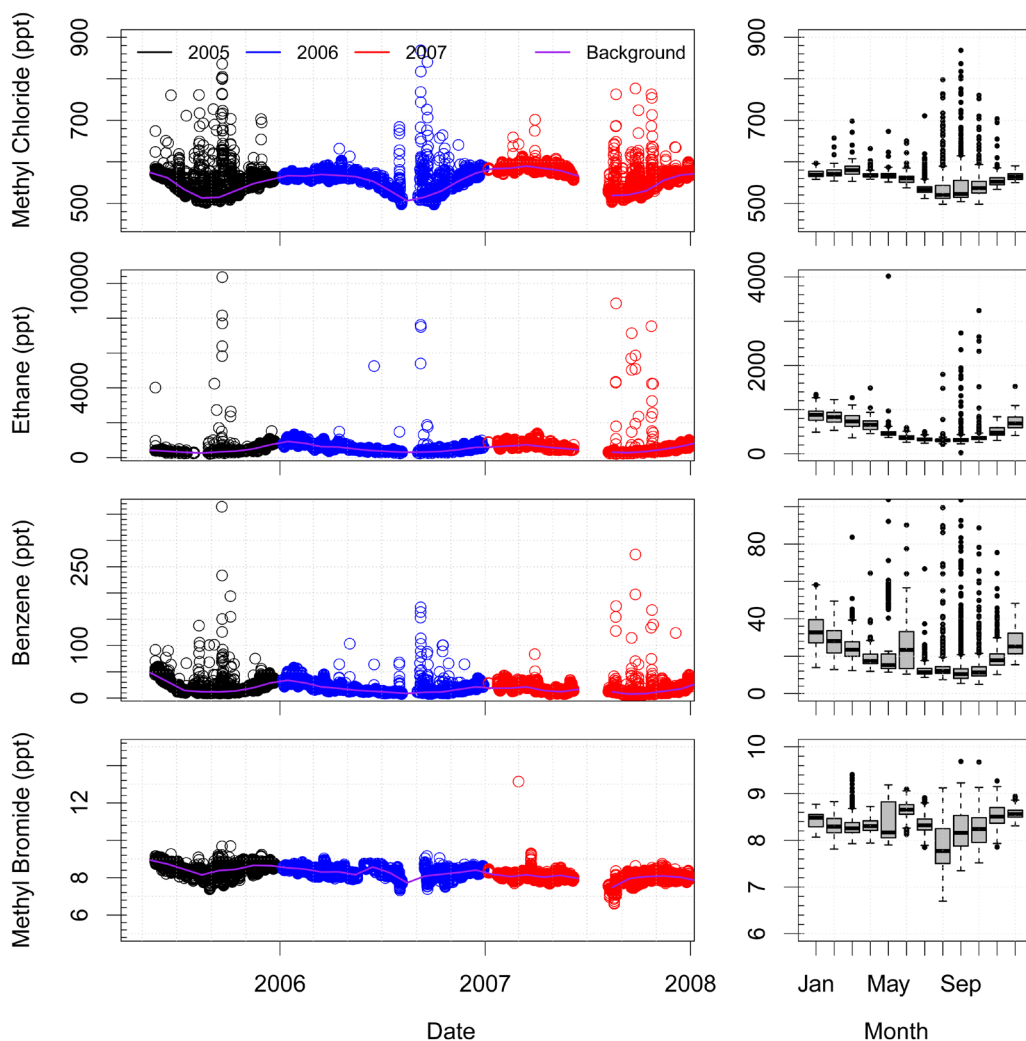


Figure 1

Time series of selected raw data observed at RPB (left hand plots).

Data gaps occur when instrument complications arise. The solid purple line represents the statistical background used in later analysis. Right hand plots show box-whisker plots of all data from 2005–2007, highlighting the seasonality of the measurements and statistical outliers (solid circles).

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via comparison to N1, an intermediate calibration scale transfer cylinder (Möhle et al., 2007). Benzene is calibrated against a dilution of a synthetic, high concentration standard (Cylinder CC144868, Apel-Reimer, USA) as per Yates et al. (2010) and the method outlined by O'Doherty et al. (2004). An important aspect of the Medusa GC-MS is its ability to check its linearity by injecting a wide range of standard gas volumes. Such measurements are regularly undertaken at each AGAGE station as part of routine diagnostics, which confirm that the Medusas are linear over wide ranges of sample volume, concentration, and composition.

Figure 1 shows an example of the data recorded at RPB for a selected subset of species. One of the notable features of the Medusa data set recorded at RPB is the occurrence of perturbations above background measurements. Many long-term measurement datasets show perturbations above background, generally driven by the advection of polluted air. Here, however, the periods of time where many of the NMHCs, and specifically methyl chloride are high, are often associated with periods of decreased concentrations of CFC's and their replacement HFC's (good markers of anthropogenic polluted air – see below and Figure 3). The patterns of spikes in these data can be more clearly seen in the right hand column of Figure 1 where the same data are displayed from the left hand plots, this time combining data from all years into one seasonal cycle (January – December). The solid horizontal bars in the plots on the right hand side of Figure 1 show the monthly median value (for all years 2005–2007) whilst the box represents the inter quartile range (IQR – 25th–75th percentiles). The right hand plots in Figure 1 show that a clear seasonal cycle exists for ethane and benzene, which are both dominated by the loss reaction with OH (which peaks in concentration in local summer). Assuming an average OH mixing ratio of 1×10^6 molecules cm^{-3} gives lifetimes with respect to reaction with OH of ~2 months and ~2 weeks for ethane and benzene respectively (Simpson et al., 2012; Volkamer et al., 2002). The seasonal cycle for methyl chloride generally follows that of ethane and benzene, with the minimum mixing ratios observed between August and October suggesting that reaction with OH again determines the local mixing ratios recorded (NB the rate coefficient for reaction of methyl

