Atmos. Chem. Phys., 15, 1939–1958, 2015
www.atmos-chem-phys.net/15/1939/2015/
doi:10.5194/acp-15-1939-2015
© Author(s) 2015. CC Attribution 3.0 License.

Atmospheric Chemistry and Physics
Open Access

Increasing concentrations of dichloromethane, CH_2Cl_2, inferred from CARIBIC air samples collected 1998–2012

E. C. Leedham Elvidge[1], D. E. Oram[2,3], J. C. Laube[2], A. K. Baker[1], S. A. Montzka[4], S. Humphrey[2], D. A. O'Sullivan[2,*], and C. A. M. Brenninkmeijer[1]

[1]CARIBIC, Max Plank Institute for Chemistry, Hahn-Meitner Weg 1, 55128 Mainz, Germany
[2]Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, UK
[3]National Centre for Atmospheric Science, University of East Anglia, Norwich, NR4 7TJ, UK
[4]National Oceanic and Atmospheric Administration, Boulder, CO 80304, USA
[*]now at: Met Office, FitzRoy road, Exeter, EX1 3PB, UK

Correspondence to: E. C. Leedham Elvidge (emma.leedham@mpic.de)

Received: 18 June 2014 – Published in Atmos. Chem. Phys. Discuss.: 12 August 2014
Revised: 17 January 2015 – Accepted: 20 January 2015 – Published: 24 February 2015

Abstract. Atmospheric concentrations of dichloromethane, CH_2Cl_2, a regulated toxic air pollutant and minor contributor to stratospheric ozone depletion, were reported to have peaked around 1990 and to be declining in the early part of the 21st century. Recent observations suggest this trend has reversed and that CH_2Cl_2 is once again increasing in the atmosphere. Despite the importance of ongoing monitoring and reporting of atmospheric CH_2Cl_2, no time series has been discussed in detail since 2006. The CARIBIC project (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) has analysed the halocarbon content of whole-air samples collected at altitudes of between ∼ 10–12 km via a custom-built container installed on commercial passenger aircraft since 1998, providing a long-term record of CH_2Cl_2 observations. In this paper we present this unique CH_2Cl_2 time series, discussing key flight routes which have been used at various times over the past 15 years. Between 1998 and 2012 increases were seen in all northern hemispheric regions and at different altitudes, ranging from ∼ 7–10 ppt in background air to ∼ 13–15 ppt in regions with stronger emissions (equating to a 38–69 % increase). Of particular interest is the rising importance of India as a source of atmospheric CH_2Cl_2: based on CARIBIC data we provide regional emission estimates for the Indian subcontinent and show that regional emissions have increased from 3–14 Gg yr^{-1} (1998–2000) to 16–25 Gg yr^{-1} (2008). Potential causes of the increasing atmospheric burden of CH_2Cl_2 are discussed. One possible source is the increased use of CH_2Cl_2 as a feedstock for the production of HFC-32, a chemical used predominantly as a replacement for ozone-depleting substances in a variety of applications including air conditioners and refrigeration.

1 Introduction

Dichloromethane, CH_2Cl_2, is a short-lived chlorocarbon of mainly (up to 90 %, Montzka et al., 2011b) anthropogenic origin. Its main applications include use in paint strippers, degreasers and solvents; in foam production and blowing applications; as a chemical feedstock; and as an agricultural fumigant (Montzka et al., 2011b). The contribution from natural sources (mainly biomass burning and an oceanic source) is uncertain. Simmonds et al. (2006) obtained a good model fit to their observations using a 10 % combined oceanic and biomass burning source, although they showed that a stronger terrestrial source could support natural emissions of up to 30 %. However, recent field measurements of biomass burning plumes have indicated that this source is likely to be smaller than previously estimated (Simpson et al., 2011). With an atmospheric lifetime of around 5 months (Montzka et al., 2011b), CH_2Cl_2 displays significant atmospheric spatial variations and temporal trends. Its seasonal cycle is mainly due to reaction with the OH radical, with maxima

in late winter/early spring and corresponding minima in late summer or early autumn (Cox et al., 2003). There are no discernible seasonal variations in emissions or end uses (Gentner et al., 2010; McCulloch and Midgley, 1996). Significantly higher concentrations are observed in the Northern Hemisphere (NH, Southern Hemisphere = SH) due to the predominant industrial source. A NH : SH mole fraction ratio of 2.7 has been reported for the lower troposphere (Simmonds et al., 2006).

Short-lived chlorocarbons, including CH_2Cl_2, contribute to stratospheric chlorine and its cycling with stratospheric ozone. Their current contribution is minor – Laube et al. (2008) found that at 15.2 km (the level of zero radiative heating) 1.4 % of chlorine from organic compounds was from short-lived chlorocarbons, of which half was from CH_2Cl_2. This level is important because air parcels at or above this level point are likely to be transported to the stratosphere. However, current and projected decreases of longer-lived anthropogenic chlorocarbons (such as CH_3CCl_3, CCl_4, halons and CFCs) could mean a greater relative importance of shorter-lived chlorocarbons with respect to stratospheric chlorine, especially if their atmospheric abundances were to increase. Due to its predominantly anthropogenic source CH_2Cl_2 is susceptible to changes in industrial emissions. CH_2Cl_2 is also of concern as it is also a toxic air pollutant and possible carcinogen and, as such, is regulated by national and European Union Law, for example the Solvent Emissions Directive, 1999/13/EC (E.C.S.A., 2007).

The earliest reported NH atmospheric measurements of CH_2Cl_2 were made in the mid-1970s and observed concentrations of 35 ± 19 ppt (Cox et al., 1976). A range of global measurements in the 1980s and 1990s (many of which will be discussed further throughout this paper and are included in Table 2, see also Simmonds et al. (2006) for an in-depth discussion of many of the observations during this period) showed a consistent picture of peaking concentrations, with an average of $\sim$30–40 ppt around 1990, followed by a decline linked to decreasing industrial use of CH_2Cl_2 (McCulloch et al., 1999). Measurements made between 1989 and 1996 at Alert, Canadian Arctic, observed a decline of around -4 % (-1.8 ppt) per year (Gautrois et al., 2003). Long-term measurements (1995–2004) at Mace Head, Ireland demonstrated a decline in CH_2Cl_2 pollution events since measurements began in 1995, although this decline had stabilised in the later years of the data set (Simmonds et al., 2006). In the SH, Advanced Global Atmospheric Gases Experiment (AGAGE) atmospheric measurements began at Cape Grim in 1998 and reported mean CH_2Cl_2 concentrations for 1998–2000 of 8.9 ($\pm$0.2) ppt (Cox et al., 2003). These early measurements were supported by firn records which indicated that SH CH_2Cl_2 concentrations increased from 1–2 ppt at the beginning of the record (pre-1940) to 9 ppt around 1990 (Trudinger et al., 2004). Due to the lack of industrial emissions in the SH the rapid decline in atmospheric concentrations seen in the NH was not observed in the AGAGE Cape Grim time series (Simmonds et al., 2006).

In recent years increasing CH_2Cl_2 concentrations have been observed in both the NH and SH. Montzka et al. (2011b) reported an increase of around 8 % between 2007 and 2008, based on updated AGAGE data from Simmonds et al. (2006). There was no corresponding increase in $CHCl_3$, 70 % of which is believed to be of natural origin (Worton et al., 2006). The increase was also noted in Montzka et al. (2011a, see their Supplementary Information) whose time series of CH_2Cl_2 between 1995 to 2009 shows increasing atmospheric concentrations in recent years. CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) CH_2Cl_2 measurements up to the end of 2012 provide the opportunity to investigate this increase from a global time series perspective and may help improve our understanding of the recent changes in atmospheric CH_2Cl_2.

2 Methods

2.1 The CARIBIC platform and whole-air samples

CARIBIC centres on a large air-freight container accommodating a range of scientific equipment which is deployed monthly aboard a commercial passenger aircraft departing from Germany for up to four consecutive long-haul flights. Details of both CARIBIC phases can be found on our website, caribic-atmospheric.com. CARIBIC phase 1 (CARIBIC1) operated between 1997 and 2002 aboard a Boeing 767 departing for several global destinations from either Düsseldorf or Munich airport. Whole-air samples were collected using twelve 21 L stainless steel tanks pressurised to 17 bar. Details of CARIBIC1, including the range of other measurements made, can be found in Brenninkmeijer et al. (1999). Halocarbon data are available for 1998–2002.

Between 2003 and 2005 a new container was developed and this system was deployed aboard a Lufthansa Airbus 340–600 departing from Frankfurt Airport. CARIBIC phase 2 (CARIBIC2) began in 2005 and, at the time of writing, is still in operation. Samples are taken en route to destinations across the globe with flights occurring approximately monthly. Two whole-air samplers consisting of fourteen 2.7 L glass flasks collect 28 air samples for halocarbon, non-methane hydrocarbon (NMHCs) and greenhouse gas measurements at pre-determined intervals during the flight, mainly within cruising altitudes of around 10–12 km. Filling times are between 30–90 s, averaging 45 s or 10 km of the flight path. Further air sampler information can be found in Baker et al. (2010) and Schuck et al. (2009). The fully automated CARIBIC2 system contains a range of other sampling equipment, including, but not limited to, equipment for the in situ or post-flight analysis of ozone (O_3), carbon monoxide (CO), aerosols and water vapour. Further information can be found in Brenninkmeijer et al. (2007).

2.2 Halocarbon analysis

During both CARIBIC1 and CARIBIC2 air samples were sent to the University of East Anglia (UEA, UK) for halocarbon analysis via gas chromatography mass spectrometry (GCMS). During CARIBIC1 subsamples were removed from the main canisters into electropolished stainless steel cans and sent to UEA. For CARIBIC2 the whole-air sampling units were sent directly to UEA for analysis. During CARIBIC1 two separate GCMS systems were used. The first was an Agilent/HP 5890A GC coupled to a double-focusing, tri-sector mass spectrometer (VG/Micromass Autospec). Each 200 mL air sample was dried by passing through magnesium perchlorate (MPC) before being trapped in a previously evacuated stainless steel loop filled with 100 µm glass beads and immersed in liquid argon (−186 °C). The bulk of the air passed into an evacuated stainless steel flask where the pressure change, and hence sample volume, was measured with a capacitance manometer (Edwards Barocel). The MPC trap was shown to have no effect on the measured CH_2Cl_2 concentration. Halocarbons were separated on a 60 m × 0.53 mm (1.5 µm film thickness) DB5 capillary column (J&W), with helium carrier gas (2 mL min^{-1}) and a temperature program of −20 °C (2 min) rising to 220 °C, at a rate of 15 °C min^{-1}. The mass spectrometer was operated in selected ion mode (voltage switching) using electron ionisation (EI). Each air sample was analysed at least twice, with a working standard analysed before and after each sample pair to allow correction for small changes in instrument response.

