

**The influence of
boreal forest fires on
non-methane
hydrocarbons**

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The influence of boreal forest fires on the global distribution of non-methane hydrocarbons

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Abstract

Boreal forest fires are a significant source of chemicals to the atmosphere including numerous non-methane hydrocarbons (NMHCs). We report airborne measurements of NMHCs, acetone and methanol from > 500 whole air samples collected over Eastern Canada, including interception of several different boreal biomass burning plumes. From these and concurrent measurements of carbon monoxide (CO) we derive fire emission ratios for 29 different species relative to the emission of CO. These range from 8.9 ± 3.2 ppt ppb⁻¹ CO for methanol to 0.007 ± 0.004 ppt ppb⁻¹ CO for cyclopentane. The ratios are in good to excellent agreement with recent literature values. Using the GEOS-Chem global 3-D chemical transport model (CTM) we show the influence of biomass burning on the global distributions of benzene, toluene, ethene and propene (species considered generally as indicative tracers of anthropogenic activity). Using our derived emission ratios and the GEOS-Chem CTM, we show that biomass burning can be the largest fractional contributor to observed benzene, toluene, ethene and propene in many global locations. The widespread biomass burning contribution to atmospheric benzene, a heavily regulated air pollutant, suggests that pragmatic approaches are needed when setting air quality targets as tailpipe and solvent emissions continue to decline. We subsequently determine the extent to which the 28 Global WMO-GAW stations worldwide are influenced by biomass burning sourced benzene, toluene, ethene and propene when compared to their exposure to anthropogenic emissions.

1 Introduction

Non-methane hydrocarbons (NMHCs) are a class of trace compounds found throughout the troposphere. Whilst typically present at mixing ratios in the parts per trillion range, they exert significant influence over the oxidizing capacity of the troposphere, the lifetime of methane and the formation of tropospheric ozone (Houweling et al., 1998). They play a central role in controlling the lifetime (τ) of OH and can influence its

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activity for volatile organic compounds (VOCs) as part of the Global Atmosphere Watch programme (WMO-GAW) (Helmig et al., 2009). NMHCs including ethane, propane, acetylene, butane and pentane form part of the target suite of compounds (WMO technical document 2007) in this network. Observations of NMHCs in remote terrestrial or oceanic environments are less easy to categorize in terms of contributing sources than comparable urban measurements. It is possible for many NMHCs that the observation of a given species will arise because of the combined releases of man-made and natural emissions, followed by transport and degradation. Extracting value and information from emerging long-term trends in background NMHCs requires therefore a robust understanding of the various contributing sources in background, non-urbanized environments. In this paper we quantify the release of 29 different NMHC species from boreal forest fires, a major emission source to the mid and high latitudes of the Northern Hemisphere. This information is combined with a global 3-D chemical transport model (CTM) and a global fire map to produce a geographically resolved estimate of the boreal and other biomass burning fraction of NMHCs in the troposphere. The contributions of overall NMHC abundance from biomass burning and anthropogenic sources are placed in context with the locations of the 28 global status stations that form WMO-GAW, providing an assessment of how NMHCs at these locations are likely to be influenced by future changes to biomass burning activity or anthropogenic emissions.

Boreal forests, defined as high latitude 50–70° N forests, account for roughly one third of total global forested area, and their fires emit many more species in addition to NMHCs. CO₂, CO and CH₄ are the largest emissions by mass with CH₃OH and HCHO the most dominant organic compounds. Of the NMHCs ethane, benzene, ethene and propene have been seen in many studies including in lab combustion experiments, relatively close to source, and many days downwind. Simpson et al. (2011) report an exceptionally comprehensive catalogue of different species released by boreal fires, including NMHCs, halocarbons, oxygenated species and organic nitrates. Laboratory evaluation of organic emissions include those reported in Christian et al. (2003, 2004);

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Yokelson et al. (2008), and Warneke et al. (2011), in the near field by Yokelson et al. (2007, 2009); Jost et al. (2003); Sinha et al. (2003); and in long range transport Holzinger et al. (2005); de Gouw et al. (2006); Duck et al. (2007); Yuan et al. (2010).

Whilst tropical biomass burning dominates total emissions, boreal fires account for around 9% of all fire carbon emissions (van der Werf et al., 2010) and can have major impacts on the global atmosphere. Perturbation to the global growth rate in CO, CH₄ and C₂H₆ have for example been attributed to single regional boreal burning events (e.g. Kasischke et al., 2005; Yurganov et al., 2005). The areal extent of burned biomass is related to regional temperature and rainfall, and there is evidence that in Canada the forest area burned has increased since the 1970s (Girardin, 2007). Published model predictions of boreal fires all show significant increases with higher temperature associated with future climate scenarios, leading to greatly increased emissions in all those species released in the burning process (Soja et al., 2007; Marlon et al., 2008; Flannigan et al., 2005; Wotton et al., 2010; Amiro et al., 2009; Kasischke and Turtesky, 2006).

Boreal forest fires have a strong influence on air quality in mid latitudes in the Northern Hemisphere. Due to convection and pyroconvection of plumes they can inject trace gases and aerosols into the upper troposphere and occasionally lower stratosphere where long-range transport can widely distribute the emissions (Fromm et al., 2000; Jost et al., 2004). Canadian forest fire signatures in NMHCs have been seen frequently at the Pico observatory on the opposite side of the Atlantic Ocean (Val Martin et al., 2010). Measurements from several different aircraft over the central and Eastern North Atlantic have shown elevations in species such as ethene and benzene of between 100 and 1000 times over the typical marine background (Lewis et al. (2007), Fehsenfeld et al. (2006) and references therein). The photochemical impact of biomass plumes over the North Atlantic ocean remains somewhat uncertain however, with literature disagreement as to whether they contribute significantly to more general tropospheric ozone production (e.g. Jaffe and Wigder, 2012). This wider atmospheric chemistry

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challenge provides the motivation for the BORTAS study, of which this dataset forms one part.

2 Experimental

The NMHC measurements reported in this paper were made as part of the BORTAS research project – Quantifying the impact of BOREal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS). The observational programme was conducted from Halifax International airport (63°30' W/44°52' N) and comprised a series of 15 different missions of either one or two flight sectors, and of durations between 3 and 8 h flying time. The data represents a total observing period of approximately 79 flight hours covering around 28 000 km in sample tracks. In addition to measurements made from Halifax, the dataset also includes observations made during the trans-Atlantic crossing from/to the United Kingdom via the Azores. The flights have FAAM catalogue numbers from B618 to B632 and all data in this paper is publicly accessible at www.badc.nerc.ac.uk/data/bortas. Figure 1 shows the flight tracks and sample points of all Whole Air Samples included in this paper. Acetylene is used as a representative tracer for both biomass burning emission and anthropogenic pollution in this plot, with substantial elevations visible on many flights.