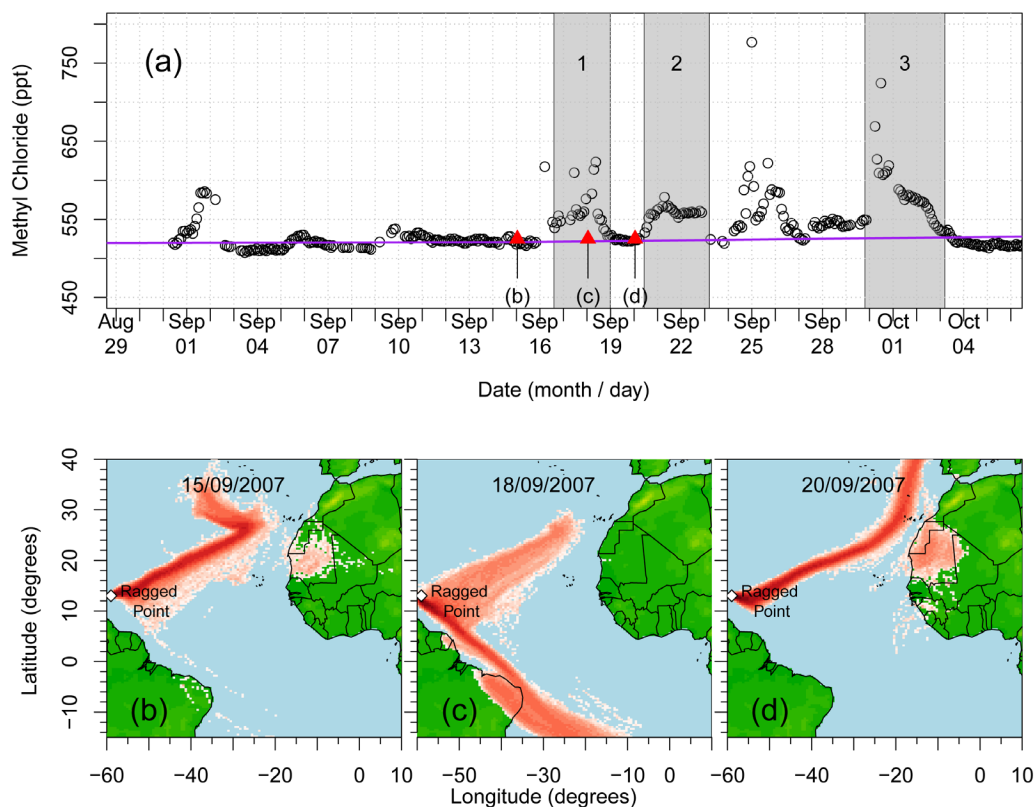


Figure 2
Methyl chloride during exemplar event in 2007.

Panel (a) - methyl chloride mole fractions observed at Ragged Point. Measurements are given by black circles, the statistical background is shown as the purple line. Panels b–d show surface (0–100m) air history maps going back in time for 10 days from the 15th, 18th and 20th September 2007 respectively.

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chloride with OH is much smaller than that for ethane and benzene and following the same assumptions as in the estimates for lifetimes of ethane and benzene results in a lifetime for methyl chloride with respect to OH of ~18 months). The methyl bromide (CH_3Br) seasonal cycle shows a very different temporal profile to the other compounds displayed in Figure 1. CH_3Br has an atmospheric lifetime similar to that of methyl chloride but with considerably different sources (the oceans being the most likely dominant source of CH_3Br ; Montzka et al., 2011b).

The right hand plots in Figure 1 show that for ethane, benzene and methyl chloride there are distinct periods where statistically significant outlying measurements are made. From this three-year data set it is clear that these outliers occur during August to October with March to June also being significant for methyl chloride. These periods correlate well with the maximum in biomass burning in southern and northern South America respectively. In addition, it should also be noted that the period August to October coincides with the Atlantic hurricane season. As a specific example of the phenomenon seen in these data we select the month of September 2007 to focus on in this paper. Figure 2a shows a time series of the recorded levels of methyl chloride at RPB from the end of August 2007 to the beginning of October 2007 (see section 3 for a discussion on the data in Figure 2b–d). A statistical method has been used to derive a background concentration that is shown as the solid purple line (O'Doherty et al., 2001). In this method averaging over 60 day periods either side of a measurement datum point is used. Several assumptions are then made; namely that background air should have a Gaussian appearance/seasonality; that polluted air should have generally large values and that meridional transport of air can bring in cleaner air than the background. Thus, values above the background correspond to enhancements in the local concentration of methyl chloride and values below the background correspond to clean air. RPB receives background air from the Northern Hemisphere and the Southern Hemisphere depending on the time of year. The difference in the concentrations based on hemispheric gradients (~11 ppt as an annual mean) can be accounted for thanks to long-term measurements made in each hemisphere at Mace Head (Ireland) and Cape Grim (Tasmania) (Simmonds et al., 2004). In any case these RPB data have very little spread (IQR of 33 ppt (~6%) over the whole 3 year period), and it can be seen that a clear number of events can be picked out where the concentration of methyl chloride exceeds the statistical background.

The periods when observations of methyl chloride are above the background often match up well with periods when anthropogenic markers (such as HFCs and CFCs) are lower than their respective statistical backgrounds. Figure 3 shows tracer-tracer correlations, in the form of scatter plots, of methyl chloride versus benzene, HCF-134a, ethane and methyl bromide during the three events when methyl chloride is above the background shown in Figure 2a (grey shading). Figure 3 shows that during the events when methyl

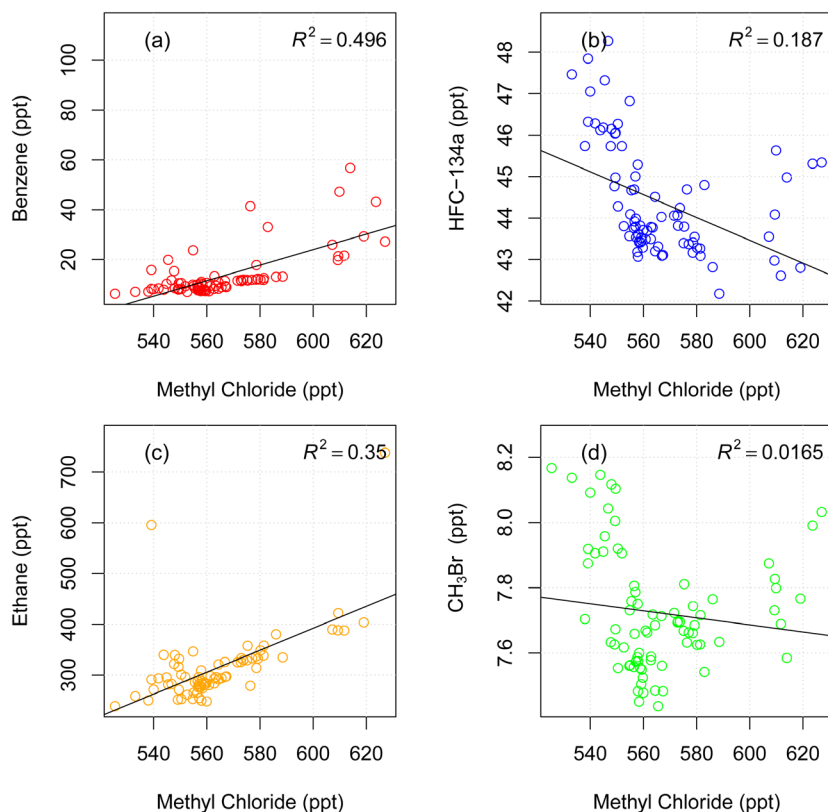


Figure 3
Relationships between measured data during events identified in Figure 2.