The VG Autospec system was used from the start of analysis at UEA in June 1998 until December 1999. In 1999 a new instrument ("Entech") was purchased by UEA and became the main instrument for CARIBIC sample analysis. This system consisted of an Agilent 6890 GC and 5973 quadrupole MS. With this system pre-concentration was achieved using a commercial, fully automated, three-stage pre-concentrator (Entech Instruments, model 7100). This system was used throughout the rest of CARIBIC1 and CARIBIC2. The Entech pre-concentrator employs multiple traps to remove water (Trap 1), CO_2 (Trap 2) and to cryo-focus the sample prior to injection into the GC (Trap 3). Typically, between 800–1000 mL of air are trapped at 100 mL min^{-1} onto a 1/8" (external diameter, OD) stainless steel trap (Trap 1) packed with glass beads and held at −150 °C. The contents of Trap 1 are then swept onto Trap 2, consisting of 1/8" OD stainless steel packed with Tenax adsorbent and held at −40 °C. Trap 3 cryo-focuses the sample on a fused silica lined stainless steel tube (1/32" OD). Until 2010 a DB-5 capillary column (J&W Scientific, 105 m × 0.32 mm ID, 1.5 µm film thickness) was used for separation. In 2010 the column was changed to an Agilent GC-GasPro column (30 m × 0.32 mm). The temperature program used with the DB-5 column was 30 °C for 8 min rising to 220 °C at a rate of 10 °C min^{-1}. The temperature program used with the GasPro column is −10 °C for 2 min rising to 200 °C at a rate of 10 °C min^{-1}. The MS is operated in selected ion mode using EI at 70 eV. The system allows for the unattended analysis of up to 16 samples, interspersed with equal volume aliquots of a working standard analysed at regular intervals. Each sample is normally analysed only once and, as the response of the quadrupole analyser is more stable than the Autospec, the working standard is analysed less frequently.

To assist with the transition between the VG Autospec and the Entech system parallel analysis was conducted for two flights in July 2000. Agreement between the two systems was excellent. Of the 24 samples analysed on both systems all but five had a difference of less than ±1 ppt (corresponding to a difference of < 3 % standard deviation, σ, or less than the precision of these instruments). For the five remaining samples the difference was less than ± 2 ppt. The CH_2Cl_2 samples that were analysed on both systems were treated in the following manner. If the difference was less than ± 1 ppt (3 %σ) the values were averaged and the variation between the two measurements incorporated into error bars plotted with these values. Where the difference was greater than ± 1 ppt the VG Autospec value was selected based on the better precision of this instrument with respect to CH_2Cl_2.

To provide additional support to the CARIBIC2 data set, three flights, one a year between 2009 and 2011, were also analysed on a highly sensitive Waters Autospec magnetic sector GCMS. This system is the direct replacement of the VG Autospec described above and, whilst a number of minor modifications have been made to the analytical procedure (see Laube et al., 2010), the system is essentially the same. Where the Entech and Autospec values agreed within ±1σ (based on replicate Autospec measurements) the values were combined. As with CARIBIC1, these values all agreed within ±1 ppt. For the remaining samples the values from the higher precision Autospec system have been used. The limit of detection for all three analytical systems was 0.1 ppt or better.

For CH_2Cl_2 the UEA calibration is tied to the 2003 GCMS gravimetric scale of the Global Monitoring Division of the Earth System Research Laboratory of the National Oceanic and Atmospheric Administration (NOAA-ESRL-GMD) in Boulder, CO, USA. A number of calibrated, high-pressure whole-air samples collected at Niwot Ridge (a remote site near Boulder) were acquired between 1994 and 2009. These were used for the propagation of mixing ratios to all CARIBIC measurements. Further details on this procedure can be found in the Supplement. The CH_2Cl_2 data are reported on the latest (2003) NOAA-ESRL calibration scale. NOAA do not provide an absolute accuracy on their calibrated gas standards but, in a recent international comparison exercise (IHALACE), the mean of the CH_2Cl_2 calibration scales from the three independent calibration laboratories was found to have a standard deviation of ± 9 % (Hall et al., 2014). In Sect. 3.1, CARIBIC data are compared to the long-term CH_2Cl_2 record from Mace Head (53.3° N,

9.9° W, 42 m a.s.l.) measured by NOAA-ESRL-GMD. These data are obtained from regularly collected flasks samples analysed by GCMS. Sampling at Mace Head is done in a manner to characterise only air that is arriving from the clean air sector, specifically when wind direction is between 180 to 320° and the wind speed is greater than $4\,m\,s^{-1}$. For further information see Montzka et al. (2011a) and http://www.esrl.noaa.gov/gmd/hats/gases/CH2Cl2.html. A comparison between NOAA and UEA calibration scales is discussed in the Supplementary Information which provides a comparison of data from Cape Grim, a ground-based site sampled by both groups. Cape Grim samples analysed by both groups compare well (65 % agree within the respective 1σ standard deviations), with no apparent offset or change in the relationship between both groups' results over time (NOAA / UEA ratio of 1.02 ± 0.06). Throughout this paper we refer to the dry air mole fraction of CH_2Cl_2 as "concentrations" to increase the accessibility and readability of this paper.

The analytical precision during CARIBIC1 was 0.9 % for the VG Autospec (based on repeat analysis of randomly selected samples, 1998–2002) and 2.4 % for the Entech (based on repeat analyses of the working standard, 1999–2002). During CARIBIC2 the Entech system was managed by several operators and the analytical precision was calculated for each of these periods, again based on repeat analysis of randomly selected samples or repeat analysis of the working standards. Average precision was 3.42 % between May 2005 and September 2006, 4.0 % between October 2006 and October 2009, 5.5 % between November 2009 and October 2012 and 3.3 % in November and December 2012. Average precision for the Autospec system during CARIBIC2 was 0.48 %. The final data set used in this study is from 1998–2002 and 2005–2012.

2.3 Ancillary measurements – CO, O_3 and back-trajectories

With a typical cruise altitude of 10–12 km CARIBIC intercepts air of both tropospheric and stratospheric origin. Data were labelled to indicate if they were of mainly tropospheric or stratospheric origin based on a chemical definition of the tropopause. O_3 is measured in situ onboard the CARIBIC platform (see Sprung and Zahn, 2010) and therefore provides a measure of upper troposphere/lower stratosphere (UTLS) structure with a temporal and spatial resolution more suited to the discrete whole-air samples than parameters derived from meteorological analyses, such as potential vorticity. Samples were classed as being predominantly stratospherically influenced if the integrated O_3 mixing ratio for that sampling period was above a seasonal threshold determined by Eq. (1), a method derived from CARIBIC data by Zahn and Brenninkmeijer (2003), confirmed by Thouret et al. (2006) and used as part of CARIBIC halocarbon analysis by Wisher et al. (2014):

$$O_3^{\text{tropopause}}\,(\text{in ppbv}) = 97 + 26\sin\left[\frac{2\pi\,(\text{Day of Year} - 30)}{365}\right]. \quad (1)$$

A detailed discussion of O_3 as a chemical marker for the structure of the UTLS is provided by Zahn and Brenninkmeijer (2003) and Sprung and Zahn (2010). Briefly, the extratropical O_3 chemical tropopause is observed around 100 ppbv O_3 and can be seen in changes in the relationship between O_3 and tropospheric tracers such as CO and acetone. Above the chemical tropopause, a compact "mixing line" between O_3 and, for example, CO, denotes the mixing of tropospheric and stratospheric air in the extratropical tropopause layer (ExTL). The ExTL extends up to a maximum of 400–500 ppbv O_3, above which lies the lowermost stratosphere (LMS). Figure 1 shows which samples were classed as being of predominantly tropospheric origin and which were stratospheric. As tropospheric trends in CH_2Cl_2 form the focus of this investigation, stratospherically influenced samples (which comprised between ∼ 6–40 % of samples, depending on the region) were excluded from the bulk of the discussion for each region. Vertical profiles incorporating stratospheric samples are discussed in Sects. 3.4 and 3.5.

CARIBIC measurements of CO were used during the analysis of CH_2Cl_2 measured on flights to South Africa and India (Sects. 3.2 and 3.3 respectively). Details of CO measurements can be found in Brenninkmeijer et al. (1999) for CARIBIC1 and Scharffe et al. (2012) for CARIBIC2. For comparison with the whole-air samples the CO values (produced every 2 s) were integrated over the sampling period of each whole-air sample. Back-trajectory analyses for CARIBIC flights are provided by the Royal Netherlands Meteorological Institute (KNMI) – further details can be found at http://knmi.nl/samenw/campaign_support/CARIBIC/ or in Scheele et al. (1996). The trajectory model used European Centre for Medium range Weather Forecasting (ECMWF) data at a $1° \times 1°$ resolution to calculate both 5-day back-trajectories at 3 min intervals along the flight track and 8-day back-trajectories for the collection interval of each whole-air sample. During the early CARIBIC flights ECMWF "first guess" fields were used to calculate the back-trajectories, changing to re-analysis data after September 2000.

