Edinburgh Research Explorer

The influence of biomass burning on the global distribution of selected non-methane organic compounds

**Atmospheric
Chemistry
and Physics**

The influence of biomass burning on the global distribution of selected non-methane organic compounds

A. C. Lewis[1], M. J. Evans[1,2], J. R. Hopkins[1], S. Punjabi[2], K. A. Read[1], R. M. Purvis[1], S. J. Andrews[2], S. J. Moller[1], L. J. Carpenter[2], J. D. Lee[1], A. R. Rickard[1], P. I. Palmer[3], and M. Parrington[3]

[1]National Centre for Atmospheric Science (NCAS), University of York, Heslington, York YO10 5DD, UK
[2]Department of Chemistry, University of York, Heslington, York YO10 5DD, UK
[3]School of Geosciences, University of Edinburgh, The King's Buildings, Edinburgh EH9 3JN, UK

Correspondence to: A. C. Lewis (ally.lewis@york.ac.uk) and M. J. Evans (mat.evans@york.ac.uk)

Abstract. Forests fires are a significant source of chemicals to the atmosphere including numerous non-methane organic compounds (NMOCs). We report airborne measurement of hydrocarbons, acetone and methanol from > 500 whole air samples collected over Eastern Canada, including interceptions of several different boreal biomass burning plumes. From these and concurrent measurements of carbon monoxide (CO) we derive fire emission ratios for 29 different organic 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 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 which are controlled for air quality purposes and sometimes used as indicative tracers of anthropogenic activity). Using our observationally 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 levels 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 decline in developed countries. We subsequently determine the extent to which the 28 global-status World Meteorological Organisation – Global Atmosphere Watch stations worldwide are influenced by biomass burning sourced benzene, toluene, ethene and propene as compared to their exposure to anthropogenic emissions.

1 Introduction

Non-methane organic compounds are a class of trace compounds found throughout the troposphere and include non-methane hydrocarbons (NMHCs) and oxygenated volatile organic compounds (OVOCs). Whilst typically present at mixing ratios in the parts per billion to 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 the hydroxyl radical OH and can influence its rate of production via ozone + alkene reactions. Some species are also now implicated in the generation of secondary oxidation products, which can aid the formation of secondary aerosols (Hallquist et al., 2009 and references therein). NMHCs are released from a wide range of biogenic and anthropogenic sources. Most individual NMHCs have a mix of sources, with isoprene (the largest global emission by mass) being the prime exception with emissions almost exclusively from terrestrial vegetation. Incomplete combustion is generally the largest individual anthropogenic source of NMHCs, including petrol and diesel engines, static power generation and the burning of wood and coal for heating and cooking (e.g. AQEG, 2007 for the UK, Badol et al., 2008 for France, Morino et al., 2011 for Japan).

Biomass burning has long been recognised as a major source of trace gases to the atmosphere, of relevance to this study, being the work of Crutzen et al. (1979) first estimating the emission of carbon monoxide (and other gases) from biomass burning. The co-emission of hydrocarbon species

along with CO has been reported extensively and the correlation with CO used to derive emission ratios for many species (e.g. Crutzen and Andreae, 1990). Vegetation burning occurs globally from the tropics in South America, Africa, SE Asia and Australia through to the boreal forests of North America and Siberia. A summary of emissions for many trace species including hydrocarbons is reported in Andreae and Merlet (2001). As a class of compound NMHCs have a wide range of atmospheric lifetimes, from a few minutes to several months, which together with their disparate regional sources, control their global distributions (Atkinson, 1994).

Long-term automated measurements of NMHCs are currently skewed in number towards urban and sub-urban locations, reflecting the important role of NMHCs in controlling urban air quality. In urban locations the sources of most NMHCs tend to be overwhelmingly anthropogenic and in many locations have shown downwards trends of the order 1–5 % per year (von Schneidemesser et al., 2010), dependant on species, arising from the effective introduction of vehicle emissions control technologies and a reduction in industrial and domestic solvent usage. Global data on emissions, disaggregated by sector, geography, time and hydrocarbon species, do not currently exist. However at a national level, using the UK as an example, exhaust emissions and solvent usage have decreased to around 1/4 and 1/3 respectively of the emissions in 1990 (see for example http://naei.defra.gov.uk/). Trends in developing countries are more difficult to estimate given a lack of observations. It may be a reasonable assumption that catalytic controls may not have as effectively penetrated vehicle fleets in these locations and growth in traffic volume may outweigh control measures. It is potentially reasonable however to assume that there has not been an increase in benzene use as a solvent since it has been replaced effectively by other less harmful solvents. Observations of NMHCs in the background atmosphere are confined largely to process studies and short-term research missions. A substantial literature exists on the subject, and we refer the reader to dedicated texts, e.g. "Volatile Organic Compounds In The Atmosphere" (Koppman, 2007).

There is an increase in the number of long-term (> 5 yr) background measurements (typically hundreds of km from urban sources) of NMHCs in the troposphere, using flask samples (Pozzer et al., 2010) and from in situ observations (e.g. Plass-Duelmer et al., 2002; Read et al., 2009; Simpson et al., 2012). Recognizing the importance of addressing the limited extent of measurements relative to other atmospheric species, the World Meteorological Organization now has a specific long-term monitoring 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, requiring a more detailed analysis of other variables such as trajectory origins, source receptor modelling and use of chemical transport models. It is possible for many NMHCs that the observation of a given species will arise because of the combined releases of anthropogenic and natural emissions, followed by transport and degradation. Extracting value and information from 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 to 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 (Kasischke and Stocks, 2000), and their fires emit many more species in addition to NMHCs. CO_2, CO and CH_4 are the largest emissions by mass with CH_3OH and HCHO the most dominant organic compounds (see most recently for Canadian boreal fires Simpson et al., 2011). 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. These and many other hydrocarbon emissions are summarised in Andreae and Merlet (2001). Simpson et al. (2011) report an exceptionally comprehensive catalogue of different species released by boreal fires, including NMHCs, halocarbons, oxygenated species and organic nitrates, and we pay particular attention in comparing to this study since it provides very good overlap in terms of chemical speciation and was made in the same geographic region. Laboratory evaluation of organic emissions include those reported in Christian et al. (2003, 2004), 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 by 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, CH_4 and C_2H_6 have 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 (Flannigan et al., 2005; Kasischke and Turtesky, 2006; Soja et al., 2007; Marlon et al., 2008; Amiro et al., 2009; Wotton et al., 2010).

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, 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 concentration (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 or not they contribute significantly to more general tropospheric ozone production (e.g. Jaffe and Wigder, 2012). This wider atmospheric chemistry challenge provides the motivation for the BORTAS study, of which this dataset forms one part.