Scatter plots of CH_3Cl versus (a) benzene, (b) HFC-134a, (c) C_2H_6 and (d) CH_3Br from periods 1–3 identified in Figure 2 (a), where CH_3Cl is elevated above the statistical background.

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chloride is above the background, there is good correlation with enhancements in other species which have strong biomass burning sources (such as ethane and benzene), weak anti-correlation with species which are not thought to be produced from biomass burning but are markers of (local) anthropogenic pollution (HFC-134a) and very weak negative correlation with methyl bromide. The anti-correlation between methyl chloride and HFC-134a in Figure 3 is an important line of evidence for rejecting the possibility of strong local emissions of methyl chloride being the cause of the enhancements observed. The lack of correlation/very weak anti-correlation between the methyl halides is interesting, given that the sources of the methyl halides are similar and they have similar lifetimes. Untangling the causes of these observations will form the basis of further work and will not be discussed further here.

As methyl chloride has a reasonably long lifetime (~1.5 years with respect to OH) and very simple photochemistry it is an ideal compound for dispersion model studies. In light of this, and the correlations noted above, the NAME model (see next section) has been used to investigate the causes of the enhancements in methyl chloride at RPB. The NAME model has been used in conjunction with AGAGE measurements in several previous investigations including estimating emissions of ozone-depleting and greenhouse gases in Europe (Manning et al., 2003, 2011) and estimates of emissions of CO and Black Carbon Aerosol (Derwent et al., 2001). The modelling results can also be easily adapted to help understand the sources of the enhancements seen in benzene and ethane. As with methyl chloride, reaction with OH represents the major loss process and there are no complex secondary sources of these gases.

3. The NAME model

To help analyse the data in Figure 1 we use the NAME model, which is a state of the art Lagrangian modelling tool developed by the Met Office (Jones et al., 2007). The model has been used in simulations of inert tracer experiments (Ryall and Maryon, 1998), tropospheric air quality (Redington and Derwent, 2002), volcanic ash transport (Webster et al., 2012) and radionuclide transport (Johnson et al., 2007; Leadbetter et al., 2014). Witham and Manning (2007) applied the model to understand the role of Russian biomass burning on UK aerosol exceedances. The model can be forced by large-scale meteorological variables coming from Numerical Weather Prediction (NWP) models, from radar rainfall observations, or from single site meteorological observations. In this study we have used NWP meteorological fields from the Met Office Unified Model (UM) (Davies et al., 2005), which for 2007 had a global horizontal resolution of ~60 km x 60 km (at the

equator) and has been archived for NAME use with 31 unequally spaced model levels from the surface to a height of 19 km. Similar to other Lagrangian models, NAME uses the UM meteorology to provide large scale information regarding the atmospheric flow and a random walk scheme to account for sub-gridscale atmospheric turbulence. NAME also has a parameterised simple deep convection scheme, details of which are discussed in the description of sensitivity tests in section 7.

As an example of the suitability of using the NAME model in combination with the RPB measurements, Figure 2b–d show air history plots derived with NAME for 00:00 UTC on the 15th, 18th and 20th September 2007 respectively. The air history information is generated by the NAME model through releasing inert particles from RPB and tracking them backwards in time over the course of 10 days (see section 4 for more details). The plots show where model particles spent time near the surface (0–100m), with the deeper shades of red indicating where surface emissions might have greater influence on the air sampled at RPB. By comparing the measurements of methyl chloride in Figure 2a with the air history plots in Figure 2b–d it is clear to see that the high levels of measured methyl chloride on the 16th–19th September occurs during a period when air has recently travelled from the south over the coastal lands of South America. The periods either side of this event (15th and 20th September, b and d) are illustrative air history plots for the NH background air arriving at RPB, which during this time of the year is from the relatively clean and well mixed North Atlantic atmosphere.

4. Air history analysis of high methyl chloride events

In this section we describe the simulations we performed with NAME to understand the air history associated with the measurements of high levels of methyl chloride displayed in Figure 2(a).

Initially NAME was run in a backwards mode to generate a series of 3-hourly surface level (0–100 m) air history maps (as shown in Figure 2b–d) for RPB, throughout August and October 2007. In these experiments 20,000 model particles were released over the three-hour period of interest and their location was tracked going back 10 days from the time of release. The benefit of this “multiple trajectory” approach, compared with simple back trajectory analysis using single trajectories, for understanding atmospheric source-receptor relationships has been discussed by Fleming et al. (2012).

Analysis of the air mass history maps generated for every measurement of methyl chloride made at RPB during August to October 2007 shows that the periods when methyl chloride concentrations are above the statistical background largely correspond to air masses that came from the South Atlantic, with many of them following the contour of the east coast of the South American continent (as in Figure 2c).

Composite air history maps were also created focusing on the three specific events highlighted in Figure 2a. These maps involved emitting particles for the specific duration of the events shaded grey in Figure 2a and following them back in time for 10 days. These data are shown in Figure 4. Figure 4 shows that for all three events highlighted in Figure 2a, a considerable influence from continental South America can be seen in the air mass history. Figure 4 also highlights the complicated nature of interpreting measurements made during these events. The modelling indicates that the measurements made during these events also have recent contributions from the surface areas of the North Atlantic and Western Africa. Using NAME we calculate

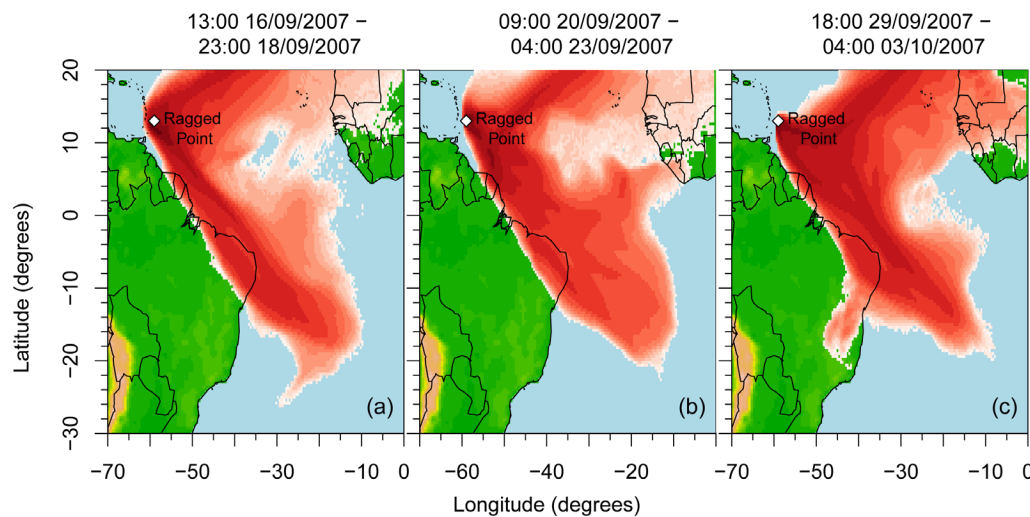


Figure 4
Air history maps for periods 1–3 identified in Figure 2a.