VOCs were sampled using the whole air sampling (WAS) system fitted to the FAAM 146 research aircraft. The WAS system consists of sixty-four silica passivated stainless steel canisters of three litre internal volume (Thames Restek, Saunderton UK) fitted in packs of 8, 9 and 15 canisters to the rear lower cargo hold of the aircraft. Each pack of canisters was connected to a 5/8 inch diameter stainless steel sample line connected, in turn to an all-stainless steel assembly double-headed three phase 400 Hz metal bellows pump (Senior Aerospace, USA). The pump drew air from the port-side aircraft sampling manifold and pressurized air in to individual canisters to a maximum pressure of 3.25 bar (giving a useable sample volume for analysis of up to 9 l). Air samples were analysed on location in Halifax within 48 h of collection using

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a dual channel gas chromatograph with two flame ionization detectors (see Hopkins et al., 2011 for full details). One litre samples of air were withdrawn from the sample canisters and dried using a glass condensation finger held at -30°C . Samples were pre-concentrated onto a multi-bed carbon adsorbent trap, consisting of Carboxen 1000 and Carbotrap B (Supelco), held at -20°C and then heated to 325°C at $16^{\circ}\text{C s}^{-1}$ and transferred to the GC columns in a stream of helium. The eluent was split in an approximately 50:50 ratio between an aluminium oxide (Al_2O_3 , NaSO_4 deactivated) porous layer open tubular (PLOT) column (50 m, $0.53\ \mu\text{m}$ id) for analysis of NMHCs and two LOWOX columns (10 m, $0.53\ \mu\text{m}$ id) in series for analysis of polar VOCs. Both columns were supplied by Varian, Netherlands. Peak identification and calibration was made by reference to a part per billion level certified gas standard (National Physical Laboratory, ozone precursors mixture, cylinder number: D64 1613) for NMHCs. This standard and instrument has in turn been evaluated as part of the WMO GAW programme and was within target operating limits. A relative response method was used for the calibration of OVOCs in the field, with reference to propane. The response values of oxygenated volatile organic compounds (OVOC) to propane were derived from laboratory calibration using ppm gas standard dilution and permeation methods. Detection limits were in the range 1 to 9 ppt and 10 to 40 ppt for NMHCs and OVOCs respectively.

3 Summary of non-methane hydrocarbon concentrations and emissions

To determine the relative emissions of NMHCs from biomass burning over other sources it is necessary to identify case studies where the overwhelming contributor to NMHC abundance is from a burning event. There are two major means of achieving this. The first is to make a case-by-case examination of data and assign data as being either “i” or “out” of a biomass burning plume. This works well where plumes are very distinct. The other means is to assign a threshold or filter for certain tracers of biomass burning and thus categorize all data above the filter threshold as having attributes of plume. In this paper we use the latter approach since on many occasions plume edges

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were indistinct, and the averaging of WAS samples smoothed across plume boundaries. The NMHCs and CO in this study have been categorized into three classes: (i) observations made in background air, as defined by CO <200 ppb; (ii) observations made in clearly identifiable biomass burning plumes (CO >200 ppb, plume confirmed by presence of furan and furfural by in-flight GC-MS) and (iii) observations made in anthropogenic plumes (CO >200ppb, no biomass burning tracers by GCMS). Classifications (i) and (ii) are summarised in Table 1, along with the highest plume mixing ratios for all observed NMHCs. In practice, the very high NMHC and CO values in biomass burning plumes dominate the slopes obtained from subsequent NMHC – CO plots, and changing the thresholds, for example to 175, 150 or 125 ppb CO has no significant impact on the slopes obtained.

A common approach is to examine the emissions of various NMHCs as a function of co-measured CO, to derive an emissions ratio (ER). This strictly refers to the ratio of the emissions at the point of release. All measurements made here were some distance downwind of the fire source and so chemical loss from the atmosphere must be appreciated. The primary loss from the plume of NMHC is likely to be through OH reaction, however in the absence of OH measurements, it is difficult to make adjustments for transport losses. A range of plumes of different ages are encountered in this study, from overhead passes to several days downwind, however in this study general plume age does not appear to substantially change the slope obtained of any given NMHC against CO. This is a somewhat surprising observation suggesting that losses of more reactive species such as alkenes are not high during transport. Overall therefore we estimate emission ratios for a range of species of differing reactivities in Table 1 without correction for plume age, but would highlight that there are increased uncertainties associated with more reactive hydrocarbons for the reasons outlined above.

The emission ratios in Table 1 are derived by subtracting a concentration value indicative of the background environment from the NMHC and CO data using a filter at 200 ppb CO to identify biomass burning. This is of course somewhat subjective, since all air masses encountered will have some degree of contribution to NMHCs and CO

from biomass burning. Subtracting the background data from plume data gives the emissions ratio defined as:

$$ER_{\text{NMHC:CO}} = \frac{[\text{NMHC}]_{\text{plume}} - [\text{NMHC}]_{\text{bkgd}}}{[\text{CO}]_{\text{plume}} - [\text{CO}]_{\text{bkgd}}}$$

The uncertainty values for our emission ratios (Table 1) are a combination of slope (from the R-squared value), the measurement uncertainty for observations of CO (assumed to be 5 %) and the compound specific uncertainties for the measurement of NMHCs. Within the stated uncertainties there is in general a very high degree of agreement between this study and the recent work of Simpson et al. (2011) that was undertaken in a similar geographical region. Some additional NMHCs are reported here which were not reported in the Simpson et al. study; these new ERs are in line with similarly structured compounds reported previously. Notable outliers include propene, which is observed in this work to have an ER around double that reported in Simpson et al. (2011), and methacrolein with an ER around five times higher here. Whilst isoprene was elevated within biomass burning plumes in this study, it was not correlated to CO to a statistically significant ($R^2 < 0.15$) degree and so we do not assign an ER, unlike Simpson et al. (2011) Its presence within the plume may be rationalized however through either close proximity vegetation releases or the heat induced distillation of biogenic volatile organic compounds (BVOCs).

We summarize graphically for a range of alkane species in Fig. 2a, showing background data, biomass plume data and distinct plumes of anthropogenic emissions. For alkanes, anthropogenic and biomass burning the NMHC:CO relationships are rather similar, and in isolation are difficult to disentangle. Figure 2b shows the relationships between a range of alkenes and CO. Here the differences between elevation caused by anthropogenic emissions and those caused by biomass burning are much clearer. Somewhat surprisingly even for very short-lived NHMCs, sampled some days downwind, the mixing ratios remain very high and are in contrast to the anthropogenic plumes, where CO is significantly elevated, but the reactive alkenes are largely

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depleted. This mirrors observations in Lewis et al. (2007) of plumes far out in the North Atlantic where ethene, for example, remained at mixing ratios >1000 ppt more than four days from emission. Figure 2c shows the relationships between selected aromatic and oxygenated species and CO. For toluene and methacrolein, again there are substantial differences in the slopes for anthropogenic and biomass plumes.