2 Experimental

The measurements reported in this paper were made as part of the research project - Quantifying the impact of **BOR**eal forest fires on **T**ropospheric oxidants over the **A**tlantic using **A**ircraft and **S**atellites (BORTAS). The observational programme was conducted from Halifax International Airport (063°30′ W/44°52′ N) between 12 July 2010 and 2 August 2010. This comprised a series of 15 different sorties, each comprising either one or two flights in a day and of duration 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. See Palmer et al. (2013) for further details of this campaign. 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 Facility for Airborne Atmospheric Measurement (FAAM) catalogue numbers from B618 to B632 and all data in this paper are publically 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 into 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 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 $16\,°C\,s^{-1}$ and transferred to the GC columns in a stream of helium. The eluent was split in a fixed ratio between an aluminium oxide (Al_2O_3, $NaSO_4$ deactivated) porous layer open tubular (PLOT) column (50 m, 0.53 μm id) for analysis of NMHCs and two LOWOX columns (10 m, 0.53 μm id) in series for analysis of polar OVOCs. This split was determined experimentally from the relative sizes of benzene peaks on both columns and in this experiment was in a ratio 54:46. 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. The detection limit for ethene was 2 ppt with a precision of 1 % and accuracy of 5 % for mixing ratios greater than 100 ppt. The detection limit for propene, benzene and toluene were 1 ppt with a precision of 1 % and accuracy of 5 % for mixing ratios greater than 100 ppt.
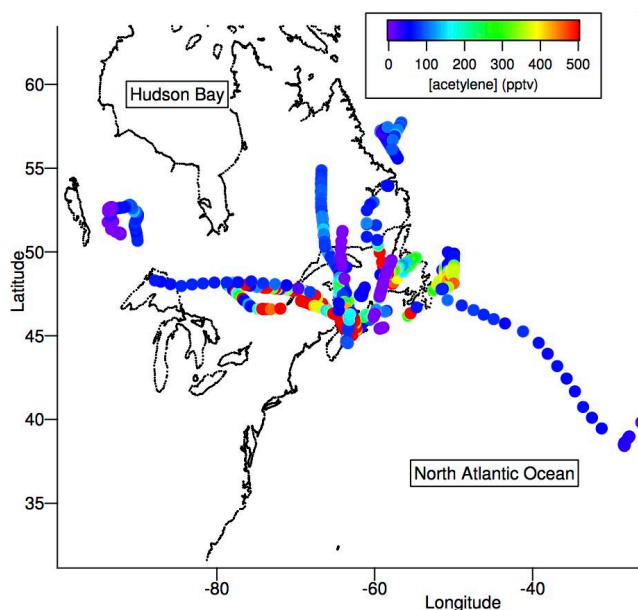
Fig. 1. FAAM146 flight tracks during August 2012, overlaid with sample locations for whole air samples. The points are coloured by acetylene mixing ratio.

3 Summary of non methane hydrocarbon concentrations and emissions

To determine the relative emissions of NMHCs from biomass burning in comparison to other sources it is necessary to identify case studies where the overwhelming contributor to NMHC abundance is from a burning event. This approach is needed so that any calculated emission ratio based on the behaviour of NMHC against CO is not influenced by, for example, non-combustion emissions of the NMHC. We do not attempt to derive emission strength for any other source, other than biomass burning. In our later modelling activities we draw on published emission values for non-biomass burning sources. There are two major means of achieving a filtering for biomass burning data. The first is to make a case-by-case examination of data and assign data as being either "in" 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 the attributes of a biomass burning plume. In this paper we use the latter approach since on many occasions plume edges 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 > 200 ppb, no biomass

burning tracers by GC-MS. 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 emission 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 chemical loss from the plume 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 plume encounters directly over fires to several days downwind. The assessment of general plume ages has been made based on forecast trajectories used for flight planning purposes. We have not attempted to place precise ages on plumes, although a range of techniques, based on transport and chemical clocks have been reported previously. In this study plume age does not appear to change substantially the slope obtained of any given NMHC against CO. When flights are taken individually the slopes obtained are all very similar to the slope obtained when all the biomass burning plume data is used in concert. 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 mixing ratio indicative of the background environment of organic compounds and CO 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:

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

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 high degree of agreement between this study and the recent work of Simpson et al. (2011) that was undertaken in a similar geographical region and also using an aircraft platform. The values obtained for benzene, toluene,

Table 1. Measurement statistics from the observations made during the BORTAS campaign. Any 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^{-1})	ER to CO (pptv ppbv^{-1}) Simpson et al.
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
methacrolein	3	2	160	754	0.8 ± 1.1	0.15 ± 0.01
methanol	40	1556	4423	10 335	8.9 ± 3.2	9.6 ± 1.9
acetone	9	1476	2550	4584	3.5 ± 0.8	1.6 ± 0.4

ethene and propene all fall within the reported ranges in the review article of Andreae and Merlet, 2001. Some additional NMHCs are reported here which were not reported in the Simpson et al. (2011), 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 half that reported in Simpson et al., and one third that reported in Akagi et al. (2011) for boreal fires. Methacrolein in this study had an ER around five

times higher than Simpson et al. 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, heat induced distillation of biogenic volatile organic compounds (BVOCs), or from emissions from peat combustion (Christian et al., 2003).

We summarize graphically for a range of alkane species in Fig. 2a showing background data, biomass plume data and distinct plumes of anthropogenic emissions. Each alkane is slightly different in terms of behaviour, but in general terms the majority of data points sit on a common slope, with a smaller number of outliers showing high alkane without enhancement in CO. These outliers may be assigned as being from a non-combustion source. The use of a CO threshold value and a secondary mass spectrometric marker means these non-combustion data points do not influence the calculated biomass burning slopes. 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 relatively clear, and in all cases are correlated to CO (but with different slopes), since the primary alkene source is also combustion. Somewhat surprisingly even for very short-lived NHMCs, in biomass burning plumes sampled some days downwind, the mixing ratios remained high and are in contrast to the anthropogenic plumes, where CO is significantly elevated, but the reactive alkenes are largely 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. A very small number of elevated benzene data points are observed without elevation in CO suggesting a localised non-combustion source in the region.

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 CO_2 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 CO_2 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., as the ER.

4 Model analysis and global impacts

The airborne observations made over Canada show strong correlations between the abundance 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 http://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
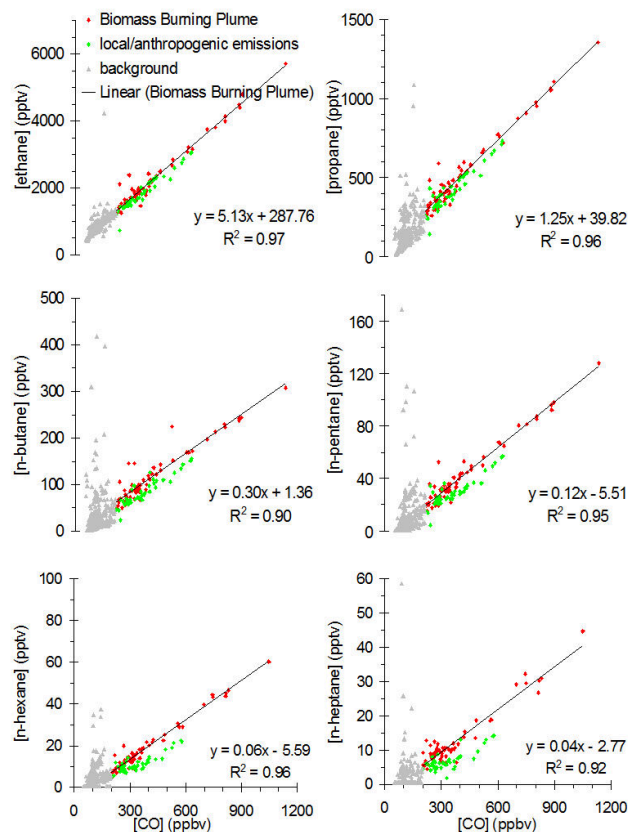

Fig. 2a. Selected plots of alkanes vs. CO. Grey triangle assigned as background air, red diamonds assigned as biomass plumes and green diamonds assigned as anthropogenic plumes.

particular for study since they are often (if erroneously) considered in atmospheric chemistry as anthropogenic tracers, rather than from natural emissions. The substantial emissions from biomass burning are potentially of growing significance in those locations (particularly in developed countries) where such species are on downwards emission trajectories, a result of control technologies, reformulation of gasoline composition and reduced solvent usage. In those locations with rapidly growing vehicle fleets, such as in developing countries, it remains an open question as to whether benzene is on an increasing or decreasing trajectory.