The plots show the time-integrated concentration [deeper red reflecting high concentration] of an inert tracer emitted from RPB and advected backwards for 10 days. The tracer concentration is output over a vertical column of 0 – 2000 m agl. Contours in light red represent lower integrated concentrations (i.e. those regions contributed less to the air arriving at RPB) while the darker shading represent higher integrated concentrations (i.e. those regions contributed more to the air arriving at RPB).

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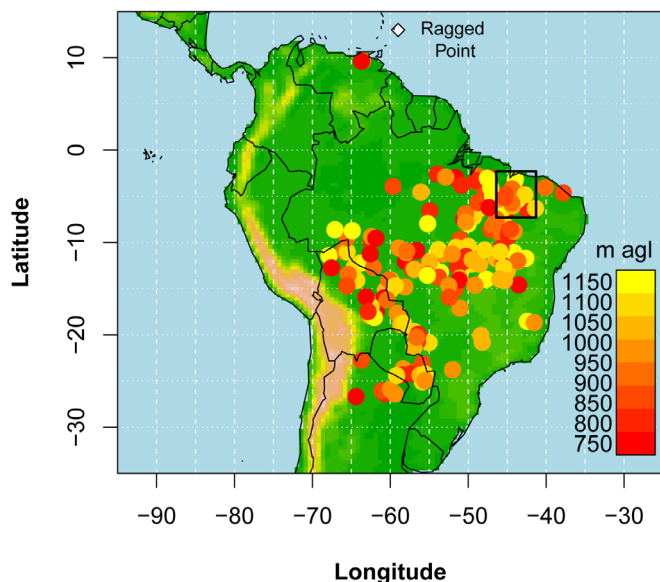


Figure 5

The locations of the modelled biomass burning sources for the time period 31/08 – 03/10/2007 are shown as filled circles.

The colour of the circle reflects the mean emission height for the source in m above ground level.

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that over the 10 day backwards simulations 12%, 8% and 16%, respectively, of surface air mass history for the three events in Figure 4 came from the SH (below 0°N).

5. Simulating biomass burning plumes with NAME

The results of the air history modelling show that the air that was sampled during the events in Figure 2, was influenced by South American continental surface sources. In section 6 we will use these air history data in combination with flux estimates of biogenic emissions to determine the role of surface biogenic emissions on the measurements made at RPB. Owing to the complex vertical profile of biomass burning plumes, the surface level air history maps are not able to provide a direct link between biomass burning and the enhanced levels of methyl chloride observed at RPB. To investigate this possible relationship further, model runs were performed to simulate the dispersion of material originating from biomass burning. The MODIS fire web mapper (<http://firefly.geog.umd.edu/firemap/>) was used to identify thermal anomalies that could be interpreted as biomass burning events. These events could then be incorporated into the NAME model (running it forward in time) as point source emissions. MODIS makes daily passes over this area of the world and records on average 2×10^6 thermal anomalies per year. In order to minimize the numerical complexity and to focus on the peak events, a time series from 31/07/2007 to 03/10/2007 was chosen to model. The fire web mapper was used to retrieve the latitude, longitude and thermal brightness temperature of thermal anomalies on a daily basis. In order to simplify the task only hot spots with 100% confidence were selected, a $5^\circ \times 5^\circ$ grid was created over South America and only one hot spot (the maximum) per grid cell per day was retrieved (using random sampling) (Figure 5). The confidence limits assigned by MODIS relate to the instruments confidence that a thermal anomaly was correctly detected. Low confidence values do not necessarily indicate that there was no thermal anomaly, but may mean that atmospheric interference, for example by clouds, made the assignment of the anomaly complicated.

Using a combination of the work of the WRAP (2005) and Hodzic et al. (2007), the fire brightness temperature (Tb_{fire}) recorded by MODIS was used to estimate the vertical distribution of the plume height (ΔP) using Equations 1 and 2:

$$\Delta P = (BE)^2 \times (P_{top} - P_{bot}) \quad (1)$$

$$BE = 0.0017 \times Tb_{fire} + 0.08 \quad (2)$$

where BE reflects the fire burning efficiency. In their study of the impact of Iberian forest fires on air quality during the European heat wave of 2003, Hodzic et al. (2007) derived a relationship where the fire brightness temperature from MODIS could be used to estimate BE (Equation 2). Hodzic et al. (2007) adjusted the form of their expression for BE so that it gave good agreement with the values of BE calculated using the WRAP method with *a priori* information of the size of the fires. Whilst much more rigorous methods for simulating fire plume rise exist (e.g. Sofiev et al., 2012; Val Martin et al., 2012), in this work we have adopted to use the undemanding relationships expressed through Equations 1 and 2.

For our main simulations with NAME we assume a P_{bot} of 1000 m agl and a P_{top} of 5000 m agl and use the observed Tb_{fire} to estimate ΔP . We input particles that represent the fire at $\Delta P/2$ m agl and use ΔP to

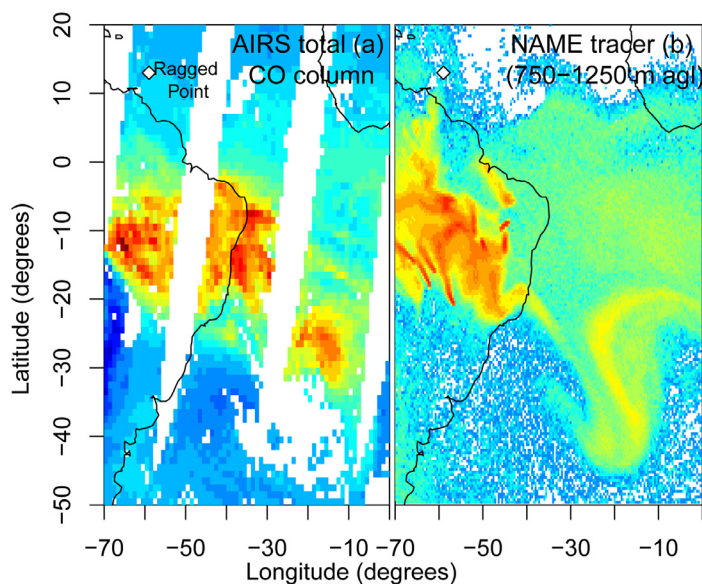


Figure 6

Comparison of CO total column measurements made by AIRS (panel a) and modelled inert tracer concentrations from simulated fires (panel b) for the 25th September 2007.

Note that the modelled data is for the average concentration of particles between 750 – 1250 m agl and is on a logarithmic scale to aid the comparison.