It is potentially possible to provide a relative assessment of emissions scaled to the amount of biomass fuel burnt, referred to as an Emission Factor (EF). This essentially relates NMHC emissions to CO₂ rather than CO via an estimated value associated to the mass fraction of carbon in the biomass fuel. We do not make this scaling here since CO₂ data for this experiment is much less complete than for CO, although when made for selected flights it shows a similarly good agreement with Simpson et al. (2011) as the ER.

4 Model analysis and global impacts

The airborne observations made over Canada show strong correlations between the concentrations of individual NMHCs and CO in plumes from both biomass burning and fossil fuel burning origins. To explore the individual contributions from the distinct source types we perform a “tagged tracer” simulation of benzene, toluene, propene and ethene within the GEOS-Chem global model (version 9.1.2 www.geos-chem.org/) (Bey et al., 2001; van der Werf et al. 2010) in which individual model tracers represent contributions of benzene, for example, emitted from a particular source and geographical region. We chose these species in particular for study since they are generally considered in atmospheric chemistry as anthropogenic tracers, rather than from natural emissions. Their large emission rates from biomass burning are potentially of growing significance given that all these species are on downwards emissions trajectories in developed countries, a result of emissions control technologies and reformulation of gasoline composition.

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We adapt the model NMHC tracers in a flexible way to simulate both tagged anthropogenic and biomass burning sources. For simplicity we ignore any other biogenic source (e.g. direct leaf-level emissions of toluene or ocean source of alkenes). We include the NMHC species as extra tracers in the full-chemistry model simulation. We simulate emissions (the rate of the emission being described below) transport by the large-scale meteorology fields, and also by convection and boundary layer mixing. The NMHC species do not directly interact with the chemistry scheme but are subject to oxidation by the time-dependent oxidant fields of OH, O₃, and NO₃. We do not consider the oxidation of these compounds in the stratosphere, which is a reasonable approximation given atmospheric lifetimes of 7 days or less and only modest convective outflow levels encountered during experiments.

The purpose of this modelling is to apply the emissions factors derived in this study and upscale the distribution of observed NMHCs on a global and annual timescale and to evaluate the model at remote surface sites, rather than to attempt along-flight-track simulations to match observations. Given the excellent agreement in ER between this study and Simpson et al. (2011), experiments conducted in different years, we consider that representative meteorology from any given year would be a reasonable approximation to simulate annual global hydrocarbon distributions from boreal biomass burning. We run the model for the year 2009 twice with the first year being considered as model spin-up. We choose this year as GFED III (Global Fire Emission Database) (van der Werf et al., 2010) emissions of CO are available for this year.

Table 2 describes the emission rates of these target compounds released in the model. The RETRO emission (Schultz et al., 2007) for 2000 are used for the anthropogenic sources and the biomass burning sources are scaled to the GFED III CO emissions used in the model. Whilst more up-to-date inventories exist at national levels, this database has the correct combinations of NMHC species, geographic and temporal disaggregation for the study here, and is well integrated with the GEOS-Chem model. Changes in emissions over recent years have occurred however, most notably for benzene, and the impacts of this on our conclusions are discussed later. The biomass

burning emissions of the hydrocarbons uses the GFED III CO emissions scaled by the ratios derived for the BORTAS data. Our estimates of global benzene and toluene emissions are comparable to previous studies (e.g. Henze et al., 2008) but tend to be lower especially for the biomass burning source due to different choices of emission ratio ($3.4 \text{ Tg}(\text{C}_6\text{H}_6) \text{ yr}^{-1}$ for that study vs. $3.5 \text{ Tg}(\text{C}_6\text{H}_6) \text{ yr}^{-1}$ for this for anthropogenic emission; $2.7 \text{ Tg}(\text{C}_6\text{H}_6) \text{ yr}^{-1}$ for that study vs. $1.8 \text{ Tg}(\text{C}_6\text{H}_6) \text{ yr}^{-1}$ for this study).

Lifetimes of individual hydrocarbons are derived as being the reciprocal of the annual globally integrated loss rate of the compound divided by the annual mean burden. For these simulations the global mean tropospheric OH concentration was calculated to be $1.12 \times 10^6 \text{ molecules cm}^{-3}$, which is broadly consistent with the available observational constraints (Krol et al., 1998).

5 Evaluation of the model against data

To evaluate the general performance of the global model in simulating global background hydrocarbon distributions from all sources we compare it against some remote NMHC measurements made as part of the WMO Global Atmosphere watch programme. The number of measurement stations for which this type of continuous data exists is very small – perhaps only 3 to 5 at any one time. More comprehensive geographic coverage is achieved for alkanes and acetylene from flask networks, but not the target species in this study. Figure 3 shows observations of the concentration of benzene (monthly means, derived from hourly data) at the Cape Verde Atmospheric Observatory in the tropical mid-Atlantic and a comparison with the model simulation under a range of emission levels. Using baseline RETRO emission data for the nominal year 2000 reproduces the annual cycle of surface NMHC concentrations, but has a large positive bias. We attain better model agreement between the concentration data only after we reduce the anthropogenic emissions by two thirds. There is some good justification for allowing a significant reduction in anthropogenic benzene over the past decade, with many developed countries having dramatically reduced emissions

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following reformulation of gasoline content and introduction of catalytic converters. We consider therefore that the model shows suitable agreement to allow us to proceed in so far as it reasonably captures the annual variability seen in measurement. Moving forward, in this study we continue to work with the RETRO database as is, but in a number of cases and figures highlight how biomass to anthropogenic contributions would be affected if a 2/3 reduction in anthropogenic benzene was applied.

6 Estimating global distribution of benzene, toluene, ethene and propene from biomass burning and anthropogenic emissions

Figure 4 shows the global annual mean mixing ratio of biomass burning benzene, and anthropogenic benzene estimated by the GEOS-Chem model, using the CO:benzene ratio from this work together with the GFED III CO emissions and the RETRO database for the year 2000 for the anthropogenic emissions. This figure highlights that for most locations the air quality or human health impact of these biomass burning emissions is generally very small – benzene released from this source contributes typically a few parts per trillion. The same is true for toluene, ethene and propene (not shown). Exceptions are locations in Arctic regions where the estimated concentrations of benzene from biomass burning reach in to the ppb range. The biomass burning impacts on global NMHCs are therefore perhaps most important to consider when attempting to evaluate trends, transport processes and longer-term behaviour of these species when measured in background locations, e.g. in those locations where the presence of these species is used as a diagnostic of, for example, long range transport.