We adapt the model NMHC tracers in a flexible way to simulate both tagged anthropogenic (the sum of combustion and non-combustion sources) and biomass burning sources. For simplicity we ignore any other biogenic sources (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-dependant oxidant fields of OH, O_3,
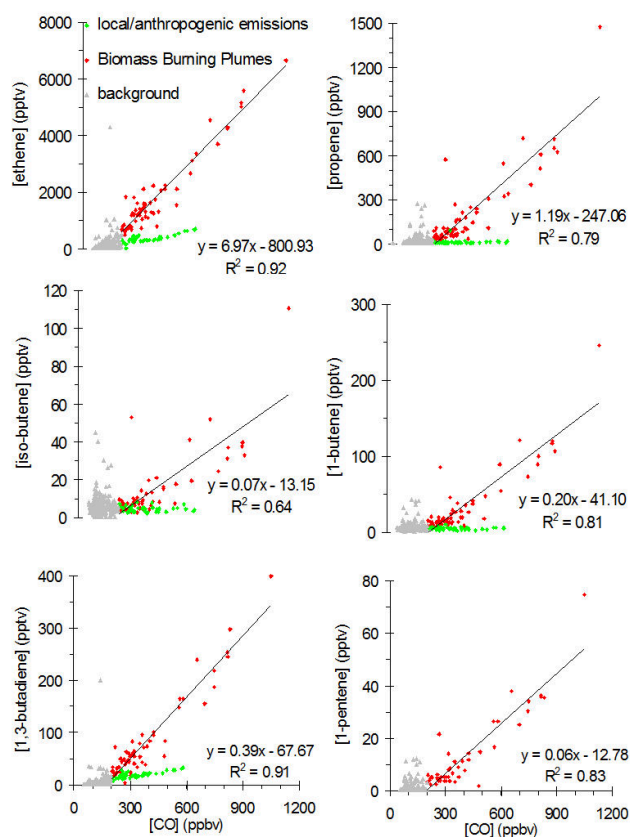
Fig. 2b. Selected plots of alkenes vs. CO. Grey triangle assigned as background air, red diamonds assigned as biomass plumes and green diamonds assigned as anthropogenic plumes.

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

and NO_3. 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 the experiments.

The purpose of this modelling is to apply the emission ratios 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. We have taken a simple approach in using a single ER for certain hydrocarbon species for the biomass burning source since that captures much of the global behaviour of the hydrocarbon relative to CO. Ideally however a more detailed biomass burning inventory that encapsulated the many different sources and fuels types would be used, but this would require far greater model sophistication in terms of input emissions and would require a source specific disaggregation of CO. Given the good to excellent agreement in ER between this study and Simpson et al., 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
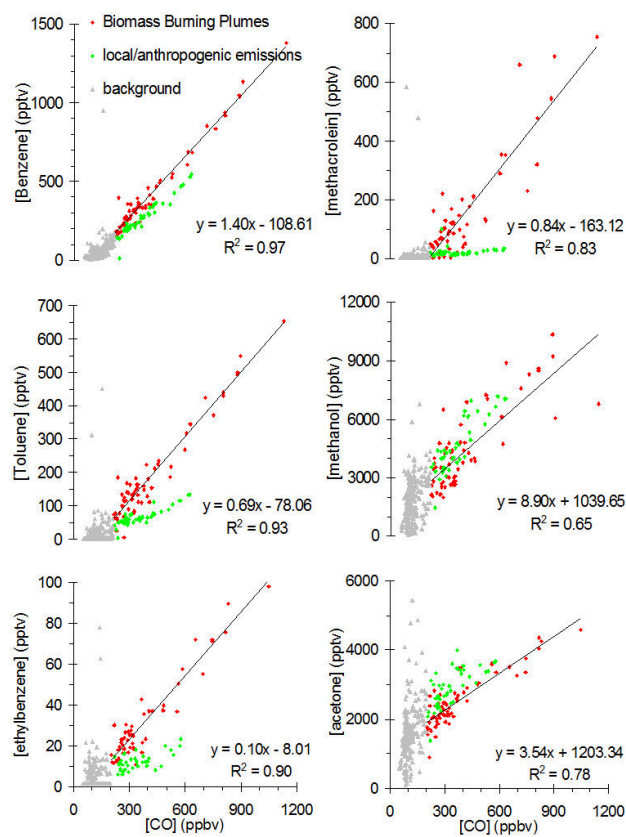
biomass burning. We run the model for the year 2009 twice with the first year being considered as model spin-up. We choose this year as GFED3 (Global Fire Emission Database) (van der Werf et al., 2010) emissions of CO are available at time of writing. Other fire emissions inventories exist, for example the NCAR model of Wiedinmyer et al. (2011), and it must be acknowledged that differences between inventories naturally add to the uncertainty in any CO derived estimate of hydrocarbon distribution. A comparison of global inventories by Stroppiana et al. (2010) would suggest that our biomass burning emission value of $350 \, Tg \, yr^{-1}$ is consistent with the NCAR (FINN) model but towards the lower end of the range given in this analysis, suggesting our hydrocarbons from biomass burning are conservatively estimated.

Table 2 describes the emission rates of these target compounds released in the model. The RETRO emissions ("Reanalysis of the tropospheric chemical composition of the last 40 years" project) (Schultz et al., 2007) for 2000 are used for the anthropogenic sources, made up of ten sectors including various combustion sources, industrial emissions, waste treatment, agriculture and solvent emissions. Whilst more up-to-date anthropogenic inventories exist at national levels,

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

Compound	Emission Type	Emission source	Emission (Tg yr^{-1})	Lifetime (days^{-1})
benzene	Biomass	$CO_{bb} \cdot 0.0014$	1.77	7.42
	Anthropogenic	RETRO 2000	3.48	10.95
toluene	Biomass	$CO_{bb} \cdot 0.00069$	1.11	1.55
	Anthropogenic	RETRO 2000	6.13	2.73
ethene	Biomass	$CO_{bb} \cdot 0.0069$	0.85	1.15
	Anthropogenic	RETRO 2000	6.47	1.19
propene	Biomass	$CO_{bb} \cdot 0.0019$	2.04	0.28
	Anthropogenic	RETRO 2000	2.74	0.30
CO	Biomass	CO_{bb}	272	

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 sources are scaled to the GFED3 CO emissions used in the model. The biomass burning emissions of the hydrocarbons uses the GFED3 CO emissions scaled by the ratios derived in earlier sections for the BORTAS data. We use a single value for the emission ratio of hydrocarbons from biomass burning and apply this to both boreal and tropical forest fires. Literature reviews of emissions indicate that whilst some species are very dependant on location and type of fuel, many hydrocarbon emissions (and indeed CO on a per dry mass burnt basis) are similar across extratropical and tropical forests. Using the summary values from Andreae and Merlet (2001) the ER of benzene in tropical forests is estimated at around 1.65 ± 0.10 ppt per ppb CO, as compared to our boreal value of 1.40 ± 0.11. A similarly close agreement is found for ethene, propene and toluene – for example our boreal estimate for toluene is 0.69 ± 0.09 ppt per ppb CO, vs. the tropical literature range of 0.73 ± 0.8. We consider therefore that the use of a single ER for all biomass burning emissions is sufficient to represent both regions in the model and that compared to uncertainty in the overall size of CO biomass burning emissions and anthropogenic benzene, this is likely to be a minor factor.