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model the uniform vertical distribution of particles at the start of the model run (as with the backwards air history runs, each individual particle is tracked in the model and is allowed to move freely using information from the NWP and NAME parameterisations to determine the trajectories they take). The choices of the absolute heights of P_{bot} and P_{top} will have some bearing on the final results, but were assigned based on those used by Hodzic et al. (2007). In order to test the sensitivity to these values, further simulations were performed where all the tracers were emitted from 50(\pm 50) m agl (results discussed in section 7). In all runs an inert non-reactive and non-depositing tracer was used to model the fire emissions.

In total 208 sources are indicated in Figure 5, and were included in the model runs for the period of interest. Although this represents a very small amount of the actual number of events recorded by MODIS, the spatial and temporal resolution is well represented which should be the most significant factors in successfully modelling this case study.

The main forward model run involved emitting an individual tracer for each of the 208 sources identified. The inert tracer was emitted with a uniform mass of 1 kg over the duration of 24 hours for each source. This arbitrary emission could then be scaled up to estimate actual emissions as presented in section 6. Initially runs were performed with a small number of model particles (\sim 9,000 per source) but it was found that only small numbers of the model particles arrived at RPB – resulting in large numerical noise. In order to reduce the numerical noise further runs were carried out with increased numbers of model particles (72,000 per source), subsequently yielding larger numbers of particles at RPB. Generally speaking, the majority of the simulated biomass burning plumes were advected eastward across the South American continent towards the South Atlantic. In the northern part of South America, however, material is able to travel via winds to the NE that advect material towards RPB. In Figure 6 total column CO data from the Atmospheric Infra Red Sounder (AIRS) operating onboard the NASA Aqua satellite, are compared with the NAME model tracer distribution of material from the simulated biomass burning sources for the 25th September 2007. Figure 6 shows that there is good qualitative agreement between the spatial location of total column CO (of which biomass burning will be a major contributor in this part of the world), and the simulated biomass burning tracers in the NAME model – providing confidence in the modeling method. It should be noted that a like for like comparison is very difficult as the NAME output shown is the average concentration of tracer from 750–1250 m agl and the satellite retrieval is the total atmospheric column. However, in general there is reasonably good agreement between the location of model tracer and observed CO. Figure 6 shows that on 25th of September both the model and observations capture the location of biomass burning related material in north eastern Brazil that was spreading into the South Atlantic.

Figure 7 compares the time series of NAME modelled tracer concentration (on log₁₀ scale) from all sources with the corresponding observations of enhanced methyl chloride ($\Delta\text{CH}_3\text{Cl} = \text{CH}_3\text{Cl}_{\text{measured}} - \text{CH}_3\text{Cl}_{\text{statistical background}}$) at RPB. The results in Figure 7 show that although there is a lot of scatter there is good correlation between the model and enhanced observations during several events. These include the periods identified in Figure 2(a) (16th – 19th of September, 20th – 24th of September and 29th September to the 3rd October) and highlighted with grey shading. The combination of the air mass history plots (Figure 4) and the results from the forward modelling (Figure 7) show that during these three periods biomass burning in northern Brazil could be a likely source of the enhanced methyl chloride (and ethane and benzene given the relationship between these in Figure 3) observed at RPB.

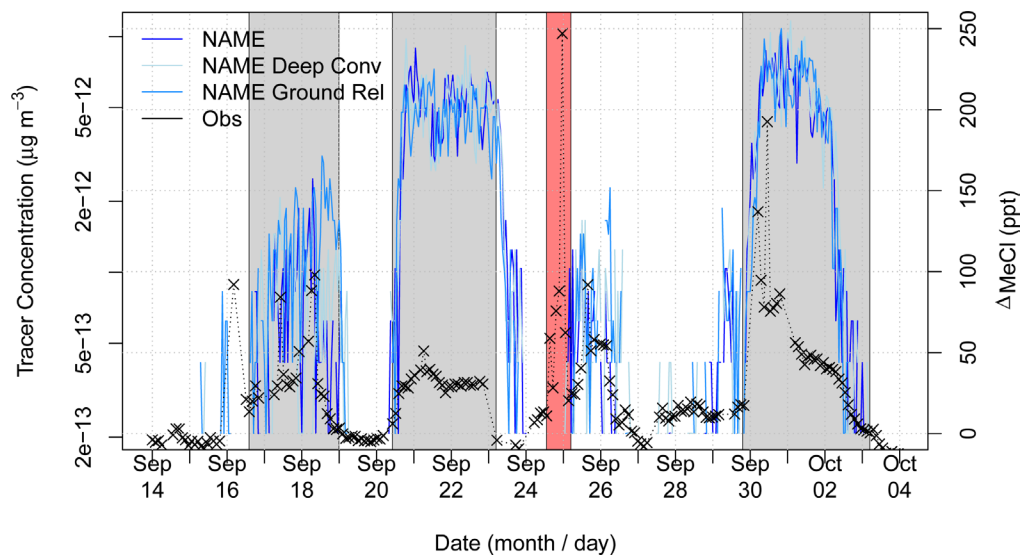


Figure 7

Hourly average modelled biomass burning tracer concentrations (log₁₀ scale) at RPB are shown on the left hand axis using the blue lines (light blue represent the sensitivity run where parameterised deep convection was included).

The observations of CH₃Cl above the background are shown on the right hand axis using the black crosses.

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However, there is some disagreement between the observations and the model, particularly on 25th September when an observation of very high methyl chloride was made (~250 ppt above the background, shown within the red shaded area in Figure 7). The air history map (extended to 20 days prior to the measurements) for this period is shown in Figure 8(a) and it is clear that the air sampled was influenced by outflow from the Iberian Peninsula/NW Europe. The fact that this is an anthropogenic signal can be seen further when correlations are plotted for methyl chloride to other measured species. Figure 8(b)(c) show that strong ($R^2 \geq 0.6$) correlations are observed between methyl chloride and anthropogenic markers such as CFC-11 and HFC-134a.

The individual NAME fire simulations can be used to quantitatively estimate the influence of individual fire sources on the enhanced observations. The fire(s) simulated from the region bounded by 41.4–46.4°W, 2.3–7.3°S on 11th September is identified as being most influential (> 80% of the total simulated tracer) for the observations made during 16th – 19th of September (indicating a travel time of 5–8 days). For the observations made during 20th – 24th September it is slightly harder to distinguish the fires on 14th and 16th of September (also from the same region as the fires on the 11th September), which were calculated to account for 40 and 50% of the simulated tracer concentration respectively. During the other periods where modelled tracer arrived at RPB coincident with the observed enhancements in methyl chloride it was very difficult to discern the influence of individual fires to the total tracer concentration. For example during the period of 29th September to the 3rd October no one single event contributes more than 6.4% to the total. Although the individual contribution can be easily calculated it makes analysis more complicated as there is no difference in weighting between the fires. Due to this the fires on the 11th, 14th and 16th September (periods 1 and 2 in Figure 2a) will be focused on for estimating emissions.