3 Results and discussion

Between 1998 and 2012 CARIBIC flights covered a substantial area of the global free troposphere (Fig. 1). However, for the purpose of this investigation several regions were selected and only the data from these flights will be discussed. These regions and the rationale behind their selection are described here. Firstly, a European region within a box spanning 40 to 55° N and −10 to 20° E (Frankfurt Airport = 50.03° N,

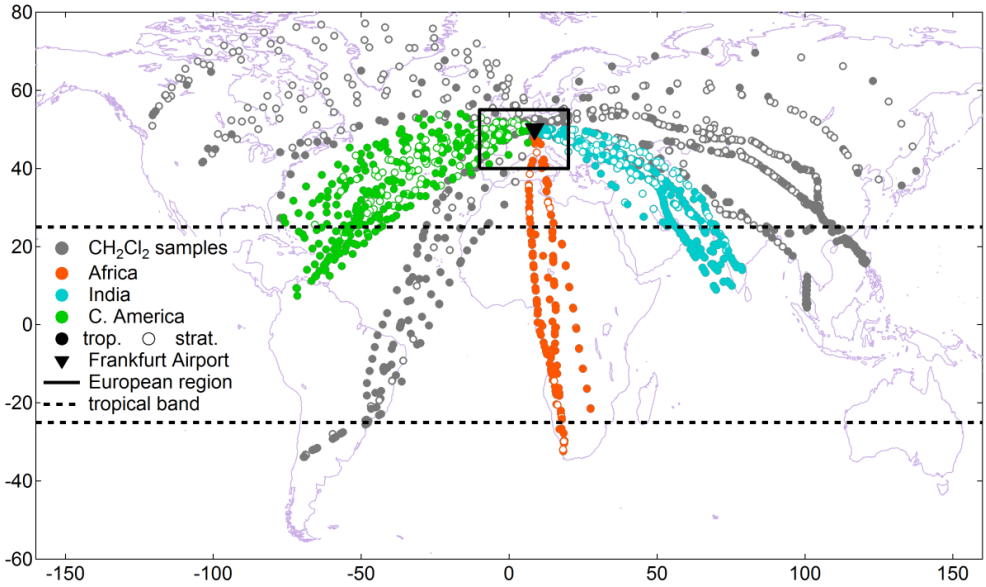

Figure 1. CARIBIC whole-air samples analysed for CH_2Cl_2 between 1998–2002 and 2005–2012. The grey points show all the CH_2Cl_2 samples collected by CARIBIC during these periods. The subset of data used in this study are also shown: (1) the samples within the European region described in Sect. 3 are marked by the black box, (2) flight routes to Africa, India and Central America are shown by coloured samples, see inset legend, and (3) samples within the tropical region are delineated by the dashed lines. More details of the regions used in this study can be found in Table 1.The identification of samples as tropospheric or stratospheric is described in Sect. 2.

8.57° E) was selected as it is the area with the greatest temporal coverage. Secondly, routes to South Africa, India and across the North and Central Atlantic were also chosen as these routes were traversed by CARIBIC over multiple years, allowing changes over time to be observed in these regions. Finally, samples collected in the tropical region covering 25° S to 25° N were used to investigate the concentration of CH_2Cl_2 in air masses with the potential to enter the tropical tropopause layer (TTL). Further details of these five case studies can be found in Table 1 and they are highlighted in Fig. 1. Throughout the paper mean values prefaced by ± refer to the 1σ standard error associated with that mean value.

3.1 Long-term time series of CH_2Cl_2 measured over Europe

The CH_2Cl_2 time series of European CARIBIC and NOAA Mace Head data can be seen in Fig. 2a. A fairly consistent seasonal cycle is observed inter-annually in the boundary layer air samples from Mace Head whereas the CARIBIC data show greater variability. This variability in the CARIBIC data is mainly because these samples represent a wide variety of air masses sampled over a large area (Fig. 2c) compared to clean-sector air sampled at Mace Head (Sect. 2.2). Analysis of back-trajectories indicates that air sampled by CARIBIC over Europe originates from a large NH geographical region, including industrial areas where high emission "pollution" events may occur as well as contrasting regions where pristine tropospheric air masses are sampled. In contrast, the Mace Head site commonly samples clean sector air. Although a previous study involving data collected by aircraft at an average altitude of 4 km (Miller et al., 2012) observed seasonality in atmospheric concentrations of CH_2Cl_2, we do not see a strong seasonal pattern at 10–12 km in our more sporadic data set. Further analysis, discussed in subsequent sections, will highlight the importance of strong source regions (e.g. India and Southeast Asia) on observed CH_2Cl_2 concentrations in the mid- and upper troposphere.

The trend in European observations of CH_2Cl_2 is shown in Fig. 2b. Error bars represent the 1σ variation associated with the mean of all tropospheric samples taken within each year (hereafter referred to as the annual tropospheric value). As seen in Fig. 2a, only a small number of NOAA samples were collected in the first few years of the data set. Due to this small sample size, biases, for example the influence of seasonality, could be introduced (see Table 3 for seasonal distributions). This adds an additional, unquantified uncertainty to these annual values. To account for this, data from Mace Head can be compared to data collected at other NOAA NH sites such as Barrow, Alaska. Data from Barrow show a very similar pattern to those from Mace Head and support the trend seen at Mace Head (data not shown but available from http://www.esrl.noaa.gov/gmd/hats/gases/CH2Cl2.html and published in Montzka et al., 2011a). Determining trends for the first few years of the database is hard due to the reduced data coverage. However, NOAA data covers the whole year from 2003 onward (Fig. 2a).

Table 1. A summary of CARIBIC data used in this study.

Region	Temporal data coverage		Number of tropospheric (stratospheric*) samples
	Annual	Monthly	
Europe	Data collected 1998–2002 and 2005–2012 Min. coverage: $n = 1$ in 1999 Max. coverage: $n = 16$ in both 2009 and 2011	All months covered	123 (87)
Africa	2000, 2009–2011. Individual flights:	Mainly NH winter	140 (21)
	2000	May, Jul, Dec	32 (4)
	2009	Mar, Oct	47 (8)
	2010	Nov, Dec	22 (6)
	2011	Jan, Feb, Mar	39 (3)
India	Data collected 1998–2001, 2008, 2011 and 2012. The summer monsoon (July, Aug and Sept) was sampled in 1998, 1999, 2000 and 2008. In other years samples were only taken outside of the monsoon season.		295 (134)
	Monsoon	Jul, Aug, Sept	105 (38)
	Non-monsoon	Rest of year	190 (95)
North and Central Atlantic	Data collected 2001–2002, 2007, 2009–2012	All months covered	282 (108)
Tropics	All data within $\pm 25°$ of equator. All years included.	All months covered	539 (34)

* Stratospheric samples have been excluded from the analysis of most regions, see Sect. 2.

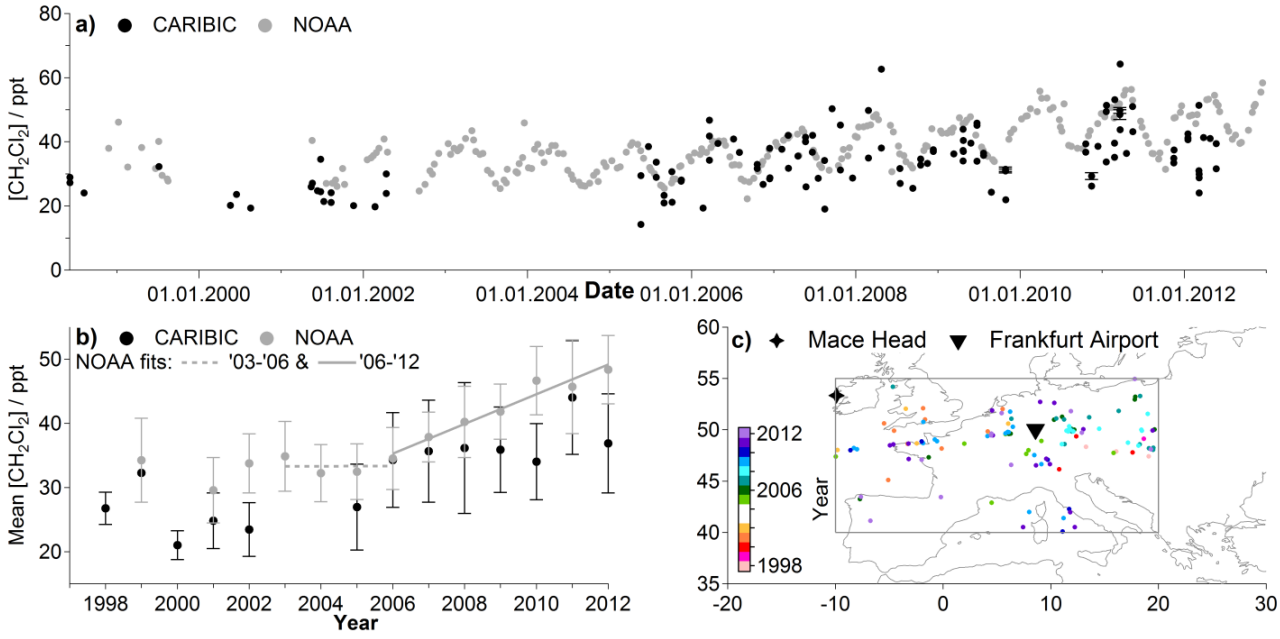

Figure 2. (a) European CH_2Cl_2 time series from June 1998 to December 2012. Where a sample was analysed multiple times an error bar is given based on the variation between these measurements, see Sect. 2. **(b)** The mean value of all CH_2Cl_2 values taken within this region for each year ("annual tropospheric value"), shown separately for CARIBIC and NOAA Mace Head data, error bars are 1σ. **(c)** Geographical distribution of CARIBIC samples within the European region 40–55° N and −10–20° E. Frankfurt Airport (CARIBIC2 base) and the NOAA sampling site at Mace Head are also shown. Samples are coloured by year.

The NOAA Mace Head data show no trend between 2003 and 2006 (linear fit is displayed in Fig. 2b) with a steadily increasing trend from 2006. Despite the 1σ annual error bars being relatively large, due to the seasonal variation seen at the Mace Head boundary layer site, a linear fit for the NOAA data between 2006 and 2012 shows a strong positive correla-

Table 2. CH_2Cl_2 descriptive statistics for regions included in this study and a comparison to data from the existing literature.