Recent work suggests that smouldering fires can consume a substantial amount of organic material but may be poorly represented in emissions estimates (see for example Bertschi et al., 2003; Hyde et al., 2011; Turetsky et al., 2011). It is clear that if our hydrocarbon ER was derived solely from near to source or fresh fire emissions then we would not capture this source in our data. However the scale of the aircraft observations, covering 28 000 km of sample tracks and from 500 ft to 30 000 ft would suggest that all type of burning emissions are represented in our data. We do not observe any substantial deviation in hydrocarbon to CO slopes for biomass influenced air suggesting that the smouldering emis-

sion is captured in our ratio. There is a wider issue of whether smouldering CO is then captured appropriately by GFED3 but that is beyond this paper. The implication is that our estimates of influence may be under-estimates if the smoldering source is not captured and is significant.

Our overall total estimates of global benzene and toluene emissions are comparable to previous studies (e.g. Henze et al., 2008). However our estimates for the biomass burning source specifically, are somewhat lower than in Henze et al. (2008); this arises due to different values for the emission ratio. For comparison, Henze et al., used $3.4 \, \text{Tg}(C_6H_6) \, \text{yr}^{-1}$ for the anthropogenic emission and $2.7 \, \text{Tg}(C_6H_6) \, \text{yr}^{-1}$ for the biomass burning, whereas we have used $3.5 \, \text{Tg}(C_6H_6) \, \text{yr}^{-1}$ for this for anthropogenic emission and $1.8 \, \text{Tg}(C_6H_6) \, \text{yr}^{-1}$ for the biomass burning source.

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 1.12×10^6 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 (GAW) programme. The number of measurement stations for which this type of continuous data exists is very small – perhaps only 3–5 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. We have used benzene measurements that have been filtered to remove any local
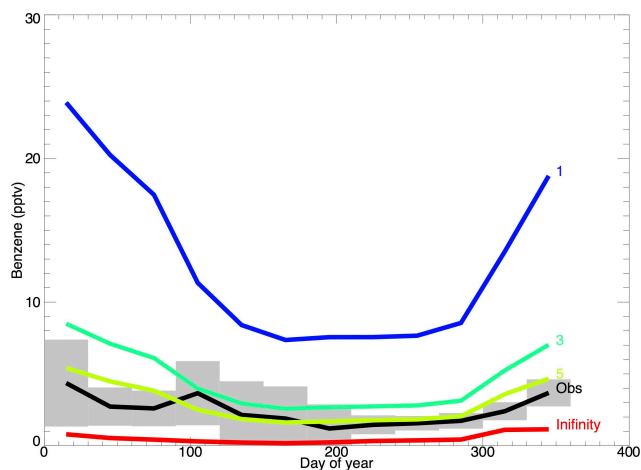
Fig. 3. Comparison of GEOS-Chem model estimate for benzene and observations made at the Cape Verde GAW observatory. Bars indicate ranges of monthly data and the black line the observed average. The blue line indicates the model estimate using biomass burning and RETRO emissions inputs. The two green 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.

contamination or sources, such that the dataset represents a good measure of tropical North Atlantic open ocean variability. The grey bars represent the standard deviation variability. 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 justification for allowing a significant reduction in anthropogenic benzene over the past decade, with many developed countries having very substantially reduced emissions following reformulation of gasoline content, the introduction of catalytic converters and the elimination of benzene as a solvent. Although sector specific data is limited for benzene sources, if one considers emissions from the UK to be a reasonable proxy for Europe and other developed regions then solvent and production processes emission of benzene had by 2009 fallen to around one-third the levels of 1990. Road transport emissions are estimated to have fallen to appropriately one-quarter the 1990 value by 2009. This is not of course to say that atmospheric concentrations have shown that same level of reduction, but studies have shown a sustained reduction of around 20 % a year during periods of emission control tightening (Dollard et al., 2007). We would stress here that we are not suggesting our model proves that RETRO should be adjusted by a multiplier of 0.33, but rather that this is the level of change that is required to make an observation match with our model.

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 and order of magnitude concentrations. 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 two-thirds 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 GFED3 CO emissions and the standard RETRO database for the year 2000 for the anthropogenic emissions. There are rather few long-term observations of benzene with which to compare to our model, and most in the literature refer to urban locations, many of which are roadside. It is not therefore appropriate to try to compare the outputs of a global scale model such as GEOS-Chem with such urban observations since these can be dominated by influences below the grid scale of the model. In very general terms however the comparison in benzene is reasonable with, for example, Baker et al. (2008) and Dollard et al. (2007). In these papers urban benzene from observation networks is reported for US and UK cities, typically at values in the range 150–450 ppt, in order of magnitude agreement with that predicted from our model.

Figure 4 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 in our model year reach into the ppb range. This study only attempts to model a single year of biomass burning emissions, and it should be appreciated that significant inter-annual variability in both intensity and location of burning exists (e.g. Simpson et al., 2006) and this of course changes the extent to which locations may be impacted by this source. Future work may want to examine how variability in burning impacts on the global hydrocarbon distribution and this is of course something that may ultimately be inferred via a network of background GAW observations. The biomass burning impacts on hydrocarbons are therefore perhaps most important to consider when attempting to evaluate trends, transport processes and longer-term behaviour in background locations. Conversely background observations of such hydrocarbons in background locations may provide a new constraint on the size and distribution of global emissions. Values indicated by the model over Africa (in the hundreds of ppt and greater occasion), fall within the range of concentrations seen
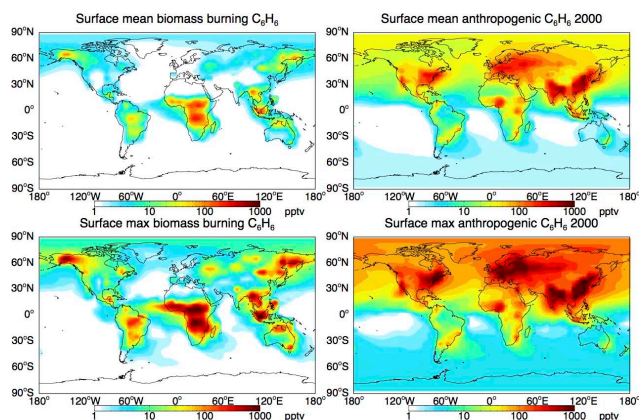
Fig. 4. Top row: model estimate of the annual surface mean mixing ratio of benzene resulting from biomass burning emissions (left) and from anthropogenic emissions (right) using the standard RETRO 2000 scenario. Second row of plots shows the monthly maximum surface mixing ratio from these two sources.

for example by Sinha et al. (2003) in biomass burning from Southern Africa.

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 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 tropical biomass burning provides a large source and fossil fuel burning (anthropogenic) is lower. Here, our model indicates that biomass burning constitutes the largest 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 very low, approaching the typical GC detection limits of around 1 ppt.