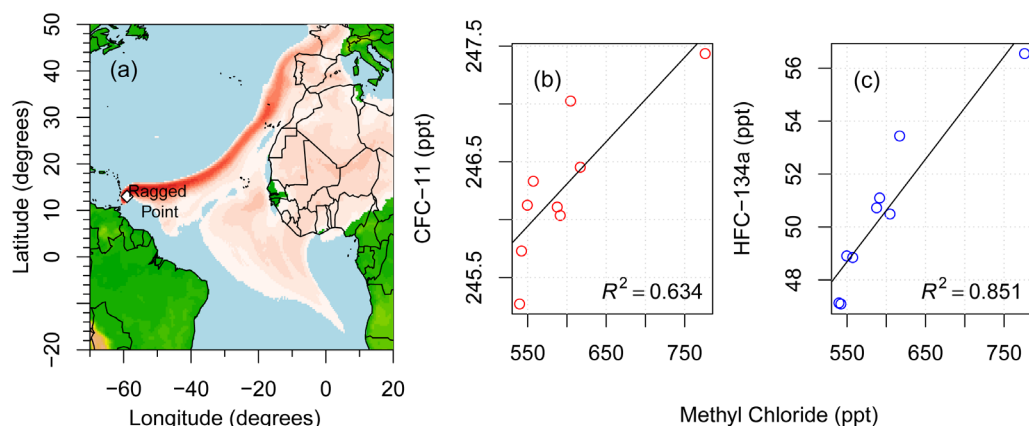


Figure 8

Evidence for Northern Hemisphere pollution impacting measurements at RPB.

Panel (a) shows a 20-day air history map for measurements made from the 24th – 25th September 2007 (event highlighted in red in Figure 7). Panels (b) and (c) show scatter plots of methyl chloride versus CFC-11 and HCF-134a during this event.

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6. Emission estimates

The following section outlines the details of the methods and calculations we have performed in order to derive estimates of emissions of the NMHC and ODS we observed at RPB using the results from the NAME model simulations. Three different approaches have been taken to estimating emissions with the aim of understanding the relative roles of biogenic emissions and biomass burning to the enhancements in ethane, benzene and methyl chloride seen at RPB.

6.1 Biogenic emissions

The first approach (Method 1) was to calculate the biogenic (vegetation) emissions contribution. Although vegetation is known to be a major source of emissions of NMHC (including isoprene, monoterpenes and methanol), biogenic emissions of ethane and benzene, are thought to be much smaller (Guenther et al., 2006). Prior to the work of Yokouchi et al. (2002) and Saito and Yokouchi (2008), vegetation was not thought to be a source of emissions of methyl chloride. Several studies have now identified the metabolic route by which vegetation can stimulate emissions of methyl chloride (e.g. Keppler et al., 2005), which involves the abiotic chloride methylation of plant pectin. Initial estimates of the tropical vegetation source of methyl chloride were on the order of 0.82 Tg yr^{-1} (Yokouchi et al., 2002), but were based on scaling up data from enclosure measurements made on tropical ferns and *dipterocarpe* from South East Asia, which yielded fluxes of $5.4 \mu\text{g m}^{-2} \text{ h}^{-1}$.

Further evidence for a large vegetation source of methyl chloride, comes from the airborne measurements of Gebhardt et al. (2008). In their study, Gebhardt et al. (2008) analysed air samples from 10 separate flights (99 samples in total) made over the pristine Amazon rainforest from 8 – 18 October 2005 with the data analysis focused on separating out the observations using air mass back trajectories. Gebhardt et al. (2008) showed that in air masses that had been heavily influenced by the boundary layer over the rainforest canopy, levels of methyl chloride were much higher than in the background air, whilst levels of other halocarbons were only slightly higher. Based on these data they were able to estimate fluxes of methyl chloride of $9.5 \pm 3.8 \text{ m}^{-2} \text{ h}^{-1}$. In calculating the biogenic emission contribution to the observations of methyl chloride at RPB in Method 1 we have used the air history maps generated for the events in Figure 2 (Figure 4), which have been analysed to determine the time that each particle spent in a land grid box prior to arriving at RPB. These data can then be combined with the area of the grid box and the range of estimates of emission fluxes from Gebhardt et al. (2008) and Yokouchi et al. (2002) to determine the total biogenic emissions of a methyl chloride. The results are presented in Table 1, which shows that the total biogenic emission of methyl chloride calculated using Method 1 for the three events investigated was $7.5(\pm 2.5)$ megagrams (where the uncertainty in the calculation is driven by the uncertainty of the emission factor for methyl chloride). For ethane and benzene, where emission estimates from tropical vegetation are likely to be small, we omit any calculations using this method. There is very little information on vegetation fluxes of ethane. In their review of BVOC emissions, Kesselmeier and Staudt (1999) show that the vegetation flux of ethane would be negligible when compared with that of methyl chloride (Yokouchi et al., 2002) (on the order of 0.07–0.2% of the methyl chloride emission flux).

6.2 NAME biomass burning emission estimates

The second approach (Method 2), was to use the NAME simulations of biomass burning dispersion in combination with the observations of above background concentrations of ethane, benzene and methyl chloride (a simple atmospheric inversion calculation) to determine the contribution of biomass burning emissions to the observations made at RPB.

Biomass burning can be described as the open combustion of any non-fossilized fuel and covers the combustion of a wide range of materials; from grass to dung (Andreae and Merlet, 2001; Akagi et al., 2011). When biomass is burnt a wide variety of compounds are emitted into the atmosphere, and accurate

Table 1. Comparison of emission estimates using the NAME air history maps to estimate biogenic emissions from land (Method 1), the NAME forest fire simulations (Method 2) and literature data on emission factors, burned area and available biomass from the regions identified by the NAME simulations (Method 3)^a

Compound	Emission estimates		
	Method 1 (g)	Method 2 (g)	Method 3 (g)
Methyl chloride	$0.005 - 0.01 \times 10^9$	$15.2 - 15.4 \times 10^9$	$2.96 - 11.22 \times 10^9$
Ethane	-	$133.0 - 141.4 \times 10^9$	$29.47 - 73.97 \times 10^9$
Benzene	-	$9.8 - 13.2 \times 10^9$	$3.01 - 20.02 \times 10^9$

^aThe range of values covers the minimum and maximum values given the associated uncertainties. Results for Method 2 incorporate the effect of travel time on oxidising emissions from the fires.

Table 2. Comparison of emission factors from Tropical and Extra Tropical biomass burning for a range of compounds measured at RPB*

Compound	Emission factor (g/kg)	
	Tropical	Extra-tropical
C ₂ H ₂	0.325 ± 0.47	0.23 ± 0.09
C ₂ H ₄	1.03 ± 1.635	1.25 ± 0.485
C ₂ H ₆	0.605 ± 1.09	1.15 ± 0.6
Benzene	0.39 ± 0.285	0.8 ± 0.08
Toluene	0.235 ± 0.21	0.44 ± 0.10
CH ₃ Cl	0.0365 ± 0.109	0.0545 ± 0.03
CH ₃ Br	0.00642 ± 0.001415	0.0036
CH ₃ I	0.00625 ± 0.001725	0.0008

*Data are averages from Andreae and Merlet (2001) and Akagi et al. (2011).