7 Biomass vs anthropogenic sources of benzene, toluene, ethene and propene

The tagged tracers in the GEOS-Chem model are then used in Fig. 5 to show the surface ratio of (i) the mean of the monthly mean ratio of simulated biomass burning tagged hydrocarbon to total hydrocarbon (biomass burning tracer + anthropogenic

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tracer) and (ii) the maximum of the same ratio observed in any of the individual twelve months in the year. The plots illustrate (with warm colours) those regions that on a mean annual basis have significant fractional biomass burning input to the observed NMHC, and also when influence can become important for shorter, monthly, periods.

Figure 5 (and Fig. 6 for benzene) shows extensive geographic regions where the abundance of all four hydrocarbons is heavily impacted by biomass burning. This is particularly the case in the Southern Hemisphere, where biomass burning is high and fossil fuel burning is proportionately lower. Here, biomass burning constitutes typically a large and sometimes dominant source to the lower atmosphere. It should be remembered of course that this is a ratio of two abundances – the absolute abundance of NMHCs in many of these remote Southern Hemisphere locations is exceptionally low.

Over the northern industrial belt (North America, Europe, Asia) the annual mean ratios indicate that benzene, toluene, ethene and propene are generally dominated by the anthropogenic source. It is worth noting however that regions of the US and Canada have, even on a mean basis, a non-trivial fraction of benzene associated with biomass burning sources. One might expect this fraction to grow in significance as vehicle emissions control further act to reduce anthropogenic emissions. Whilst health exposure limits for benzene vary widely internationally they move generally only in a downwards and tightening direction. The model simulations highlight that ultimately pragmatic approaches are needed in setting reasonable and achievable lower limits for benzene in the atmosphere given the apparent large and widespread source from biomass burning.

The figure also shows the maximum monthly mean percentage, which indicates that for many regions biomass burning can, for shorter periods, make up the dominant source of the hydrocarbon observed. The feature is most striking for benzene, not unsurprising given it has the longest lifetime, but this is also the case for shorter-lived hydrocarbons as well. For fast reacting hydrocarbons such as propene the concentrations in remote areas, particularly over the oceans, become very low and this leads to

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numerical issues in the model. Areas where the concentrations approach the numerical resolution of the model are indicated in white.

As identified earlier there is some potential that the RETRO database may now overestimate the total amount of anthropogenic benzene (and to a lesser extent other NMHCs) released due to clean technology infiltration into the vehicle fleet and gasoline reformulation in many places. Our comparison earlier of remote background benzene data with the model suggested that a two-thirds reduction in emissions would bring model and measurement into reasonable agreement. Whilst this study cannot provide any quantitative measure of whether this is globally an appropriate figure to apply, the impact of a reduction of this scale is shown in Fig. 6. By reducing the anthropogenic emissions of benzene, the proportional impact of the biomass burning contribution grows significantly (plots marked 2010).

In broad terms we conclude from these simulations that for much of the planet the observed abundance of these benzene, toluene, ethene and propene can be significantly influenced by a proportion of emissions from biomass burning, and that continued reductions in anthropogenic hydrocarbons will grow this impact. The effects are largely realised in the background environment and away from localised urban anthropogenic sources.

8 Impacts on background measurement stations

Most detailed measurements of NMHCs have historically been focused on urban centres, however there are increasing efforts now made to establish trends in the background atmosphere through the WMO Global Atmosphere Watch programme. GAW covers a wide range of parameters relating to atmospheric composition, and is considered the atmospheric chemistry component of the Global Climate Observing System (GCOS). Details can be found at www.wmo.int/gaw. Reactive gases form a subset of species to be observed including surface ozone (O_3), carbon monoxide (CO), volatile organic compounds (VOCs), oxidised nitrogen compounds (NO_x , NO_y), and sulphur

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dioxide (SO₂). GAW comprises several hundred observing sites, classified as “Contributing”, “Regional” and “Global” depending on the scope of the measurement programme at each location. We consider it useful to examine the major NMHC source influences on the primary Global measurement stations in that network, accepting that at present only a small number make continuous NMHC measurements. We focus here on the 28 Global GAW stations that make the most comprehensive range of measurements. The names and locations of the Global stations are shown in Table 3 and in Fig. 7.

Using output from the GEOS-Chem model we simulate an annual time series for benzene (biomass burning derived and total) for four “clean” background surface GAW sites from around the world. Figure 8 shows for four selected GAW locations, the simulated total benzene at each site, the benzene derived from biomass burning, and a separate plot showing the fractional contributions. At present none of these sites has online measurements year round. Those sites in reasonable proximity to biomass burning sources, (e.g. Barrow, Alaska and Bukit Kototabang, Indonesia) are subject to significant impacts with modelled benzene events of ~ 500 pptv due almost entirely due to burning. Very remote GAW sites (e.g. Samoa, Halley) show very low absolute concentrations but show a significant fraction of that coming from biomass burning.

Taking all the Global GAW locations from Table 3, we then place them into categories based on the annual mean fraction of likely experienced benzene that is from biomass and the maximum monthly fraction of benzene that is biomass (Table 4). The categories are for fraction values 0–20%, 20–40%, 40–60%, 60–80% and 80–100%. Using the standard RETRO emission values for benzene the majority of GAW Global stations on a mean annual basis are in the lowest 0–20% impact category and all but one station covered by that and the 20–40% category. An analysis of monthly maximum impact however is rather different, indicating that benzene at the majority of stations can be dominated on occasion by biomass burning sources. As discussed previously, the likely anthropogenic emissions may be lower than expressed in RETRO and so we include separate rows that show how the stations would partition if a 66.7% anthropogenic

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reduction in benzene was implemented in the model. In this case on an annual mean basis a significant number of stations would be in the 40–60 and 60–80 % biomass burning benzene category, and the majority in the highest category when considered on a monthly maximum basis.

9 Conclusions

An extensive set of airborne measurements of NMHCs have been made in boreal forest fire plumes over Canada. The data expands on the global dataset adding some new emissions estimates for certain hydrocarbon species and providing confirmatory measurements to some species previously published. The generally very good agreement between emissions derived from different aircraft studies by different groups provides significant confidence in making extrapolations from these estimates in models. Using the GEOS-Chem CTM we examine the relative contributions of anthropogenic and biomass burning emissions to the background abundance of benzene, toluene, ethene and propene. We chose these species in particular since they are traditionally thought of as being anthropogenic in nature and are species with generally declining urban concentrations in developed economies. The tagged model showed that in most of the Southern Hemisphere likely much of the observed benzene at any given location is from biomass burning, and that this source dominance extends at times to the Northern Hemisphere also. It is only over heavily industrialized regions that these NMHC distributions are dominated by the anthropogenic source. The behaviour of benzene is particularly interesting here since it is a heavily regulated pollutant that is often considered as having no safe lower limit. The study here shows that pragmatic air quality targets are needed for benzene given that regional and transboundary biomass burning sources can make up a significant fraction of the benzene experienced globally.