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 burn-
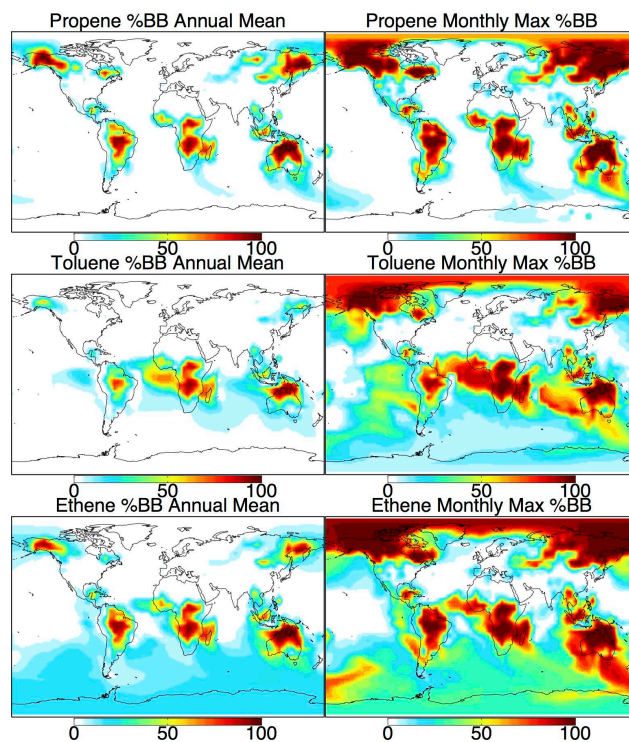

Fig. 5. Fractional contribution to the total propene (top) toluene (middle) and ethene (bottom) from biomass burning. Left hand plots show annual mean contributions and right hand plots the monthly maximum fraction from biomass burning.
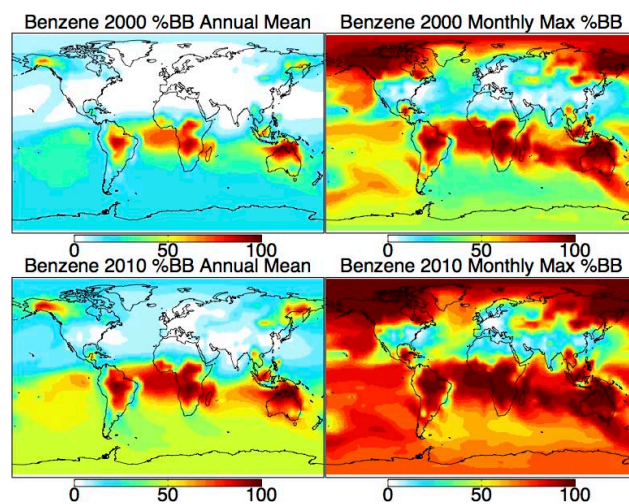

Fig. 6. Fractional contribution to benzene from biomass burning as an annual mean (left top) and as the monthly maximum (top right). Left bottom plot show how this fractional contribution is enhanced if a reduced $0.33 \cdot$ RETRO anthropogenic emissions for benzene is implemented in line with the fit to Fig. 3 based on Cape Verde observations for the year 2010.

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	75.5833	−26.5667
South Pole (Antarctica)	SPO	−89.99695	−24.8

ing sources. One might expect this fraction to grow in significance as vehicle emission controls further act to reduce anthropogenic emissions. Whilst health exposure limits for benzene vary widely internationally – from no limits in certain US states to $5\,\mu g\,m^{-3}$ in Europe, where controlled, they move generally only in a downwards direction; e.g. in Europe from $10\,\mu g\,m^{-3}$ in the 2000 Second Daughter Directive 2000/69/EC to $5\,\mu g\,m^{-3}$ in the 2008 Directive 2008/50/EC. 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 surprising 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 numerical issues in the model. Ar-

eas where the concentrations approach the numerical resolution of the model (< 0.01 ppt) are indicated in white.

As identified earlier it appears that the RETRO database may overestimate the present day amount of anthropogenic benzene (and to a lesser extent other NMHCs) released, when comparison is made with a very remote background GAW observatory. The resolution of our model is not appropriate to allow it to be sensibly compared to urban observations. Literature reports suggest that ambient urban concentrations have fallen significantly over the past 15 yr, in some locations at rates of 20 % pa. Our comparison earlier of remote background benzene data with the model suggested that a two-thirds reduction in RETRO 2000 emissions would bring model and measurement into reasonable agreement on a global scale. This study is severely limited by the lack of appropriate background observations and it is very uncertain whether this is globally an appropriate figure to apply. The work reported here does however provide an indication of the general impacts of a reduction of this scale, as is shown in Fig. 6. By reducing the anthropogenic emissions of benzene such that they agree better with real observations from

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 × 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 · 0.33)	Monthly Maximum	Monthly Maximum (RETRO · 0.33)
0.0–0.2	TAM CVO KEN IZA WAL MIN DAN NEP MLO ARE TRI PAL ZUG MAC MON JUN HLF	IZA WAL NEP PAL ZUG MAC MON JUN HLF	NEP ZUG MON JUN	ZUG MON JUN
0.2–0.4	AMS CPP CPG LAU SAM USH ALE BAR ZEP NEU SPO HAL	TAM CVO KEN MIN DAN MLO ARE ALE TRI ZEP	IZA	NEP
0.4–0.6	BUK	CPP CPG LAU USH BAR	TAM CVO WAL ARE	
0.6–0.8		AMS BUK SAM NEU SPO HAL	KEN CPP MIN DAN SAM TRI PAL MAC NEU SPO HAL HLF	TAM IZA WAL ARE
0.8–1			AMS CPG BUK LAU MLO USH ALE BAR ZEP	CVO AMS KEN CPP CPG BUK MIN DAN LAU MLO SAM USH ALE BAR TRI PAL MAC ZEP NEU SPO HAL HLF

2010 at Cape Verde, the relative 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 benzene, toluene, ethene and propene can be significantly influenced by emissions from biomass burning, and that continued reductions in anthropogenic hydrocarbons will enhance this impact. The effects are largely realised in the background environment and away from localised urban anthropogenic sources.

8 Impacts on background measurement stations

Whilst sporadic research grade measurements of hydrocarbons have been made throughout the background troposphere, and some long-term records do exist, most routine and long-term observations continue to be focused on urban centres, reflecting air quality drivers. 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 dioxide (SO_2). 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. For this we continue to use the standard RETRO emissions. 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. Should we apply our calculated two-thirds reduction in anthropogenic emissions then naturally these plots are shifted substantially to show increasing biomass burning influence and this is reflected in our later Table 4. At present none of these sites has online measurements year round. Those sites in reasonable

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

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.

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. Remote GAW sites (e.g. Samoa, Halley) show very low absolute concentrations but show a significant fraction of that coming from biomass burning. Taking Barrow as a test case, the implied CO concentrations during the burning maximum would be of the order 600–800 ppb. Publically available data on the NOAA ESRL website indicates peak CO values in 2009, derived from flask samples, as 678 ppb, in good agreement with the model.