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estimates of these emissions are acknowledged to be very important for global model studies of atmospheric chemistry and composition. Emissions of compounds from biomass burning are often quoted relative to either CO or CO₂ as an excess of the compound observed over the excess in observed CO or CO₂ but can also be expressed as an emission fraction (EF_x) of a compound released (M_x) per amount of fuel consumed (M_{biomass}), often in units of g kg⁻¹:

$$EF_x = \frac{M_x}{M_{biomass}} \quad (3)$$

There is extensive literature on studies that calculate EF_s from laboratory and real world measurements (e.g. Christian et al., 2003 and refs therein). These EF_s are generally based on hundreds of measurements from controlled burns or wild fires made close to the emission source (100–1000's m downwind) and so can be viewed as our best knowledge of the emissions of trace gases and aerosols from burning. Table 2 shows that the EF_s for methyl chloride are greater than any of the other methyl halides, but significantly smaller than the EF_s for benzene, ethane and other light NMHCs listed. It is also important to note that the factors that control the emissions of gases and aerosols are multifarious; one should not expect a canonical value for emission factors for a compound from a biome (as highlighted by the considerable uncertainty on most of the EF_s listed in Table 2).

In Method 2, the dilution from an individual fire source (as modelled by NAME) is used in combination with the enhancements of methyl chloride, ethane and benzene in the observations to constrain an emission estimate for the respective trace gas. The modelled dilution is calculated from the concentration of modelled tracer that arrives at RPB compared with the mass of tracer emitted in NAME from the fire source. It should be noted that an additional term to account for photochemical oxidation of the compounds is included. This term accounts for the loss of mass along the course of the trajectory from the location of the fire hot spot to RPB owing to reaction with OH. We assume that the level of OH is fixed along the trajectory to a 24 hr mean value of 1×10⁶ molecules cm⁻³ (reflective of the MCF lifetime data; Montzka et al., 2011a). The observed enhancements are calculated as the difference between the observations and the statistical backgrounds for the trace gases under investigation (e.g. the right hand y axis in Figure 7). These observed enhancements are then converted from mole fractions (pico moles/mole) into concentrations assuming a pressure of 1,000 mb and temperature of 25°C (assumed average parameters under which the instruments making the measurements are run at). As we are able to distinguish particles from different sources we are able to calculate the individual contribution of any modelled fire to the total mass of simulated biomass burning plume that arrives at RPB. From these pieces of information it is then possible to work out the mass emission of the trace gas from a particular fire and scale this up for all fires.

Our estimates for the emissions of methyl chloride, ethane and benzene during the events under consideration using the NAME model in combination with the observations at RPB are 15.3(±0.1), 137(±4.2), 11.5(±1.7) gigagrams respectively.

6.3 Bottom-up biomass burning emission estimates

The third approach for estimating emissions (Method 3) is a purely bottom up technique based on remote sensing data and the application of literature biomass burning emission estimates for ethane, benzene and methyl chloride (Table 2). The mass of a compound, X, emitted from a fire can be calculated from:

$$X(\text{kg}) = \rho_{\text{Biomass}}(\text{kg km}^{-2}) \times \text{Area Burnt}(\text{km}^2) \times \text{BE} \times \text{EF}_x \quad (4)$$

where ρ_{Biomass} is the density of biomass, EF_X the emission factor for species X (see Table 2) and BE the burning efficiency (a simple measure of completeness of burning). For estimates of the burnt area we have used literature data from the L3JRC project (Tansey et al., 2008) using a climatology of burnt area estimates for 2005–2007. Unfortunately this dataset does not cover our exact period of interest. However, the use of a climatology has its advantages as we are able to propagate uncertainties (in the form of inter-annual variations) into our calculations.

Estimates of biomass density used in Equation 4 are based on average values for forest type material from Table 2 of Hoelzemann et al. (2004) calculated using the Global Wildland Fire Emissions Model (GWEM). These estimates range from $5,958(\pm 304) - 25,695(\pm 214)$ g m⁻² depending on the type of forest (temperate and tropical respectively) and model version used and compare reasonably well with available literature data ($12,000 - 43,500$ g m⁻²; Kauffman et al., 1995; Guild et al., 1998). It should be noted that the estimates for savanna type fuel loads are approximately a factor of two lower. The value of BE was calculated from Equation 2 using the MODIS retrieved Tb_{fire} . For the first period investigated, Tb_{fire} was taken from the single modelled source. For the second period the average Tb_{fire} from the two sources was used. It should be noted that as MODIS has fixed overpass times, the diurnal evolution of Tb_{fire} was not recorded and so the Tb_{fire} we use is reflective of a snapshot and so is a limitation of this work.

Following the approach outlined above we calculate emissions of methyl chloride, ethane and benzene of $7.09(\pm 5.8)$, $51.72(\pm 31.5)$, $11.6(\pm 12.0)$ gigagrams respectively. The figures quoted in brackets refer to the standard deviation of the mean of the range of emission estimates and can be used as an estimate of the uncertainty of the calculated values.

7. Discussion

The results from the three emission estimates presented in Table 1 broadly agree on only a small influence of biogenic emissions from South America impacting the observations made at RPB during the events we have investigated. Local biogenic emissions from the landmass of Barbados may contribute to the enhancements we observe. However, a strong role for these dominating our observations would be inconsistent with the concomitant decreases observed in other local contaminants e.g. HFC134-a (Figure 3), so we rule them out.

The results in Table 1 suggest that biomass burning emissions are the driver for the perturbations recorded in the time series' at RPB of methyl chloride, ethane and benzene and highlight that there is a good level of agreement between the top-down (Method 2) and the upper limits of the bottom up (Method 3) techniques. Our study highlights that long-term high frequency measurements can be used to help constrain the wide ranging estimates of emissions of trace gases from biomass burning, even over distances of 1000s of km. Whilst there is in general very good agreement between these two methods the agreement between ethane is less good, with NAME simulating emissions which are ~ a factor of two higher. As such it's important to consider any potential errors with the NAME technique that could explain this difference.

In part, the higher emissions predicted by the NAME model (i.e. Method 2) could be a result of poor representation of the dynamics in this region given the low resolution of the driving meteorology ($\sim 60\text{km} \times 60\text{km}$). However, a comparison of measured meteorological variables (surface temperature, wind speed and wind direction – not shown) at RPB highlight that the NAME model (specifically the UM data used by the model) had sufficient ability to capture these meteorological fields at the observation site. Moreover, good agreement in the spatial comparison between satellite total column CO and biomass burning tracer from the NAME simulations (Figure 6) adds further support for the large scale meteorological data being used in NAME to be of high fidelity. Furthermore, LPDM studies using the FLEXPART model simulating the transport of CO over similar spatial and temporal scales determined that the errors associated with meteorology/transport are on the order of 30–40% (Angevine et al., 2014), much smaller than the level of disagreement here.