Although very limited experimental data exists for the long-term trends in NMHCs in the background atmosphere, comparison of model against an annual cycle of benzene in the tropical Atlantic is generally reasonable, although suggesting that the model

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emissions database is overestimating anthropogenic emissions. When the model is used to estimate the contribution of biomass burning to the NMHC experienced at GAW Global stations the picture is mixed. At some locations such as Barrow and Alert high absolute and fractional biomass contributions are predicted, whilst in some tropical and polar regions the absolute amounts are predicted to be low but with significant fraction from biomass burning. An assessment is made of the likely biomass burning input to all 28 GAW Global stations as a hopefully useful precursor exercise prior to the practical extension to the GAW-VOC measurement programme.

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Table 1. Measurement statistics from the observations made during the BORTAS campaign. Values observed below the limit of detection (LOD) have been assigned a value of half the LOD to enable a background value to be calculated. Median averages have been reported for the background mixing ratios in order to reduce the effect of a small number of samples with higher than expected VOC mixing ratios (likely corresponding to localised emissions from an unknown source) which would otherwise yield unrepresentatively high background values.

Species	LOD pptv	Background median (pptv)	Plume average (pptv)	Plume maximum (pptv)	ER to CO (pptv/ppbv)	ER to CO (pptv/ppbv) Simpson et al. (2011)
CO		97.72 ppb	380.52 ppb	1049.03 ppb	–	–
ethane	9	773	2236	5721	5.13 ± 0.35	4.6 ± 0.9
propane	3	103	517	1355	1.26 ± 0.10	1.3 ± 0.3
iso-butane	1	6	37	85	0.077 ± 0.02	0.09 ± 0.02
n-butane	1	18	116	307	0.30 ± 0.04	0.32 ± 0.05
cyclopentane	1	8	10	16	0.007 ± 0.004	
iso-pentane	1	4	19	41	0.034 ± 0.01	0.07 ± 0.02
n-pentane	1	5	42	128	0.13 ± 0.021	0.14 ± 0.02
2,3methylpentane	2	1	8	24	0.021 ± 0.007	0.05 ± 0.01
n-hexane	1	1	18	60	0.063 ± 0.01	0.08 ± 0.01
n-heptane	1	0.50	13	45	0.041 ± 0.008	0.06 ± 0.01
2,2,4 TMP	1	0.50	10	33	0.027 ± 0.01	
n-octane	2	1	11	101	0.028 ± 0.03	
ethene	7	49	1848	6663	6.9 ± 0.72	7.3 ± 0.1
propene	3	12	205	1475	1.19 ± 0.29	2.3 ± 0.1
propadiene	3	1.5	18	62	0.070 ± 0.02	
Trans-2-butene	1	4	4	12	–	0.09 ± 0.01
1-butene	1	5	35	246	0.20 ± 0.06	0.34 ± 0.01
iso-butene	1	5	15	111	0.074 ± 0.04	0.03 ± 0.02
cis-2-butene	1	0.50	2	2	–	0.07 ± 0.004
1,3-butadiene	1	0.50	83	398	0.39 ± 0.07	0.32 ± 0.02
t-2 pentene	1	0.50	6	21	0.019 ± 0.01	
1 pentene	1	0.50	14	75	0.064 ± 0.02	
isoprene	1	0.50	112	820	–	0.27 ± 0.05
acetylene	3	80	767	2046	2.07 ± 0.31	2.1 ± 0.9
benzene	2	27	424	1383	1.40 ± 0.11	1.70 ± 0.3
toluene	2	6	187	653	0.69 ± 0.09	0.67 ± 0.16
Ethyl benzene	3	1.50	33	98	0.10 ± 0.03	0.058 ± 0.02
m+p xylene	3	1.50	420	161	0.17 ± 0.04	0.14 ± 0.01
o-xylene	3	1.50	24	82	0.078 ± 0.03	0.064 ± 0.003
MACR	3	2	160	754	0.8 ± 1.1	0.15 ± 0.01
Methanol	40	1556	4423	10335	8.9 ± 3.2	9.6 ± 1.9
Acetone	9	1476	2550	4584	3.5 ± 0.8	1.6 ± 0.4

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Table 2. Emissions and derived lifetimes of the simulated species.

Compound	Emission Type	Emission source	Emission (Tg yr ⁻¹)	Lifetime (days ⁻¹)
Benzene	Biomass	CO _{bb} ·0.0014	1.77	7.42
	Anthropogenic	RETRO 2000	3.48	10.95
Toluene	Biomass	CO _{bb} ·0.00069	1.11	1.55
	Anthropogenic	RETRO 2000	6.13	2.73
Ethene	Biomass	CO _{bb} ·0.0069	0.85	1.15
	Anthropogenic	RETRO 2000	6.47	1.19
Propene	Biomass	CO _{bb} ·0.0019	2.04	0.28
	Anthropogenic	RETRO 2000	2.74	0.30
CO	Biomass	CO _{bb}	272	

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Table 3. List of the 28 GAW Global stations with three letter code names and locations.

Station name (Country)	CODE	Latitude	Longitude
Assekrem/Tamanrasset (Algeria)	TAM	23.26667	5.63333
Cape Verde Atmospheric Observatory (Cape Verde)	CVO	16.848	-24.871
Amsterdam Island (France)	AMS	-37.7983	77.5378
Mt. Kenya (Kenya)	KEN	-0.0622	37.2972
Cape Point (South Africa)	CPP	-34.35348	18.48968
Izaña (Tenerife, Spain)	IZA	28.309	-16.4994
Cape Grim (Australia)	CPG	-40.68222	144.6883
Mt. Waliguan (China)	WAL	36.2875	100.8963
Bukit Kototabang (Indonesia)	BUK	-0.20194	100.3181
Minamitorishima (Japan)	MIN	24.2852	153.9813
Danum Valley (Malaysia)	DAN	4.98139	117.8436
Nepal Climate Observatory – Pyramid (Nepal)	NEP	27.9578	86.8149
Lauder (New Zealand)	LAU	-45.038	169.684
Mauna Loa (United States)	MLO	19.53623	-155.5762
Samoa (United States)	SAM	-14.24747	-170.5645
Ushuaia (Argentina)	USH	-54.84846	-68.31069
Arembepe (Brazil)	ARE	-12.76667	-38.16667
Alert (Canada)	ALE	82.45	-62.51667
Barrow (United States)	BAR	71.32301	-156.6115
Trinidad Head (United States)	TRI	41.0541	-124.151
Pallas/Sodankylä (Finland)	PAL	67.97361	24.11583
Zugspitze/Hohenpeissenberg (Germany)	ZUG	47.4165	10.9796
Mace Head (Ireland)	MAC	53.32583	-9.89945
Monte Cimone (Italy)	MON	44.16667	10.68333
Zeppelin Mountain (Norway)	ZEP	78.92358	11.92366
Jungfraujoch (Switzerland)	JFJ	46.54749	7.98509
Neumayer (Antarctica)	NEU	-70.666	-8.266
Halley (Antarctica)	HAL		
South Pole (Antarctica)	SPO	-89.99695	-24.8

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Table 4. GEOS-Chem model estimated fraction of annual benzene associated with biomass burning, given as the annual mean and as the monthly maximum. The anthropogenic emissions used are that of RETRO and $0.33 \times$ RETRO. GAW sites (see Table 3 and Fig. 7) are binned according into which biomass burning fraction range they lie.