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 burning and the maximum monthly fraction of benzene that is from biomass burning. 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 current anthropogenic emissions are likely lower than expressed in RETRO and so we include separate rows that show how the stations would partition if a two-thirds anthropogenic 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. Uncertainty here is dominated by the emissions term (factor of 2), rather than by meteorology or chemistry (OH term uncertain to around 20 %). Given the uncertainty in the actual change
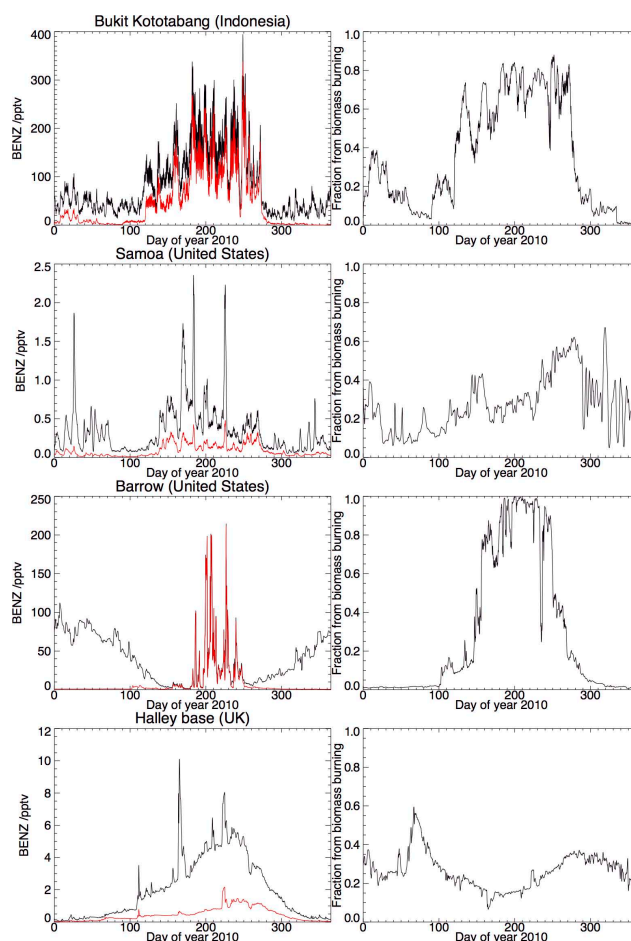
in benzene emissions to include in the model, reality is likely to lie somewhere between these two scenarios in Table 4.

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 emission estimates for certain hydrocarbon species and provides confirmatory measurements of some species previously published. There is generally very good agreement between emissions derived from different aircraft studies by different groups in the same region and this provides some confidence in making extrapolations from these estimates in models. A comparison of the ERs obtained here with earlier studies from other geographic regions indicates that many hydrocarbon ERs do not vary substantially between tropical and extra-tropical

burning, although some sources such as smouldering may not be fully represented. 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 often controlled in an air quality context and are species with generally declining urban concentrations in developed economies. The tagged model showed that in most of the Southern Hemisphere a significant fraction of observed benzene at any given location can be from biomass burning, and that biomass burning as a major contributor to the global hydrocarbon abundance extends at times to the Northern Hemisphere also. The largest sources of uncertainty in the model arise from the emission estimates rather than chemistry or meteorology, however even varying the emissions by a factor of three (moving from the 2000 RETRO base emissions to a value reduced by two-thirds in line with observations) does not change this general conclusion. It is only over heavily industrialized regions that these hydrocarbon distributions are dominated by the anthropogenic source. The lack of appropriate background monitoring sites to compare our modelling to is a major limitation. The expansion of the GAW network should help in this regard. The behaviour of benzene is particularly interesting here since it is a heavily regulated pollutant that is often considered in terms of toxicology as having no safe lower limit (Duarte-Davidson et al., 2001). 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.

Very limited experimental data exist for the long-term trends in hydrocarbons in the background atmosphere, however comparison of the model against benzene in the tropical Atlantic shows that the annual cycle can be reasonably captured, although suggesting that the model emissions database is overestimating anthropogenic emissions. When the model is used to estimate the contribution of biomass burning to the hydrocarbons experienced at GAW Global stations the picture is mixed. At some locations such as Barrow and Alert high absolute and fractional biomass contributions are suggested from model simulations, up to several hundred ppt of benzene for example, whilst in some tropical and polar regions the absolute amounts are predicted to be low, (single figure ppt mixing ratios) but with a significant fraction (20–60 %) 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.

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039–4072, doi:10.5194/acp-11-4039-2011, 2011.

Amiro, B. D., Cantin, A., Flannigan, M. D., and de Groot, W. J.: Future emissions from Canadian boreal forest fires, Can. J. For. Res., 39, 383–395, 2009.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955–966, doi:10.1029/2000GB001382, 2001.

AQEG: Air quality and climate change: a UK perspective. Report of the UK Air Quality Expert Group, AQEG. Prepared for the Department for Environment Food and Rural Affairs, the Scottish Executive, the Welsh Assembly and the Department of the Environment in Northern Ireland, Defra publications, London, April 2007. ISBN 0-85521-172-5, 2007.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monogr., 2, 216–234, 1994.

Badol, C., Locoge, N., and Galloo, J.-C.: Using a source-receptor approach to characterise VOC behaviour in a French urban area influenced by industrial emissions. Part II: Source contribution assessment using the Chemical Mass Balance (CMB) model, Sci. Total Environ., 389, 429–440, 2008.

Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Measurement of nonmethane hydrocarbons in 28 United States cities, Atmos. Environ., 42, 170–182, 2008.

Bertschi, I. T., Yokelson, R. J., Ward, D. E., Babbitt, R. E., Susott, R. A., Goode, J. G., and Hao, W. M.: Trace gas and particle emissions from fires in large diameter and belowground biomass fuels, J. Geophys. Res., 108, 8472, doi:10.1029/2002JD002100, 2003.

Bey, I., Jacob, D. J., Yantosca, R. M, Logan, J. A., Field, B. D., Flore, A. M., Li, Q. B., Liu, H. G. Y., Mickley, L. J., and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106, 23073–23095, 2001.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Saharjo, B. H., and Ward, D. E.: Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, J. Geophys Res., 108, doi:10.1029/2003JD003704, 2003.

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R.: Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC- MS/FID/ECD, J. Geophys Res., 109, D02311, doi:10.1029/2003JD003874, 2004.

Crutzen P. J. and Andreae, M. O.: Biomass burning in the tropics – impact on atmospheric chemistry and biogeochemical cycles, Science, 4988, 1669–1678, 1990.

Crutzen, P. J., Heidt, L. E., Kransec, J. P., Pollock, W. H., and Seiler, W.: Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl and COS, Nature, 282, 253–256, 1979.

de Gouw, J. A., Warneke, C., Stohl, A., Wollny, A. G., Brock, C. A., Cooper, O. R., Holloway, J. S., Trainer, M., Fehsenfeld, F. C., Atlas, E. L., Donnelly, S. G., Stroud, V., and Lueb, A.: Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, J. Geophys Res., 111, D10303, doi:10.1029/2005JD006175, 2006.

Dollard, G. J, Dumitrean, P., Telling, S., Dixon, J., and Derwent, R. G.: Observed trends in ambient concentrations of C2-C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, Atmos. Environ., 41, 2559–2569, 2007.

Duarte-Davidson, R., Courage, C., Rushton, L., and Levy, L.: Benzene in the environment: an assessment of the potential risks to the health of the population, Occupational and Environmental Medicine, 58, 2–13, 2001.