Other sources of error/disagreement between the emission methods include problems with calibration of the measurements and issues related to simulating the fires themselves. Given the extensive work undertaken to characterise the Medusa (Miller et al., 2008; Yates et al., 2010) we neglect any further discussion on measurement errors. The issue of simulating the vertical profile of emissions from the fires was addressed by performing two sensitivity simulations with NAME. The first sensitivity simulation (NAME Dep Conv, Figure 7) assessed the role of switching on the NAME model's deep convection parameterization. Deep convection is an important transport process over much of the tropics (Russo et al., 2011). The second sensitivity simulation (NAME Ground Rel, Figure 7) looked at the sensitivity to emitting the fire tracers at near ground level (50 ± 50 m agl). The results from both of these simulations demonstrate that these two processes have little impact on the results of the modeling. Emissions over the South American continent are simulated by NAME to be rapidly mixed during the day via a relatively deep boundary layer. Hence the simulations produce similar results, as boundary layer mixing is a strong component of the overall transport process. The fact that the deep convection routine in NAME has only a small impact on the simulations is largely due to the simplicity of the scheme where model particles are randomly distributed throughout the column of diagnosed convective cloud. This is not an ideal parameterization and very recently an improved routine has been developed (Meneguz and Thomson, 2014).

Another large possible source of error in calculating emissions is in the choice of the statistical background. In this study a monthly statistical background was applied to these data using the method of O'Doherty et al. (2001). Analysis of the NAME air history maps highlights that this background is representative of a North Atlantic (Hemisphere) background (Figure 2b–d). In order to test the sensitivity of the results to this background method further calculations were performed where the NAME model was used to classify each measurement made at RPB as being “background” or not. This technique has been used widely for emission estimates for a range of species and the details are omitted here (see e.g. Manning et al., 2011 for more details). Comparing the results (not shown) of the emission estimates using the NAME derived backgrounds for RPB with the statistical background (O'Doherty et al., 2001) result in changes in the emissions of methyl chloride and benzene by up to ~25%, whilst for ethane there are much smaller differences as a result of changing the background method (~5%). The larger differences are statistically significant when compared to the range of emission estimates from Method 2 that originate from the uncertainty in estimating the travel time of the biomass burning plume.

One way to explain the higher ethane emissions in Method 2 would be to invoke strong local pollution affecting the observations, but this is not well supported by the tracer-tracer correlations in Figure 3. As with benzene, biogenic emissions of ethane have not been considered to be important in this study (based on Guenther et al., 2006). However, very recently Misztal et al. (2015) have shown that contrary to previous beliefs, benzenoid compounds have major emission sources from terrestrial vegetation. We postulate that an as yet unidentified vegetation source of ethane could help reconcile the two estimates of ethane emissions and vegetative emissions of ethane are in need of more research.

8. Conclusions

In this study we have used a Lagrangian particle dispersion model (NAME) to investigate the causes of observed enhancements in methyl chloride, ethane and benzene made at the AGAGE monitoring site at Ragged Point, Barbados, during an exemplar event occurring throughout September 2007, and to then estimate emissions for the compounds investigated. NAME was run backwards in time from Ragged Point to produce air history maps for each measurement made. Analysis of these air history maps revealed that the majority of air mass history during September 2007 (a period of the year when biomass burning peaks in South America) was reflective of background/clean air from the North Atlantic, and that during the enhancement events, air masses originated from the Southern Hemisphere – heavily influenced by North East Brazil (Figure 2). Tracer-tracer correlations revealed strong positive relationships between species associated with biomass burning, whilst negative correlations were found for species that have strong anthropogenic sources (Figure 3). This evidence provided further support for the hypothesis of biomass burning contributing strongly to the observed enhancements of methyl chloride, ethane and benzene. To test whether biomass burning was indeed the source of the enhancements NAME was used to model the dispersion of simulated biomass burning plumes. The plumes were initialized using hot spot information from MODIS and a series of sensitivity tests were performed to investigate the role of the plume height injection on the simulations. Excellent agreement was found between the timing of the simulated biomass burning plumes modeled by NAME and the observed enhancements of (specifically) methyl chloride whilst the sensitivity simulations suggested that assumptions about plume height had little bearing on the models ability to simulate these events (Figure 7).

Based on the results of the NAME simulations a range of emissions estimates were made. The air mass histories were used along with literature emission factors to estimate biogenic emissions of methyl chloride from the South American land mass and it was found that these were very small when compared to the emission estimates for biomass burning. Two techniques were used to estimate biomass burning emissions. The first utilized the NAME simulations of biomass burning plume dispersion and the observations of enhancements in methyl chloride, ethane and benzene. The second method utilized literature data on biomass density, burned area and the MODIS data on FRP (to estimate burning efficiencies) for the regions that the NAME model simulated contributed to the observed enhancements. Very good agreement was found between the NAME method and the upper limits of the bottom up method with both methods highlighting that emissions were greatest for ethane, with emission estimates for benzene and methyl chloride being comparable (in relative magnitude). However, there was some disagreement between the methods on the absolute emissions for ethane, with the estimates using NAME and the in situ observations calculating emissions a factor of 2 greater.

The disagreement between the two emission estimates for ethane can be viewed as being caused by either, poor characterisation of the background mixing ratios of these compounds during the enhancement events at RPB used in the NAME estimates, or errors in the emission factors, biomass density or burning efficiency used in the bottom up calculations. By using a climatology of burned area and a range of literature estimates of biomass density we were able to reject those as sources of disagreement between the two methods. By comparing the background mixing ratios (as defined by Manning et al., 2011) of ethane at Mace Head, Ireland, and Cape Grim, Tasmania, we were able to conclude that uncertainty on the assigned background

mixing ratio could contribute up to 25% error on the NAME inversion calculations. Therefore, we conclude that in order to reconcile the two emission estimates either unaccounted for sources of these emissions need to be included in the calculations (e.g. local anthropogenic sources) or slight enhancements of the biomass burning emission factors or significant enhancements in the biogenic emissions of ethane are required.

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Contributions

- Contributed to conception and design: ATA, DES, S'OD, BRG.
- Contributed to acquisition of data: S'OD, BRG, DY.
- Contributed to analysis and interpretation of data: ATA, DES, AJM, MJA, CSW.
- Drafted and/or revised the article: ATA and all.
- Approved the submitted version for publication: ATA and all.

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Competing interests

The authors declare no competing interests.

Data accessibility statement

All data used in the analyses are available from the URLs in the text and from the author upon request.

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