Study and Region	Time period[a]	Values[b]/ ppt
This paper		
Europe	(a)[c] 1998–2002	$\bar{x} = 24.6, \sigma = 4.3, n = 21$
CARIBIC data	(b) 2009–2012	$\bar{x} = 38.6, \sigma 8.4, n = 49$
Mace Head NOAA data	Increase (a→b)	14
	(a) 1998–2002	$\bar{x} = 32.9, \sigma = 5.4, n = 28,$
	(b) 2003–2004	$\bar{x} = 33.6, \sigma = 5.1, n = 48,$
	(c) 2009–2012	$\bar{x} = 45.7, \sigma = 6.1, n = 88$
	(d) 2011–2012	$\bar{x} = 47.0, \sigma = 6.5, n = 45$
	Increase (a→c)	13
	Increase (a→d)	13.5
Africa	2000	$\bar{x} = 21.7, \sigma = 1.3, n = 3$
Above 30° N	2009–2011	$\bar{x} = 34.2, \sigma = 7.6, n = 23,$
Below 30° N	2000	$\bar{x} = 15.8, \sigma = 3.1, n = 29$
	2009–2011	$\bar{x} = 22.7, \sigma = 5.1, n = 85$
	Increase	7
India	1998–2000	$\bar{x} = 21.5, \sigma = 3.8, n = 56$
Summer monsoon (Jul–Sept)	2008	$\bar{x} = 36.4, \sigma = 9.4, n = 50$
Non-monsoon months	Increase	15
	(a) 1998–2000	$\bar{x} = 20.1, \sigma = 4.9, n = 81$
	(b) 2008	$\bar{x} = 30.4, \sigma 9.7, n = 62$
	(c) 2011–2012	$33.4, \sigma = 15.6, n = 30$
	Increase (a→b)	10
	Increase (a→c)	13
North and Central Atlantic	2000–2002	$\bar{x} = 23.2, \sigma 3.6, n = 89$
	2009–2011	$\bar{x} = 32.0, \sigma 7.8, n = 180$
Other aircraft studies		
TTL (Schauffler et al., 1993)	1991–1992	$\bar{x} = 14.9, \sigma = 1.1, n = 12$
Tropical Indian Ocean 1.2–12.5 km altitude (Scheeren et al., 2002)	1999	$\bar{x} = 29$, SD = 12, $n = 71$
ASM outflow, E. Mediterranean 6–13 km alt. (Scheeren et al., 2003)	2001	$\bar{x} = 23, \sigma = 3$
Canada & Greenland, commonly 0.8–4.7 km but up to 12 km alt. (Simpson et al., 2011)	2008	$\bar{x} = 35.8 \pm 2.9$
Tropics ($0 \pm 25°$), 345–350 K θ band (HIPPO, Wofsy et al., 2012)	2009–2011	$\bar{x} = 26.3, \quad R = 15.87 - 49.83,$ $n = 20$
Ground-based		
Atlantic cruise 45° N–30° S (Koppmann et al., 1993)	1989	$\bar{x} = 18 \pm 4$
SH		$\bar{x} = 36 \pm 6$ ppt
NH		
Alert, Canada (Gautrois et al., 2003)	1989–1996	$\bar{x} = 47.2 \pm 2, \tilde{x} = 45.8$ $r = 24.2 - 71.6$
Cape Grim, Tasmania (Cox et al., 2003)	1998–2000	$\bar{x} = 8.9 \pm 0.2$
Chinese cities (Barletta et al., 2006)	2001	$\bar{x} = 28, \sigma = 4$
Background		$\bar{x} = 226, \sigma = 232$
Urban		

[a] Time period should be viewed alongside Table 3 which shows the seasonal distribution of samples. [b] $\bar{x}$ = mean, $\tilde{x}$ = median, σ = standard deviation, R = range and n = number of samples. [c] See Sect. 3.1 for a description of the different time periods selected for Europe.

tion (see Fig. 2b, $r^2 = 0.97$). The increase between the mean of all values collected within the first 5 years (1998–2002) and the final 4 years (2009–2012) of the NOAA data set was from 32.9 ppt ($\sigma = 5.4$, sample size, $n = 28$) to 45.7 ppt ($\sigma = 6.1, n = 88$), an increase of ~ 13 ppt. A test of the robustness of the trend is to compare the change from 2003–2004 (the first period with coverage across the entire year) to 2011–2012. During this period CH_2Cl_2 increased from 35.6 ppt ($\sigma = 5.1, n = 48$) to 47.0 ppt ($\sigma = 6.5, n = 45$), an increase of 13.5 ppt. CARIBIC data broadly mirror the increasing trend between 2006–2012, bearing in mind the more sporadic nature of the data set and the wider distribution of air mass sources, discussed above. The increase between the mean of all values collected between 1998–2002 and 2009–2012 was also similar to that seen at Mace Head, increasing from 24.6 ppt ($\sigma = 4.3, n = 21$) to 38.6 ppt ($\sigma = 8.4, n = 49$), an increase of 14 ppt.

Whilst the overall trends are similar, mean annual values are higher at Mace Head (Fig. 2b). This is likely to be because the NOAA samples were collected at a lower altitude than the CARIBIC samples. Calibration scales between NOAA and UEA compare well, as described in Sect. 2 and in the Supplement. Vertical profiles of CH_2Cl_2 are discussed in Sects. 3.4 and 3.5.

Flight-based measurements in the NH were made by Simpson et al. (2011) (comparative data from the literature is outlined in Table 2 for all regions). Although they flew up to 12 km their flight altitudes were generally lower than CARIBIC (0.8–4.7 km). They reported a 2008 summer average of 35.8 ± 2.9 ppt over Canada and Greenland. CARIBIC mean values for the 3 summers around this time (2007, 2008 and 2009) were around 35, 27 and 37 ppt respectively, however as sample sizes were small ($n = 6$, 4 and 6 respectively) we combined these three summer periods to obtain a mean for summers 2007–2009 of 33.9 ± 2.2 ppt. Our value is similar to that of Simpson et al. (2011), the higher values over industrial Europe possibly offsetting some of the decrease we would expect with altitude.

3.2 Flights to Africa – investigating biomass burning emissions and NH : SH gradients

Flights to South Africa (Table 1) allow us to investigate the NH : SH gradient in CH_2Cl_2, see Fig. 3a. A strong latitudinal gradient is observed, in accordance with a strong industrial NH source of CH_2Cl_2. The increase is largest over the northern section of the flight route, which crosses Europe. We have a limited data set ($n = 3$) for the section of the flight route that crosses Europe (here defined as $> 30°$ N to provide a clear delineation between samples taken over Africa and those taken within our European box, see Fig. 1) and so we do not wish to quantify an increase over time, but from the limited data available it is similar to that seen for our European box in Sect. 3.1. During the previous peak in CH_2Cl_2 concentrations (around 1990, see Sect. 1) a difference of ~ 18 ppt between NH and SH average concentrations was observed in the Atlantic region by Koppmann et al. (1993) (Table 2). Whilst our results do not provide full SH coverage, and so cannot be used to estimate a NH : SH ratio, they do show an increasing latitudinal variation indicative of increasing NH industrial activity with respect to CH_2Cl_2.

Annual tropospheric values are shown in Fig. 3b, separated into samples taken above and below 30° N. The 44 % increase seen at latitudes $< 30°$ N is smaller than that seen over Europe, although still statistically significant (Mann-Whitney test at $p < 0.001$). Further details of the concentrations observed above and below 30° N are provided in Table 2. Inferring year-on-year trends is difficult given the varying data coverage between years. However, the increase seen between 2009 and 2011 (Fig. 3b), along with the European data set (Fig. 2), suggest that concentrations continue to increase into the 2010s.

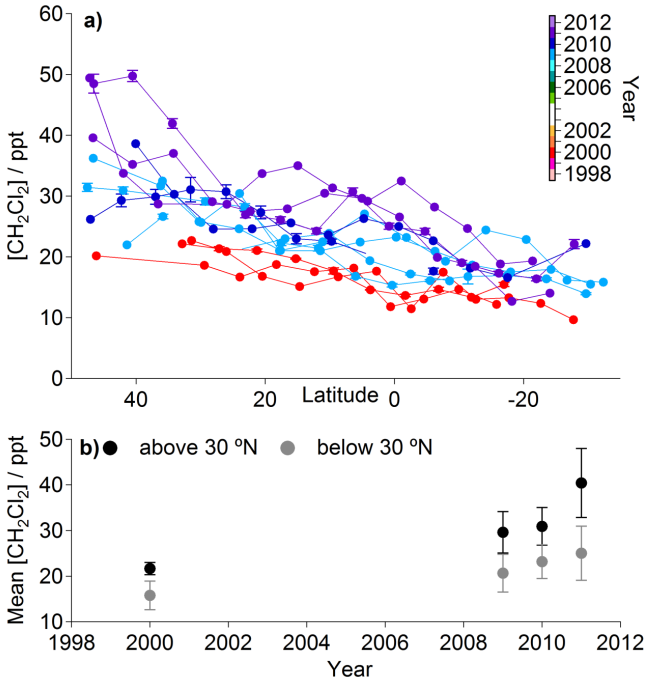

Figure 3. (a) Latitudinal distributions of CH_2Cl_2 observed during flights to South Africa where colour = year (see inset colour bar, colour scale is consistent with Figs. 2, 4 and 6). Where multiple measurements of the same sample have been made 1σ error bars are given, see Sect. 2. **(b)** Annual tropospheric values (see Fig. 2) with 1σ error bars. These average values have been split into above and below 30° N.

Despite the importance of biomass burning with respect to atmospheric trace gas emissions over Africa (Roberts et al., 2009) no correlation ($r = 0.14$, $p > 0.05$) was observed between CH_2Cl_2 and the common combustion tracer CO. Enhancements of CO, which commonly peak near the equator in CARIBIC data (Umezawa et al., 2014), are predominantly from biomass burning sources. In contrast to the latitudinal distribution of CO, CH_2Cl_2 decreased constantly from north to south (Fig. 3). Observations of CH_2Cl_2 along the CARIBIC flight track to South Africa appear to be dominated by a strong NH source and subsequent decline towards lower latitudes, with little impact from biomass burning. This observation fits with a recent study which saw no evidence for CH_2Cl_2 emissions in boreal biomass burning plumes, suggesting that previous calculations of CH_2Cl_2 emissions from biomass burning (e.g. Rudolph et al., 1995) were overestimates (Simpson et al., 2011). Whilst emissions from boreal and tropical forest fires may differ, recent analysis of air samples collected during flights over biomass burning events in the Brazilian rainforest also showed no significant fire emissions of CH_2Cl_2 (A. Wisher, UEA, personal communication, 2014).

3.3 Emissions of CH_2Cl_2 from India investigated during the Indian monsoon

CARIBIC data collected during flights to India in 2008 have previously been used to demonstrate the impact of the Indian/Asian Summer Monsoon (ASM) on UTLS trace gas concentrations (Baker et al., 2011, 2012; Schuck et al., 2010). As these studies reported elevated concentrations of many trace gases linked to the persistent convection and anticyclonic flow of the ASM, we have divided flights to India into "monsoon" (July–September, inclusive) and "non-monsoon" (rest of year) for this study (Tables 1 and 2). Latitudinal distributions of CH_2Cl_2 along routes to Indian destinations are shown in Fig. 4, displayed with the oldest flights at the top of the plot.