Biomass burning/ anthropogenic benzene fraction	Annual Mean			Annual Mean (RETRO \times 0.33)			Monthly Maximum			Monthly Maximum (RETRO \times 0.33)				
0.0–0.2	TAM IZA DAN ARE ZUG JUN	CVO WAL NEP TRI MAC	KEN MIN MLO PAL MON	IZA PAL MON	WAL ZUG JUN	NEP MAC HLF	NEP	ZUG	MON	JUN	ZUG	MON	JUN	
0.2–0.4	AMS LAU ALE NEU	CPP SAM BAR SPO	CPG USH ZEP HAL	TAM MIN ARE ZEP	CVO DAN ALE TRI	KEN MLO TRI	IZA				NEP			
0.4–0.6	BUK			CPP USH	CPG BAR	LAU	TAM	CVO	WAL	ARE				
0.6–0.8				AMS NEU	BUK SPO	SAM HAL	KEN SAM NEU	CPP TRI SPO	MIN PAL HAL	DAN MAC HLF	TAM	IZA	WAL	ARE
0.8–1							AMS MLO ZEP	CPG USH	BUK ALE	LAU BAR	CVO LAU ALE ZEP	AMS MLO NEU	KEN SAM SPO	CPP DAN USH MAC HAL



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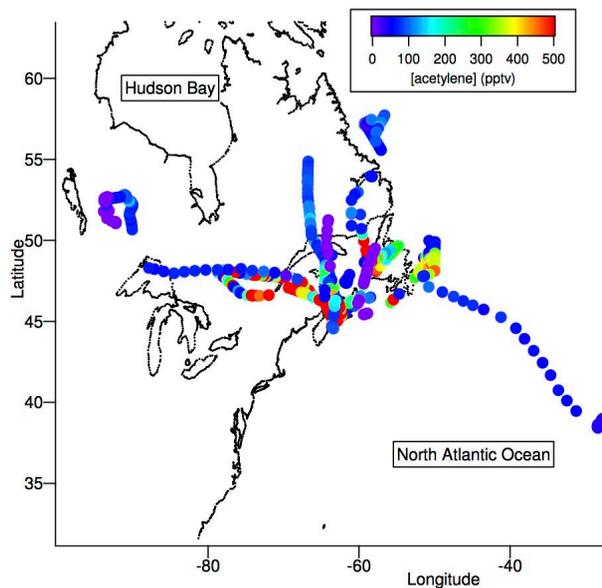


Fig. 1. FAAM146 flight tracks during August 2012, overlaid with sample locations for whole air samples. The points are coloured by acetylene mixing ratio.

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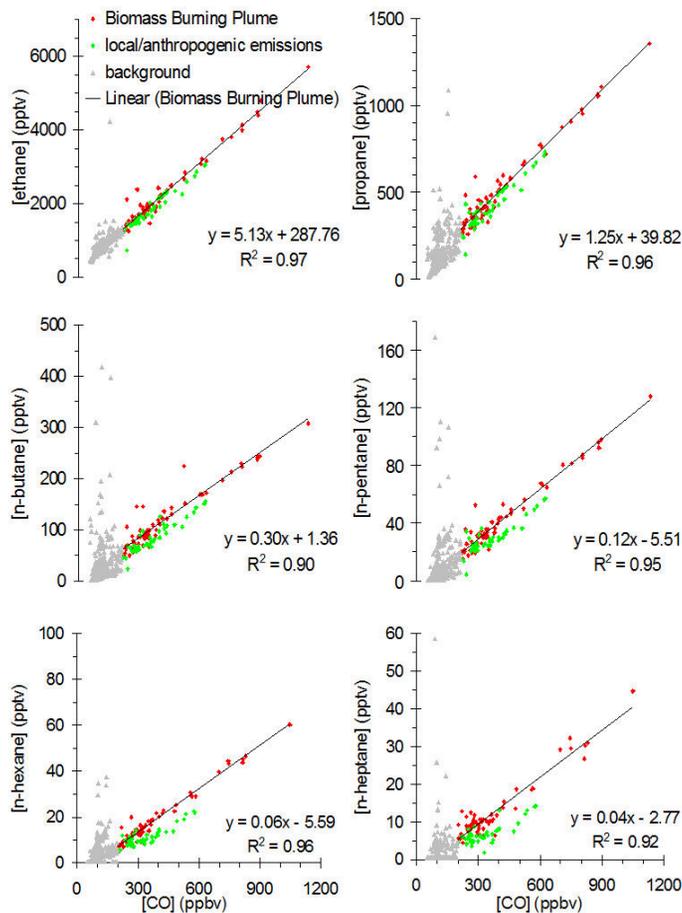


Fig. 2a. Selected plots of alkanes vs CO. Grey triangle assigned as background air, red diamonds assigned as biomass plumes and green diamonds assigned as anthropogenic plumes.

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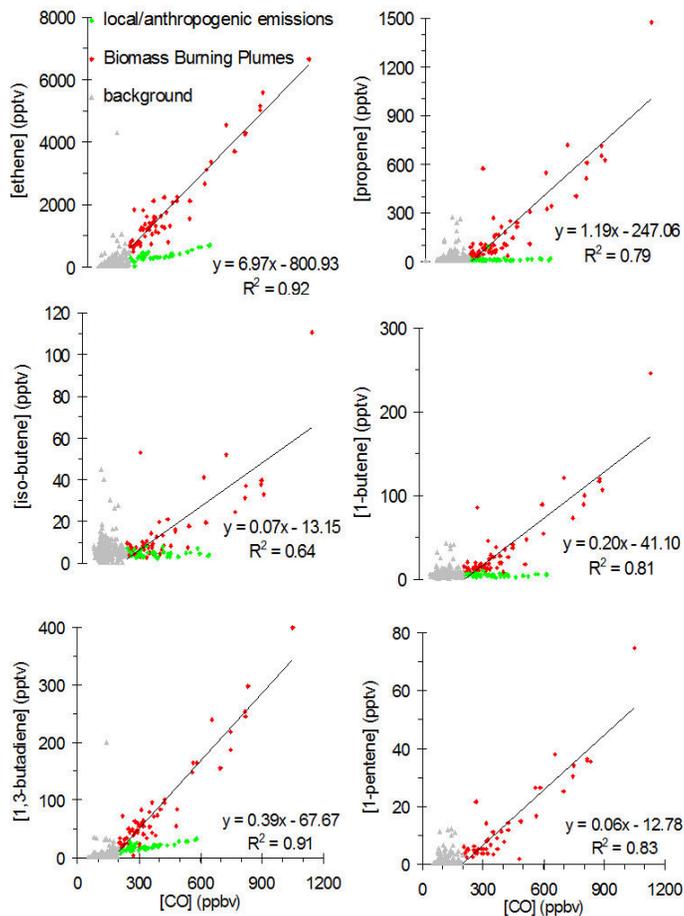


Fig. 2b. Selected plots of alkenes vs CO. Grey triangle assigned as background air, red diamonds assigned as biomass plumes and green diamonds assigned as anthropogenic plumes.