Duck, T. J., Firanski, B. J., Millet, D. B., Goldstein, A. H., Allan, J., Holzinger, R., Worsnop, D. R., White, A. B., Stohl, A., Dickinson, C. S., and van Donkelaar, A.: Transport of forest fire emissions from Alaska and the Yukon Territory to Nova Scotia during summer 2004, J. Geophys. Res., 112, D10S44, doi:10.1029/2006JD007716, 2007.

Fehsenfeld, F. C., Ancellet, G., Bates, T., Goldstein, A., Hardesty, M., Honrath, R., Law, K., Lewis, A. C., Leaitch, R., McKeen, S., Meagher, J., Parrish, D. D., Pszenny, A. A. P., Russell, P. B., Schlager, H., Seinfeld, J., Trainer, M., and Talbot, R.: International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America To Europe: Overview Of The 2004 Summer Field Study, J. Geophys. Res., 111, D23S01, doi:10.1029/2006JD007829, 2006.

Flannigan, M. D., Logan, K. A., Amiro, B. D., Skinner, W. R., and Stocks, B. J.: Future area burned in Canada, Clim. Change, 72, 1–16, 2005.

Fromm, M., Alfred, J., Hoppel, K., Hornstein, J., Bevilacqua, R., Shettle, E., Servranckx, R., Li , Z. Q., and Stocks, B.: Observations of boreal forest fire smoke in the stratosphere by POAM III, SAGE II, and lidar in 1998, J. Geophys Res., 27, 1407–1410, doi:10.1029/1999GL011200, 2000.

Girardin, M. P.: Interannual to decadal changes in area burned in Canada from 1781 to 1982 and the relationship to Northern Hemisphere land temperatures, Global Ecol. Biogeogr., 16, 557–566, 2007.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and im-

pact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Helmig, D., Bottenheim, J., Galbally, I. E., Lewis, A. C., Milton, M. J. T., Penkett, S. A., Plass-Duelmer, C., Reimann, S., Tans, P., and Thiel, S.: Volatile Organic Compounds In The Global Atmosphere, EOS Transactions, 90, 513–514, 2009.

Henze, D. K., Seinfeld, J. H., Ng, N. L., Kroll, J. H., Fu, T.-M., Jacob, D. J., and Heald, C. L.: Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high-vs. low-yield pathways, Atmos. Chem. Phys., 8, 2405–2420, doi:10.5194/acp-8-2405-2008, 2008.

Holzinger, R., Williams, J., Salisbury, G., Klüpfel, T., de Reus, M., Traub, M., Crutzen, P. J., and Lelieveld, J.: Oxygenated compounds in aged biomass burning plumes over the Eastern Mediterranean: evidence for strong secondary production of methanol and acetone, Atmos. Chem. Phys., 5, 39–46, doi:10.5194/acp-5-39-2005, 2005.

Houweling, S., Dentener, F. and Lelieveld, J.: The impact of non-methane hydrocarbons on tropospheric photochemistry, J. Geophys. Res., 103, 10673–10696, 1998.

Hyde, J. C., Smith, A. M. S., Ottmar, R. D., Alvarado, E. C., and Morgan, P.: The combustion of sound and rotten coarse woody debris, Int. J. Wildfire, 20, 163–174, 2011.

Jaffe, D. A. and Wigder, N. L.: Ozone production from wildfires: A critical review, Atmos. Environ., 51, 1–10, doi:10.1016/j.atmosenv.2011.11.063, 2012.

Jost, C., Trentmann, J., Sprung, D., Andreae, M. O., McQuaid, J. B., and Barjat, H.: Trace gas chemistry in a young biomass burning plume over Namibia: Observations and model simulations, J. Geophys. Res., 108, 8482, doi:10.1029/2002JD002431, 2003.

Jost, H. J., Drdla, K., Stohl, A., Pfister, L., Loewenstein, M., Lopez, J. P., Hudson, P. K., Murphy, D. M., Cziczo, D. J., Fromm, M., Bui, T. P., Dean-Day, J., Gerbig, C., Mahoney, M. J., Richard, E. C., Spichtinger, N., Pittman, J. V., Weinstock, E. M., Wilson, J. C., and Xueref, I.: In-situ observations of mid-latitude forest fire plumes deep in the stratosphere, Geophys. Res. Lett., 31, L11101, doi:10.1029/2003GL019253, 2004.

Kasischke, E. S. and Stocks, B. J.: Fire, climate change and carbon cycling in the boreal forest. Springer-Verlag, New York, New York, USA, 2000.

Kasischke, E. S. and Turetsky, M. R.: Recent changes in the fire regime across the North American boreal region – Spatial and temporal patterns of burning across Canada and Alaska, Geophys. Res. Lett., 33, L09703, doi:10.1029/2006GL025677, 2006.

Kasischke, E. S., Hyer, E. J., Novelli, P. C., Bruhwiler, L. P., French, N. H. F., Sukhinin, A. I., Hewson, J. H., and Stocks, B. J.: Influences of boreal fire emissions on Northern Hemisphere atmospheric carbon and carbon monoxide, Global Biogeochem. Cy., 19, GB1012, doi:10.1029/2004GB002300, 2005.

Koppman, R.: Volatile Organic Compounds in the Atmosphere, Blackwell Publishing, Oxford, UK, 2007.

Krol, M., van Leeuwen, P. J., and Lelieveld, J.: Global OH trend inferred from methylchloroform measurements, J. Geophys. Res.,103, 10697–10711, doi:10.1029/98JD00459, 1998.

Lewis, A. C., Evans, M. J., Methven, J., Watson, N., Lee, J. D., Hopkins, J. R., Purvis, R. M., Arnold, S. R., McQuaid, J. B., Whalley, L. K., Pilling, M. J., Heard, D. E., Monks, P. S., Parker, A. E., Reeves, C. E., Oram, D. E., Mills, G., Bandy, B. J., Stewart,

D., Coe, H., Williams, P., and Crosier, J.: Chemical composition observed over the mid-Atlantic and the detection of pollution signatures far from source regions, J. Geophys. Res., 112, D10S39, doi:10.1029/2006JD007584, 2007.

Marlon, J. R., Bartlein, P. J., Carcaillet, C., Gavin, D. G., Harrison, S. P., Higuera, P. E., Joos, F., Power, M. J., and Prentice, I. C.: Climate and human influences on global biomass burning over the past two millennia, Nature Geosci., 1, 69–702, 2008.

Morino, Y., Ohara, T., Yokouchi, Y., and Ooki, A.: Comprehensive source apportionment of volatile organic compounds using observational data, two receptor models, and an emission inventory in Tokyo metropolitan area, J. Geophys. Res.-Atmos., 116, D02311, doi:10.1029/2010JD014762, 2011.

Palmer, P. I., Parrington, M., Lee, J. D., Lewis, A. C., Rickard, A. R., Bernath, P. F., Duck, T. J., Waugh, D. L., Tarasick, D. W., Andrews, S., Aruffo, E., Bailey, L. J., Barrett, E., Bauguitte, S. J. B., Curry, K. R., Di Carlo, P., Chisholm, L., Dan, L., Drummond, J. R., Forster, G., Franklin, J. E., Gibson, M. D., Griffin, D., Helmig, D., Hopkins, J. R., Hopper, J. T., Jenkin, M. E., Kindred, D., Kliever, J., Le Breton, M., Matthiesen, S., Maurice, M., Moller, S., Moore, D. P., Oram, D. E., O'Shea, S. J., Owen, R. C., Pagniello, C. M. L. S., Pawson, S., Percival, C. J., Pierce, J. R., Punjabi, S., Purvis, R. M., Remedios, J. J., Rotermund, K. M., Sakamoto, K. M., Strawbridge, K. B., Strong, K., Taylor, J., Trigwell, R., Tereszchuk, K. A., Walker, K. A., Weaver, D., Whaley, C., and Young, J. C.: Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) experiment: design, execution and science overview, Atmos. Chem. Phys. Discuss., in review, 2013.