As the ASM was a particular focus of CARIBIC during 2008 we begin our discussion of Fig. 4 with these flights. A pronounced difference in the CH_2Cl_2 distribution along the latitudinal flight track can be seen between monsoon and non-monsoon months. During the 2008 monsoon (Fig. 4d) concentrations between $\sim$25–40° N are elevated compared to non-monsoon months (Fig. 4c). During non-monsoon months a relatively flat latitudinal distribution of CH_2Cl_2 is observed along the majority of the flight path with some elevated concentrations at latitudes less than 20° N. Analysis of back-trajectories indicates that these elevated samples (Fig. 4c) probed air that had recently been at low altitude over Southeast Asia. The pattern during the monsoon season is consistent with previous CARIBIC studies, referenced above, which reported elevated concentrations of NMHCs, methane and other compounds within $\sim$25–40° N due to interception of air masses with influence from the continental boundary layer.

The difference between monsoon and non-monsoon months can also be observed in the earlier (CARIBIC1) data, although the monsoonal elevation between $\sim$25 and 40° N (Fig. 4b) is superimposed on a north–south latitudinal gradient more clearly seen outside of the monsoon season (Fig. 4a). This north–south gradient is similar to that seen in the data from flights to South Africa. An important feature of Fig. 4 is the shift in the dominant latitudinal feature over time. In the 1998–2001 period a north–south gradient, suggesting low CH_2Cl_2 emissions from India, is clear. In contrast, very high concentrations at low latitudes are observed in later flights conducted in 2008 and 2011–2012 (Fig. 4e). High values at lower latitudes are in contrast with results for Africa (Sect. 3.2) and to Central America (Sect. 3.4). These results suggest a shifting latitudinal profile and an increase in emissions within the Indian region. One 2011 flight in particular showed exceedingly high levels of CH_2Cl_2 (Fig. 4e). Analysis of back-trajectories indicate that these air masses originated from a low altitude over India and Southeast Asia. This region is discussed further in Sect. 3.5.

Increases were calculated for the period between 1998–2000 and 2008 and between 1998–2000 and 2011–2012. These are provided in Table 2 for both monsoon and non-monsoon months. However, as was illustrated in our discussion of Fig. 4 (previous paragraph), during the non-monsoon months we may sample air masses that originate from outside the Indian region. During the monsoon months air masses within the monsoon anticyclone are much more isolated (full details provided below) and so the increases during the monsoon period are more likely to represent changing CH_2Cl_2 emissions from India and its neighbours. The increase between the 1998–2000 and 2008 monsoon periods was 15 ppt (69 %, further details in Table 2). Measurements of air masses from the Indian and South Asian region were made by Scheeren et al. (2002, 2003) during two campaigns in 1999 and 2001. Their observations averaged 29 ($\sigma = 12$) ppt in 1999 and 23 ppt ($\sigma = 3$) in 2001 (see Table 2). Their 2001 average, in particular, corresponds well to our early measurements over India which averaged $\sim$20–22 ppt.

As the strong convection associated with the ASM quickly elevates air masses from the Indian continental boundary layer and then isolates them within the monsoon anticyclone, UT mixing ratios over India during the monsoon are closely coupled to boundary layer emissions (Baker et al., 2011, 2012; Rauthe-Schöch, et al., 2015; Schuck et al., 2010). This makes the ASM an ideal case study for calculating emission estimates using the CARIBIC data set. As the majority of CH_2Cl_2 emissions are industrial we assume that emissions do not change during the monsoon and so the increase in UT concentrations seen during this period can be attributed wholly to meteorological changes. This assumption is justified based on findings by Gentner et al. (2010) who showed an absence of seasonality in CH_2Cl_2 emissions based on measurements made in California and a study by McCulloch and Midgley (1996) who also reported an absence of seasonality based on their analysis of data on the global industrial use of CH_2Cl_2. Previous analyses of meteorological parameters during 2008 (Rauthe-Schöch, et al., 2015; Schuck et al., 2010) have demonstrated that the monsoon anticyclone was present in July–September. For emission estimates we take all tropospheric samples where both CO and CH_2Cl_2 were measured and which were collected < 40° N (for further explanation and justification of this method see Baker et al., 2011; Schuck et al., 2010) in July–September 2008, a total of 35 samples.

Emission estimates are often calculated using ratios whereby the compound of interest is compared to a compound with which it correlates and for which emissions are quantified, in this case CO. The emission estimate is based on the slope of the linear correlation between the two tracers using Eq. (2) (where $E_{CH_2Cl_2}$ and E_{CO} are the emission estimates for CH_2Cl_2 and CO respectively):

$$E_{CH_2Cl_2} = E_{CO} \times \left(\frac{\Delta CH_2Cl_2}{\Delta CO}\right). \quad (2)$$

The CH_2Cl_2 vs. CO correlation within the monsoon (< 40° N, July–September 2008) can be seen in Fig. 5a. The

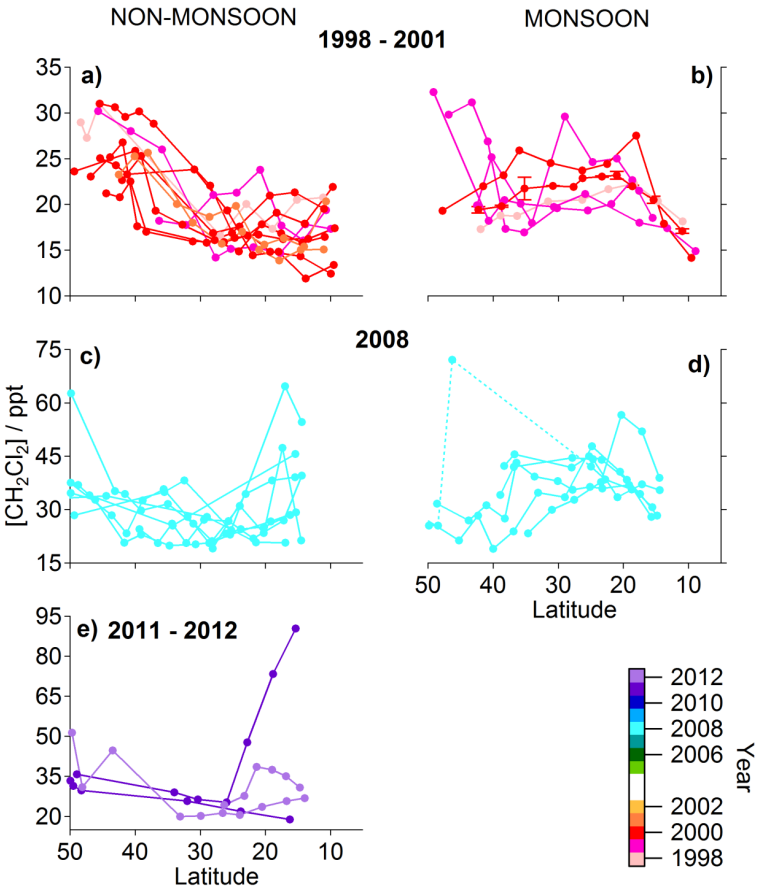

Figure 4. Latitudinal distributions of CH_2Cl_2 observed during flights to India for non-monsoon months on the left and monsoon months (July, August, September) on the right where colour = year (see inset colour bar; colour scale is consistent with Figs. 2, 4 and 6). Where multiple measurements of the same sample have been made 1σ error bars are given, see Sect. 2.

correlation has a statistically significant (Pearson's correlation coefficient, $p < 0.05$) r value of 0.62. Correlations for individual months are also shown in Fig. 5a. No statistical difference (Fisher's z test with a z-crit. value of 0.05) exists between the slopes for individual months, allowing us to use the slope of the correlation for the whole ASM period for our emission estimate. Table 4 includes ΔCH_2Cl_2 / Δ CO values from this study as well as a range of published values from a variety of sources. Lower ratios are seen for wildfire and biomass burning plumes, with higher ratios (more similar to the ones we observed) for urban (likely industrial) emissions.

Before discussing our emission estimates we provide details of the assumptions and potential errors associated with this method and our treatment of these factors. Firstly, this method assumes that the two compounds share a common, dominant source and/or that emissions are co-located. Whilst CH_2Cl_2 is of predominantly industrial origin (see Sect. 1) with emissions likely to be dominated by areas of heavy anthropogenic influence (e.g. cities), CO has a more diffuse source. It has a large combustion source which, in India, is dominated by the burning of biofuels and biomass (Dickerson et al., 2002). Despite this, we believe that CO provides the best option for emission estimates in this region. On the scale of a regional emission estimate, CO and CH_2Cl_2 sources are co-located: both show strong signatures from the Indian subcontinent where it is known that air masses sampled within the monsoon anticyclone have likely originated from. CO emissions are also well quantified, and comparisons between CO and anthropogenic chlorocarbons, including CH_2Cl_2, have also been conducted in several other studies including Gentner et al. (2010); Millet et al. (2009); Simmonds et al. (2006) and Palmer et al. (2003) (Table 4) Schuck et al. (2010) discussed the use of SF_6 as a tracer. However, its extremely patchy distribution (strong point sources) results in a poor correlation with CH_2Cl_2 and a poorer representation of the Indian monsoon plume.

To further support the suitability of the CH_2Cl_2–CO ratio for estimating CH_2Cl_2 emissions we describe two analyses which demonstrate that the variability we observe is due to recent emissions, as opposed to variations in transport time or route prior to sampling. Firstly, we compared the ΔCH_2Cl_2 / ΔCO value from our sample set ($n =$

Table 3. Seasonality of available CARIBIC data for regions included in this study.[a] Black squares show that samples were taken during that month and the number refers to the number of samples.[b]

Period[c]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Europe, CARIBIC												
1998–2001					3	6	2	4			1	
2009–2012	7	3	12	20	24	5	4	13	9	8	5	1
Mace Head NOAA												
1998–2001	1	1		1		1	3	4	1	3	1	
2003–2004	4	4	4	4	4	4	4	3	5	3	5	4
2009–2012	6	9	6	8	10	8	7	7	7	5	8	7
Africa > 30° N												
2000					1		1					1
2009–2011	3	3	8							4	4	2
Africa < 30° N												
2000					9		9					11
2009–2011	10	10	31							18	6	10
Atlantic/Central America												
2001–2002		11		20	17	9	11	10			11	
2009–2011	26		31	19	13	20	21	18		8	10	19

[a] India is not included as focus is on summer monsoon and so seasonality throughout the whole year is not relevant. Tropical region not included due to reduced seasonality in the tropics. Samples sizes for both these regions can be found in Tables 1 and 2.
[b] Samples are an average of two flask samples (NOAA) or at least two analyses of sample (UEA).
[c] Relates to any discrete time period mentioned in the text or Tables 1 and 2.