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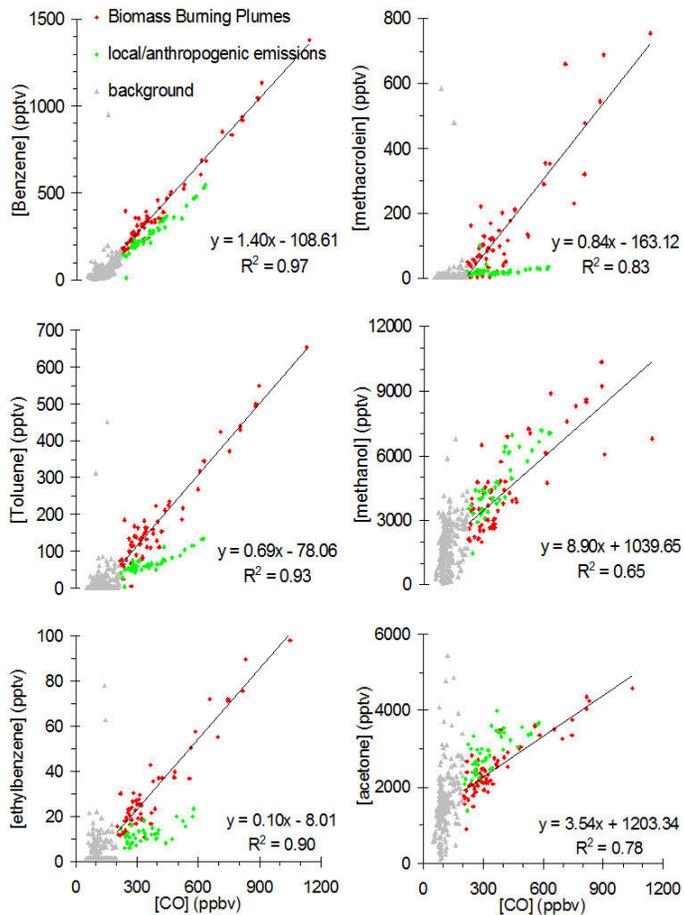


Fig. 2c. Selected plots of aromatics and oxygenates vs. CO. Grey triangle assigned as background air, red diamonds assigned as biomass plumes and green diamonds assigned as anthropogenic plumes.

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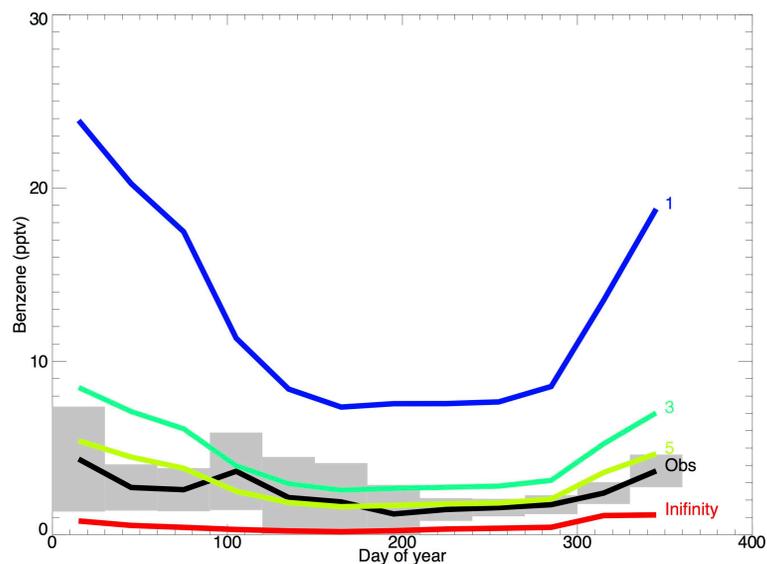


Fig. 3. Comparison of GEOS-Chem model estimate for benzene and observations made at the Cape Verde GAW observatory. Bars indicate ranges of monthly data and the black line the observed average. The blue line indicates the model estimate using biomass burning and RETRO emissions inputs. The two green lines (3) and (5) show the estimated benzene reducing benzene in RETRO by -0.2 and -0.33 respectively. The red line shows the model when no anthropogenic emissions are included.

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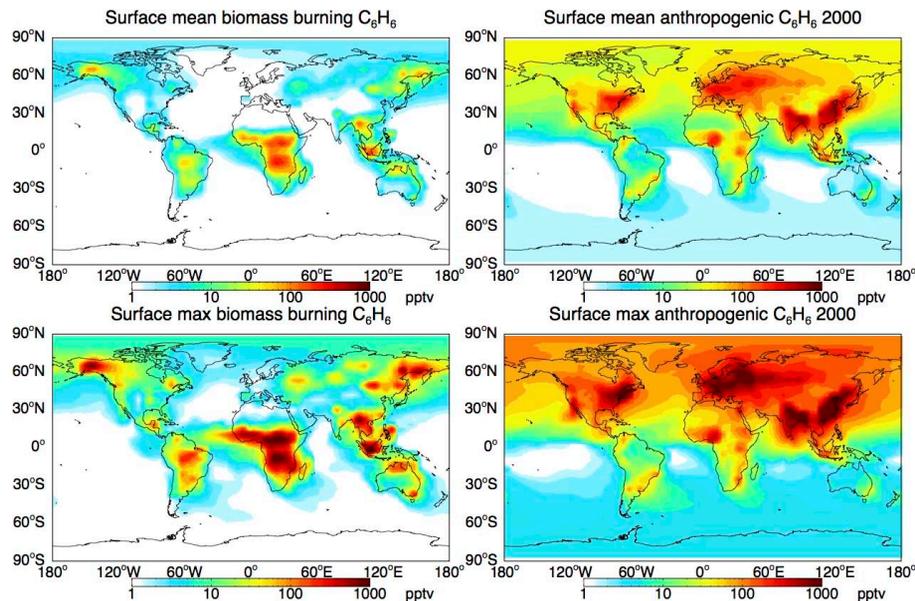


Fig. 4. Top row: model estimate of the annual surface mean mixing ratio of benzene resulting from biomass burning emissions (left) and from anthropogenic emissions (right). Second row of plots shows the monthly maximum surface mixing ratio from these two sources.