Plass-Duelmer, C., Michi, K, Ruf, R., and Berresheim, H.: C_2-C_8 hydrocarbon measurement and quality control procedures at the Global Atmosphere Watch observatory Hohenpeissenberg, J. Chrom. A, 953, 175–197, 2002.

Pozzer, A., Pollmann, J., Taraborrelli, D., Jöckel, P., Helmig, D., Tans, P., Hueber, J., and Lelieveld, J.: Observed and simulated global distribution and budget of atmospheric C_2-C_5 alkanes, Atmos. Chem. Phys., 10, 4403–4422, doi:10.5194/acp-10-4403-2010, 2010.

Read, K. A., Lee, J. D., Lewis, A. C., Moller, S. J., Neves, L. M., and Carpenter, L. J.: Intra-annual cycles of NMVOC in the tropical marine boundary layer and their use for interpreting seasonal variability in CO, J. Geophys. Res., 114, D21303, doi:10.1029/2009JD011879, 2009.

Schultz, M., Rast, S., van het Bolscher, M., Pulles, T., Brand, R., Pereira, J., Mota, B., Spessa, A., Dalsøren, S., van Nojie, T., and Szopa, S.: Emission data sets and methodologies for estimating emissions, RETRO project report D1-6, Hamburg, available at: http://retro.enes.org/reports/D1-6_final.pdf, 2007.

Simpson, I. J., Rowland, F. S., Meinardi, S., and Blake, D. R.: Influenceof biomass burning during recent fluctuations in the slow growth of global tropospheric methane, Geophys. Res. Lett., 22, L22808, doi:10.1029/2006GL027330, 2006.

Simpson, I. J., Akagi, S. K., Barletta, B., Blake, N. J., Choi, Y., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., Rowland, F. S., Vay, S. A., Weinheimer, A. J., Wennberg, P. O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R. J., and Blake, D. R.: Boreal forest fire emissions in fresh Canadian smoke plumes: C_1-C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN, Atmos. Chem. Phys., 11, 6445–6463,

doi:10.5194/acp-11-6445-2011, 2011.

Simpson, I. J., Andersen, M. P. S., Meinardi, S., Bruhwiler, L., Blake, N. J., Rowland, F. S., and Blake, D. R.: Long-term decline of global atmospheric ethane concentrations and implications for methane, Nature, 488, 490–494, 2012.

Sinha, P., Hobbs, P. V., Yokelson, R. J., Bertschi, I. T., Blake, D. R., Simpson, I. J., Gao, S., Kirchstetter, T. W., and Novakov, T.: Emissions of trace gases and particles from savanna fires in southern Africa, J. Geophys. Res., 108, 8487, doi:10.1029/2002JD002325, 2003.

Soja, A. J., Tchebakova, N. M., French, N. H. F., Flannigan, M. D., Shugart, H. H., Stocks, B. J., Sukhinin, A. I., Parfenova, E. I., Chapin III, F. S., and Stackhouse Jr., P. W.: Climate-induced boreal forest change: Predictions versus current observations, Global Planet. Change, 56, 274–296, 2007.

Stroppiana, D., Brivio, P. A., Grégoire, J.-M., Liousse, C., Guillaume, B., Granier, C., Mieville, A., Chin, M., and Pétron, G.: Comparison of global inventories of CO emissions from biomass burning derived from remotely sensed data, Atmos. Chem. Phys., 10, 12173–12189, doi:10.5194/acp-10-12173-2010, 2010.

Turetsky, M. R., Kane, E. S., Harden, J. W., Ottmar, R. D., Manies, K. L., Hoy. E., and Kasischke, E. S.: Recent acceleration of biomass burning and carbon losses in Alaskan forests and peatlands. Nature Geosci., 4, 27–31, 2011.

Val Martin, M., Logan, J. A., Kahn, R. A., Leung, F.-Y., Nelson, D. L., and Diner, D. J.: Smoke injection heights from fires in North America: analysis of 5 years of satellite observations, Atmos. Chem. Phys., 10, 1491–1510, doi:10.5194/acp-10-1491-2010, 2010.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. Phys., 10, 11707–11735, doi:10.5194/acp-10-11707-2010, 2010.

von Schneidemesser, E., Monks, P. S., and Plass-Duelmer, C.: Global comparison of VOC and CO observations in urban areas, Atmos. Environ., 44, 5053–5064, 2010.

Warneke, C., Roberts, J. M., Veres, P., Gilman, J., Kuster, W. C., Burling, I., Yokelson, R., and de Gouw, J. A.: VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS, Int. J. Mass Spectrom., 303, 6–14, doi:10.1016/j.ijms.2010.12.002, 2011.

Wiedinmyer, C., Akagi, S. K., Yokelson, R. J., Emmons, L. K., Al-Saadi, J. A., Orlando, J. J., and Soja, A. J.: The Fire INventory from NCAR (FINN): a high resolution global model to estimate the emissions from open burning, Geosci. Model Dev., 4, 625–641, doi:10.5194/gmd-4-625-2011, 2011.

WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds (VOCs) (Geneva, Switzerland, 30 January–1 February 2006) (WMO Technical Document No. 1373), 2007.

Wotton, B. M., Nock, C. A., and Flannigan, M. D.: Forest fire occurrence and climate change in Canada, Int. J. Wildland Fire, 19, 253–271, 2010.

Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crounse, J. D., Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L., Adachi, K., Buseck, P. R., and Hao, W. M.: Emissions from forest fires near Mexico City, At-

mos. Chem. Phys., 7, 5569–5584, doi:10.5194/acp-7-5569-2007, 2007.

Yokelson, R. J., Christian, T. J., Karl, T. G., and Guenther, A.: The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data, Atmos. Chem. Phys., 8, 3509–3527, doi:10.5194/acp-8-3509-2008, 2008.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys., 9, 5785–5812, doi:10.5194/acp-9-5785-2009, 2009.

Yuan, B., Liu, Y., Shao, M., Lu, S., and Streets, D. G.: Biomass Burning Contributions to Ambient VOCs Species at a Receptor Site in the Pearl River Delta (PRD), China. Environ. Sci. Technol., 44, 4577–4582, doi:10.1021/es1003389, 2010.

Yurganov, L. N., Duchatelet, P., Dzhola, A. V., Edwards, D. P., Hase, F., Kramer, I., Mahieu, E., Mellqvist, J., Notholt, J., Novelli, P. C., Rockmann, A., Scheel, H. E., Schneider, M., Schulz, A., Strandberg, A., Sussmann, R., Tanimoto, H., Velazco, V., Drummond, J. R., and Gille, J. C.: Increased Northern Hemispheric carbon monoxide burden in the troposphere in 2002 and 2003 detected from the ground and from space, Atmos. Chem. Phys., 5, 563–573, doi:10.5194/acp-5-563-2005, 2005.