Table 4. A comparison of enhancement ratios from this study (air mass age corrected) and existing literature.

Source	$\Delta CH_2Cl_2/\Delta CO$ / mol mol^{-1}
India, summer monsoon period (this study)[a]	
1998	1.0×10^{-4} ($\pm 4.3 \times 10^{-5}$) $r = 0.69$
1999	1.6×10^{-4} ($\pm 6.4 \times 10^{-5}$) $r = 0.53$
2000	2.5×10^{-4} ($\pm 3.7 \times 10^{-5}$) $r = 0.86$
2008	4.0×10^{-4} (8.7×10^{-5}) $r = 0.62$
Other studies[b]	
Biomass burning, Africa savanna, ground-based,1991[1]	2.5×10^{-5} (error = 26 %) $r = 0.65$
Wildfires, Cape Grim, ground-based, 1998-2004[2]	< 1–6×10^{-7}
Asian pollution outflow, Bay of Bengal, boundary layer flights, 1999[3]	4.4×10^{-5} ($\pm 4.7 \times 10^{-5}$) $r = 0.39$
Urban, California, ground-based, 2005[4]	3.1×10^{-4} ($\pm 3.0 \times 10^{-5}$) $r = 0.58$=0.66
Urban, USA, boundary layer flights, 2004[5]	2.4×10^{-4} (1.8×10^{-4}–2.9×10^{-4}) $r = 0.56$–0.83
Urban, Mexico, ground-based, 2006[5]	1.9×10^{-4} (1.1×10^{-4}–2.9×10^{-4}) $r = 0.43$–0.81

[a] CARIBIC fits are orthogonal distance regression fits using IGOR Pro software. [b] described by: emission source, location, sampling location, year of study [1] (Rudolph et al., 1995); [2] (Simmonds et al., 2006); [3] (Scheeren et al., 2002); [4] (Gentner et al., 2010); [5] (Millet et al., 2009).

35) to the ΔCH_2Cl_2 / ΔCO value obtained from a smaller data set based on the method used in Baker et al. (2011). Baker et al., when performing emission estimates for the same CARIBIC 2008 monsoon data set, minimised the influence of variability with respect to processing or other transport effects by selecting a data set that included only those samples whose back-trajectories indicated low-level (pressure > 600 hPa) contact within the monsoon anticyclone in the previous 5 days ($n = 15$). Comparing this subset of samples to our full sample set gives a very similar

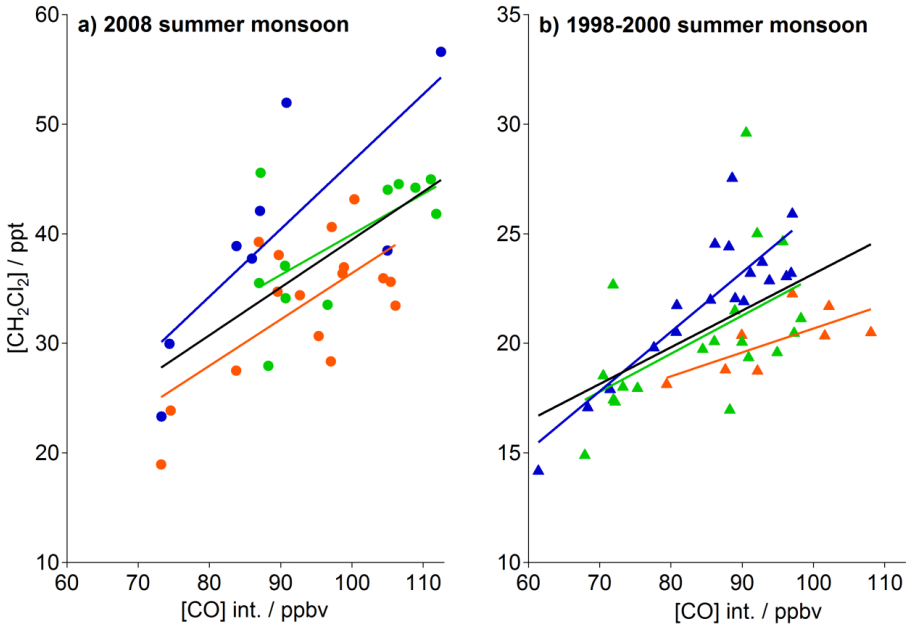

Figure 5. Correlation plots of CH_2Cl_2 and integrated CO (see Sect. 2) for **(a)** the 2008 summer monsoon period (coloured by individual months) and **(b)** the early years of the CARIBIC India data set (coloured by individual years). Further details in Table 4.

ΔCH_2Cl_2 / ΔCO and r value. The ΔCH_2Cl_2 / ΔCO and r values for our data set are shown in Table 4 and for the Baker et al. (2011) subset the age-corrected slope was 4.9×10^{-4} ($\pm 8.7 \times 10^{-5}$) and $r = 0.67$. The similarity between the two values suggests that the correlation observed in our data set (Fig. 5) is influenced by local emissions and not differences in transport times or source regions. This is supported by a second method in which we compared the CH_2Cl_2 vs. CO correlation for the ASM samples with the correlation calculated for samples taken within the same 14–40° N latitudinal band but along flight routes to Africa (Sect. 3.2) and across the Atlantic (Sect. 3.4). The correlation for the Africa and Atlantic flights are much weaker and do not show the same dynamical range as the correlation for the India data. This supports our assumption that samples taken during the ASM provide a unique correlation that represents local emissions due to the rapid convection and isolation that occurs within the monsoon system.

Secondly, there are errors and assumptions associated with the measured emission ratio. This includes the assumption that the emission ratio measured by CARIBIC is similar to that at the source, i.e. it has not been affected by dilution and/or photochemical/chemical loss processes. We believe this assumption to be valid with respect to dilution based on analysis conducted by Baker et al. (2011) on the same CARIBIC data set as used in this paper. Baker et al. (2011) reported an i-butane / n-butane ratio in the ASM of 0.77 ± 0.07 pptv pptv^{-1}, suggesting that the invariability of this ratio provided evidence of minimal dilution. A broader investigation of the ASM by Randel and Park (2006) using back-trajectory models found that 70 % of parcels initialised within the anticyclone were still there after 10 days.

Dilution is also considered in our discussion of the validity of our ratio with respect to the transport time between emission source and sampling (previous paragraph), assuming that variations in transport time lead to variations in the degree of mixing, and in the bootstrapping error analysis of the ΔCH_2Cl_2 / ΔCO regression line (subsequent paragraph). With respect to photochemical loss processes we assume transport times from the boundary layer to our sampling altitude of around 4 days based on Baker et al. (2011). Within this time, CH_2Cl_2, with a lifetime of around 5 months, does not experience large losses. However, the lifetime of CO ($\sim$2 weeks in mid-latitude summer (Scharffe et al., 2012 referencing Warneck, 1988) is short enough that concentration changes are likely to have occurred during this time and so we age-correct our emission ratios with respect to CO using Eq. (3), a method used by both Baker et al. (2011) and Scheeren et al. (2002). Here, the emission ratio at time 0, ER_0, is related to the emission ratio at time t, ER_t, by accounting for the change in time, Δt (4 days), the reaction rates, k, of CO and CH_2Cl_2 with OH at 298 K and the average concentration of OH predicted at 20° N and 500 hPa (estimated uncertainty of ± 25 %). Both k_{CO} at 2.1×10^{-13} cm^3 molec^{-1} s^{-1} and $\langle[OH]\rangle$ at 2.48×10^6 molec cm^{-3} are taken from Baker et al. (2011, and refs. within) and $k_{CH_2Cl_2}$ at 1.1×10^{-13} cm^3 molec^{-1} s^{-1} from Villenave et al. (1997). This procedure leads to a correction in our emission ratio for the 2008 monsoon season of

around −8 %:

$$ER_0 = ER_t e^{(k_{CO} - k_{CH_2Cl_2})\langle[OH]\rangle^{\Delta} t}. \quad (3)$$

Also associated with the emission ratio are errors arising during the calculation of the $\Delta CH_2Cl_2 / \Delta CO$ slope. These errors arise from two sources: (1) uncertainties in the analytical measurements of both CH_2Cl_2 and CO (see Sect. 2) and (2) uncertainties associated with using a slope calculated from a discrete set of samples to calculate a regional emission estimate. The errors associated with (1) are small compared to those associated with (2), see Sect. 2.2, and so we use (2), calculated using a bootstrapping procedure, to set bounds on our emission estimates. Using the Wood (2003) bootstrapping procedure we resampled, with replacement, our CH_2Cl_2 and CO data sets 10 000 times, each time calculating $\Delta CH_2Cl_2 / \Delta CO$. The output from the resampling procedure provides a probability distribution for the slope of CH_2Cl_2 / CO, allowing us to understand how dependent $\Delta CH_2Cl_2 / \Delta CO$ may be on the sampled data and allowing us to provide an idea of the potential variation in $\Delta CH_2Cl_2 / \Delta CO$. The bootstrapping procedure has been used to calculate a possible range of emission values to aid the comparison between years. In the following text this $\pm 1\sigma$ range is given in brackets following each emission estimate.

CO emissions for the Indian region are taken from the Emission Database for Global Atmospheric Research (EDGAR) v. 4.2 (JRC & PBL, 2009). We include emissions from the following countries; Bangladesh, Bhutan, India, Sri Lanka, the Maldives, Nepal and Pakistan. EDGAR emissions are provided per year and are split into categories including various industrial and domestic processes, transport and biomass and biofuel burning. Baker et al. (2012) used the Global Fire Emission Database (GFED, v.3.2, van der Werf et al., 2010) to show that CO emitted from biomass burning was greatly reduced during the monsoon, accounting for around 0.5 % of total annual CO fire emissions during 2008. To account for this reduction, the EDGAR biomass burning emissions were corrected for the effect of the monsoon using the GFED data and the method in Baker et al. (2012). As we had no evidence that anthropogenic Indian CO emissions had seasonality we divided these emissions evenly throughout the year. We believe any errors arising from this assumption are likely to be within the general errors associated with the EDGAR emissions (see below), in particular due to the dominance of burning as a source of CO in India (Dickerson et al., 2002). This method gave an average monthly emission during the 2008 monsoon of 4.2 Tg CO month^{-1}. Maximum errors on the EDGAR CO database are given as up to ±50 % (Olivier et al., 1999), likely reduced by our additional use of the GFED database. We do not consider the given error on the EDGAR data further as the main objective of these emission estimates is to provide a comparison of CH_2Cl_2 emissions over time and we assume that this error remains constant throughout the EDGAR database.