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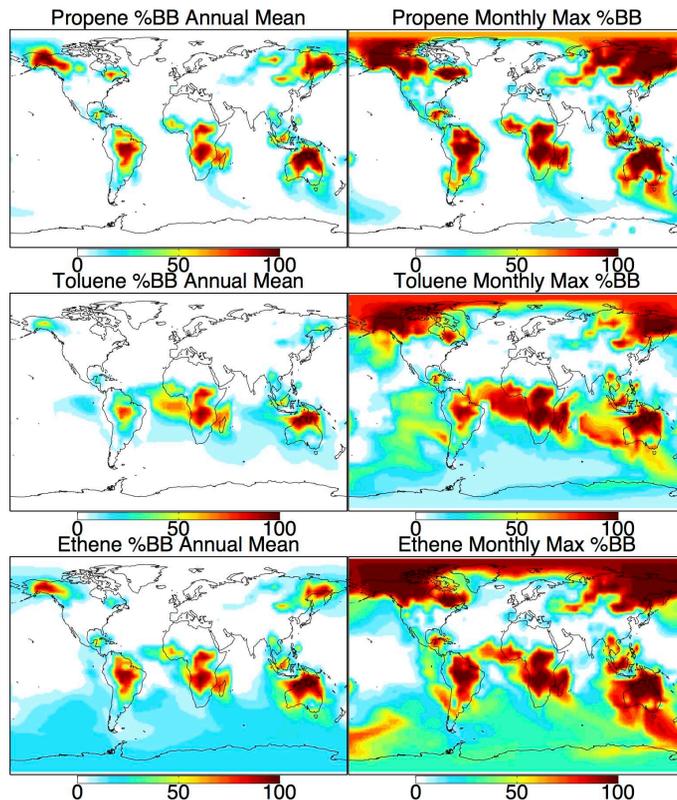


Fig. 5. Fractional contribution to the total propene (top), toluene (middle) and ethene (bottom) from biomass burning. Left hand plots show annual mean contributions and right hand plots the monthly maximum fraction from biomass burning.

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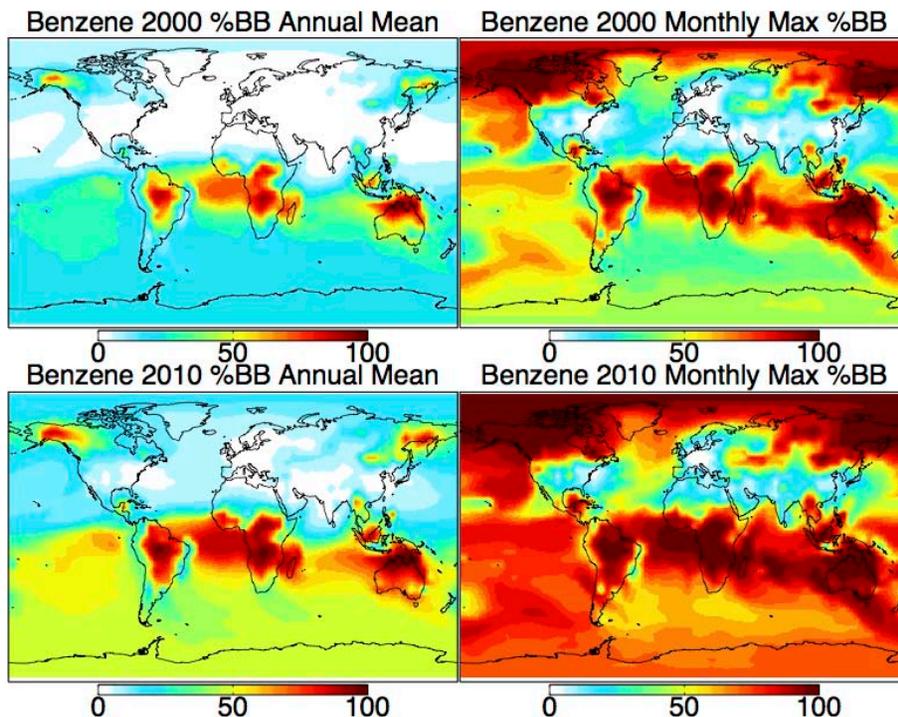


Fig. 6. Fractional contribution to benzene from biomass burning as an annual mean (left top) and as the monthly maximum (right top). Bottom plots show how this fractional contribution is enhanced if a reduced 0.33· RETRO anthropogenic emissions for benzene is implemented in line with fit to Fig. 3 observations.

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Fig. 7. Locations of the WMO GAW Global observatories.

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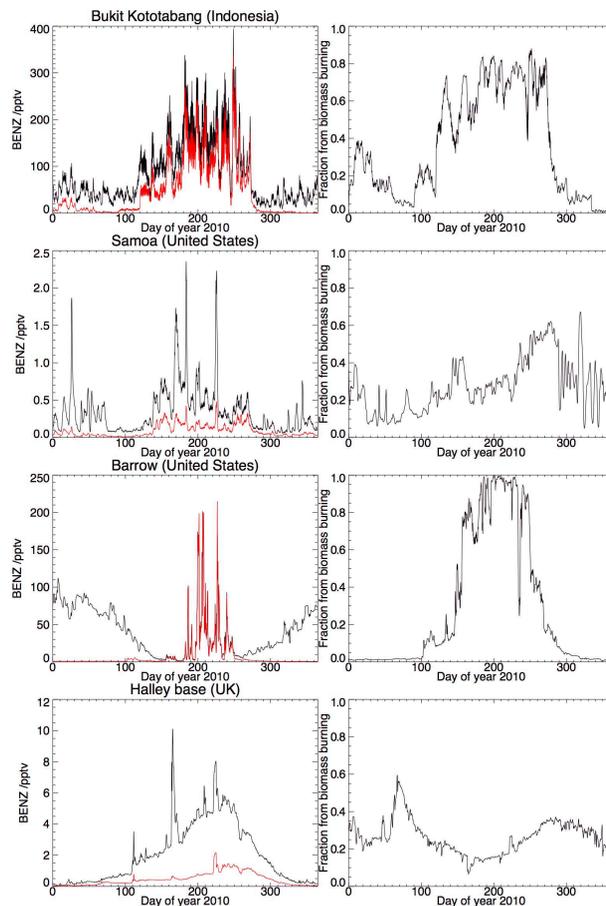


Fig. 8. Model estimates of the biomass burning inputs to benzene at four GAW observatories currently without NMHC online measurements. From top: Bukit Kototabang, Indonesia; Samoa, Pacific; Halley, Antarctica; Barrow, Arctic. Left figures show estimated mixing ratios (black) and biomass contribution (red). Right hand figures show % biomass contribution.

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