Using the 2008 CH_2Cl_2 / CO slope (Table 4) and the EDGAR CO emissions of 4.2 Tg CO month^{-1} gives an emission estimate of 1.7 (1.3–2.1) Gg CH_2Cl_2 month^{-1} from the Indian region. As industrial sources of CH_2Cl_2 have no seasonality we assume that this emission rate is constant over the year and so estimate that 20.3 (15.8–24.8) Gg of CH_2Cl_2 were emitted from the Indian region in 2008. The most recent estimate of global emissions is 515 ± 22 Gg yr^{-1} given in Montzka et al. (2011b) which is based on top-down estimates from Simmonds et al. (2006) from data collected between 1999 and 2003. Considering the caveat that global emissions are likely to have increased since this figure was published, our estimate for emissions from the Indian region in 2008 is roughly 5 % of the global total. These estimates are discussed further in Sect. 3.6.

CH_2Cl_2 emissions from the Indian subcontinent were also estimated for the 1998, 1999 and 2000 ASM seasons using the same analysis described above for 2008. Figure 5b shows the CH_2Cl_2 vs. CO correlation for 1998–2000, coloured by year. No significant difference (Fisher's z test with a z-crit. value of 0.05) was observed between the three years but we consider the three years individually to provide similar data sets for comparison with the 2008 data set (with respect to sample size and length of sampling period, see Table 2). EDGAR monthly CO emissions, modified to account for reduced burning during the monsoon, as described above, were 4.1, 4.2 and 4.2 Tg CO month^{-1} for 1998, 1999 and 2000 respectively. As CO has anthropogenic sources one may expect its emissions to have increased over time, however the monthly emissions for 1998–2000 are similar to those for 2008. To investigate this result we compared the EDGAR data to three previous studies. EDGAR monthly emissions compare well to those of Fortems-Cheiney et al. (2011) who reported relatively stable CO emissions from South Asia between 2000 and 2010. EDGAR monthly emissions also compare well to the GIS-based emission estimate of Dalvi et al. (2006) and the air pollutant emission inventory of Streets et al. (2003) who estimated that CO emissions from India in 2000 were 69 and 63 Tg respectively, similar to the 66 Tg annual emission estimated from the EDGAR database for 2000. We use only the EDGAR data in the subsequent emission estimates for consistency with both our 2008 emission estimate as well as previous studies, referenced above. The resulting annual CH_2Cl_2 emissions are estimated at 4.9 (2.7–7.2) Gg yr^{-1} in 1998, 7.9 (5.1–10.8) Gg yr^{-1} in 1999 and 12.6 (10.8–14.4) Gg yr^{-1} in 2000. Our emission estimates suggest that emissions have increased significantly over time, from a range of 3–14 Gg in the late 1990s to around 16–25 Gg in 2008.

3.4 CH_2Cl_2 measured during flights across the Atlantic to Central America

The final flight route with the temporal resolution needed for identifying CH_2Cl_2 trends is across the Atlantic to Cen-

tral America (Cuba, the Dominican Republic and northern Venezuela). Figure 6 shows the distribution of CH_2Cl_2 against both latitude and longitude sampled on flights to these destinations. The gradient along the flight tracks, shown in Fig. 6 as average values binned for every 5° latitude and 10° longitude, show very little variation in the early years of the data set (2001–2002). For example, the average CH_2Cl_2 value in the 5° latitude bins varied between 20 and 25 ppt along the entire transect. The mean CH_2Cl_2 concentration was 23.8 (σ 3.9, $n = 9$) ppt between 50 and 55° N and 19.5 (σ 2.6, $n = 8$) ppt between 20 and 25° N. The latitudinal gradient increases over time and can be seen in the binned mean values for 2009–2011 which is to be expected as the northern section of the flight route crosses western Europe (Sect. 3.1). Due to the smaller number of samples collected at the far ends of the transect (e.g. $n = 5$ and $n = 3$ for the far northern and southern bins during the 2009–2011 flights) we do not quantify the gradient along the flight track. However, it is still less pronounced than the latitudinal gradients observed en route to Africa or India, likely due to the influence of clean Atlantic air.

Annual tropospheric values (Fig. 6c) show an increase in time, as discussed in previous sections, although the magnitude of the increase is much smaller and within the levels of variation observed. Unlike previous sections, where we had defined spatial and temporal regions (e.g. Europe, Indian monsoon) for which to calculate CH_2Cl_2 increases, this flight route can provide an idea that we see CH_2Cl_2 increases, albeit small (from 23.2 ppt ($\sigma = 3.6$) to 32.0 ppt ($\sigma = 7.8$)), even in cleaner air masses from over the Atlantic and Central America. There is a lack of CH_2Cl_2 measurements in the Central American region with which to compare the CARBIC data.

Quasi-vertical profiles of CH_2Cl_2 along this route can also provide information on changes in CH_2Cl_2 over time. In Fig. 7 profiles of CH_2Cl_2 are plotted as a function of O_3, as described in Sect. 2. To investigate changes over time, Fig. 7 shows CH_2Cl_2–O_3 profiles for 2000–2002, 2009–2010 and 2011–2012. Samples within each of these 2-year periods are distributed evenly across many months and so it is unlikely that seasonal bias plays a role in the changes observed over time. Between 400 and 500 ppbv O_3 ($n = 4$ for each 2-year period) the median CH_2Cl_2 value increased from 11 ppt in 2001–2002 to 16.0 ppt in 2011–2012. However, due to the low sample number and the high variability this increase is within the uncertainties of these averages.

3.5 Vertical profiles of CH_2Cl_2 in the tropics

Air in the TTL may move quasi-horizontally into the ExTL or the LMS, or vertically into the stratospheric overworld. Despite the fact that only a portion of the air from the TTL moves into the free stratosphere, for short-lived species rapid convective transport to the TTL followed by ascent to the free stratosphere is the most efficient transport pathway to the stratosphere (Law et al., 2007). With a common cruise altitude of 10–12 km, CARIBIC flies at the lower edge of the TTL, which is commonly defined as covering a potential temperature, θ, region of between around 345 K ($\sim$ 12 km) and 380 K ($\sim$ 17 km). For this reason, we present only an upper limit on the changing input of CH_2Cl_2 into this important region.

All data sampled within the tropical latitude band of 25° S to 25° N (the distribution of which can be seen in Fig. 1, with further information in Table 1) were plotted as quasi-vertical profiles relative to θ in Fig. 8. A clear increase in the magnitude of high CH_2Cl_2 "pollution" events can be seen. Because of this skew, median values and the range (min–max) are given for each 5 K altitude bin. In 1998–2002 the median CH_2Cl_2 concentration between 345–350 K was 18.1 (13.4–25.0, $n = 20$) ppt. The median value within this altitude bin between 2009–2012 was 23.2 ppt with a range spanning 12.4 to 90.4 ppt ($n = 97$). The increase in median values is modest due to the inclusion of the 2009–2010 data (see Sect. 3.4). However, despite the variability there is a statistically significant (Mann–Whitney test, $p < 0.05$) difference between the CH_2Cl_2 concentration observed between 345 and 350 K.

With the exception of 2009–2010, see Sect. 3.4, CH_2Cl_2 concentrations observed in this vertical band increased over time, reaching 26.8 (12.4–90.4, $n = 63$) ppt in 2011–2012. Other measurements of CH_2Cl_2 within this region are sparse. In 1991–1992 Schauffler et al. (1993) measured a mean CH_2Cl_2 concentration of 14.9 ($\sigma = 1.1$, $n = 12$) in the TTL between 15.3 and 17.2 km (366–409 K). Schauffler's average is lower than that seen in the early CARIBIC data, although this is likely to be due to the fact that (1) their measurements were taken a few years earlier than CARIBIC; (2) their measurements were taken at a higher altitude; and (3) their suggestion that their mean value was biased low due a high degree of mixing with stratospheric air during their sampling period. Point (3) demonstrates the influence that stratospheric mixing may have in this region and may explain the low values we observed in the 2009–2010 period (see also Sect. 3.4). Between 2009 and 2011 tropical CH_2Cl_2 measurements were made by the HIAPER Pole-to-Pole Observations (HIPPO) project (Wofsy et al., 2012). The HIPPO database contains 20 samples taken within the latitude band $0° \pm 25°$ and within the 345–350 K θ band. These values are reported on the NOAA scale and are therefore comparable with CARIBIC data. The HIPPO results, an average CH_2Cl_2 value of 26.3 (15.9–49.8) ppt, compare well to the CARIBIC results discussed above.

The data in Fig. 8 have been coloured by sampling route, thus providing a rough indication of possible air mass source regions. Of interest is the group of high values in Fig. 8e sampled on the one flight made to Bangkok and Kuala Lumpur at the end of 2012. With the rise of industrial activity in Asia it is likely that emissions of industrial solvent emissions have also increased. Studies in China have shown exceedingly high ground-level concentrations of CH_2Cl_2. For

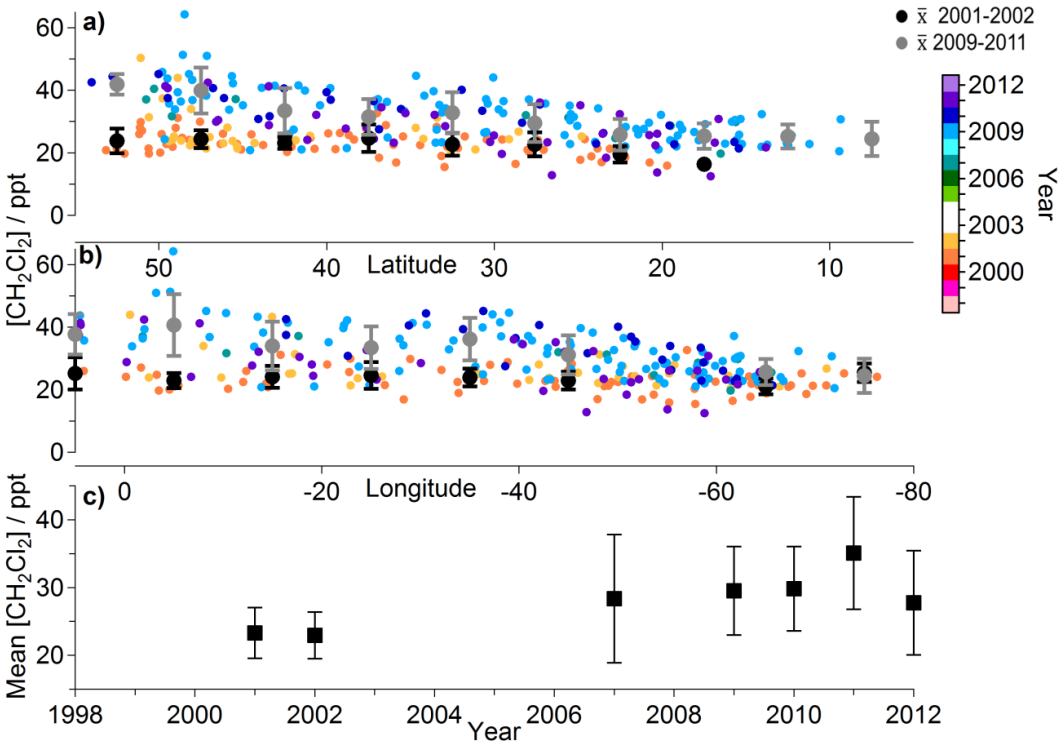

Figure 6. (a) Latitudinal and **(b)** longitudinal distributions of CH_2Cl_2 along flight routes across the North and Central Atlantic to Central America where colour = year (see inset colour bar, colour scale is consistent with Figs. 2, 4 and 6). Average, $\bar{x}$, values for 5° latitude and 10° longitude bins are shown for 2001–2002 and 2009–2011 (see Sect. 3.4), error bars are the 1σ variation within these bands. **(c)** Annual tropospheric values (see Fig. 2) with 1σ error bars.

example, a 2001 study in 45 different Chinese cities by Barletta et al. (2006) saw an urban average of 226 ppt (σ 232) and individual occurrences of up to 3 ppb. It is possible that high levels are also emitted in other industrial parts of Asia, although there are little, if any, ground-based measurements to support this.

3.6 Potential causes for increasing CH_2Cl_2

One likely contributor to the increase in CH_2Cl_2 is the increasing use of hydrofluorocarbons (HFCs) as replacements for ozone-depleting CFCs and HCFCs, the production and consumption of which are strictly controlled by the Montreal Protocol. Specifically, CH_2Cl_2 is used in the production of difluoromethane, also known as HFC-32 (Ramanathan et al., 2004). HFC-32 is used in combination with HFC-125 to make the refrigerant R410A, a direct replacement for HCFC-22. It is estimated that about 96 % of HFC-32 emissions are in the NH (McCulloch, 2004), where the majority of production and consumption of this HFC is likely to occur. Recent analysis of archived and AGAGE air samples shows that HFC-32 has increased from around 0.7 ppt, when the first measurements were made in 2004, to around 6.2 ppt in 2012, with the growth rate reaching 17 % yr^{-1} in recent years (O'Doherty et al., 2014; Montzka et al., 2011b). As HFCs do not deplete stratospheric ozone they are not controlled by the Montreal Protocol. However, they are potent greenhouse gases and, as such, are covered by European legislation controlling their production, consumption and emission. This legislation is likely to reduce CH_2Cl_2 emissions from HFC production in Europe in the coming years. In contrast, it is expected that much of the future demand for HFCs is likely to come from developing countries (Velders et al., 2009). The use of air conditioning systems is growing rapidly in India (e.g. NRDC, 2013); it is the world's third largest consumer of CH_2Cl_2 (IHS, 2014) and HFC-32 production plants have opened in recent years (Daikin, 2012). A rapidly expanding air conditioning industry and increased consumption of CH_2Cl_2 in India could at least partly explain the occurrence of high CH_2Cl_2 observations in the latter years of the CARIBIC data set (Sect. 3.3 and Fig. 4e). A shift in the main consumers and emitters of HFCs is supported by O'Doherty et al. (2014) who suggest that East Asian emissions are underestimated in some inventories (e.g. EDGAR) and that emissions from East Asia are growing in importance.

There are other uses for CH_2Cl_2 which could be contributing to the increasing atmospheric concentrations. Industrial sources include use in office (plastic) materials and electronics (Bin Babar and Shareefdeen, 2014; Kowalska and Gierczak, 2012), the production and use of which is increasing in

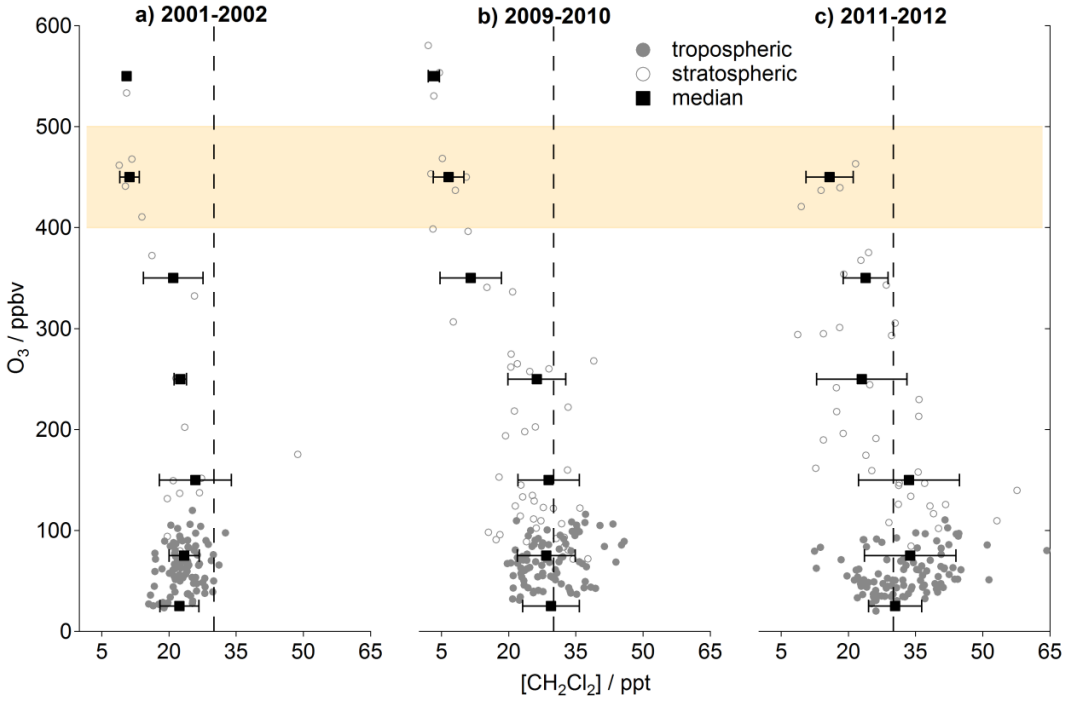

Figure 7. Profiles of CH_2Cl_2 relative to O_3 from samples collected on flights across the North and Central Atlantic to Central America. Median values are for 50 ppb O_3 bins between 0–100 ppbv and 100 ppbv O_3 bins above this, error bars are 1σ. The coloured band highlights the region between 400–500 ppbv O_3 discussed in Sect. 3.4. The dashed line represents 30 ppt of CH_2Cl_2 (see Sect. 1), provided as a visual marker to illustrate the shift over time to higher concentrations of CH_2Cl_2.

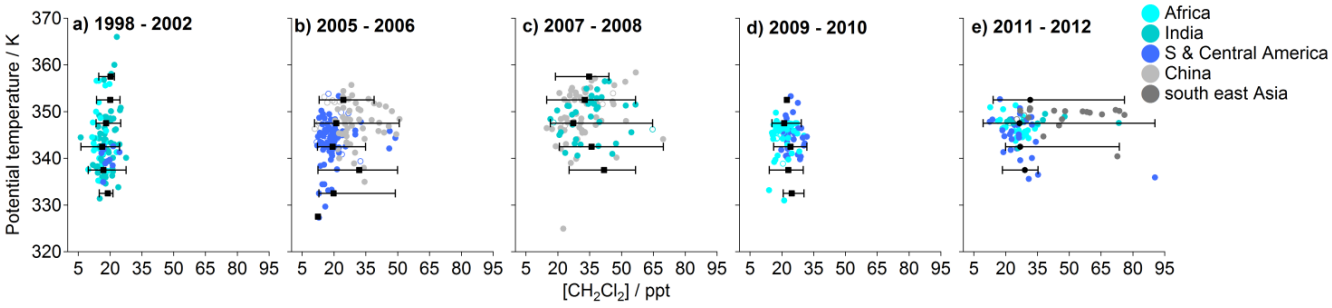

Figure 8. Profiles of CH_2Cl_2 relative to potential temperature for samples taken within the latitude range $0° \pm 25°$. Median (error bars are range) values for 5 K bins are overlaid in black. Colour represents flight route, as shown by the inset colour bar.

developing nations such as India and those in Southeast Asia. A CH_2Cl_2 source from municipal waste disposal (Majumdar and Srivastava, 2012) may be of particular importance for India where mismanagement of waste disposal has been found to lead to high levels of fugitive volatile organic compound emissions from waste disposal sites. CH_2Cl_2 is also used by the pharmaceutical industry in drug preparation, where its use may be increasing as a replacement for CCl_4 which is regulated by the Montreal Protocol (UNEP CAP, 2009).

The likely sources of increased CH_2Cl_2 emissions over the past decade suggest that India might be an increasingly important source of industrial CH_2Cl_2 emissions, as seen in the CARIBIC data set, although its emissions are still small on a global scale. We estimate CH_2Cl_2 emissions from the Indian region in 2008 to be in the region of 20.3 (15.8–24.8) Gg. This is similar to an estimate of 24 (16–33) Gg yr^{-1} for 2005 USA emissions calculated by Millet et al. (2009). The latest global estimate provided by the WMO (Montzka et al., 2011b) gave global emissions of 515 Gg yr^{-1} for 1999–2003 based on Simmonds et al., 2006). Both the India and USA emissions are small fractions of this total (which is a lower limit due to the time frame it was based upon and the increasing emissions over time) suggesting that other regions contribute significantly. Significant growth in industrial production and consumption of HFCs in Asia, in particular in China, was projected by Velders et al. (2009), suggesting that these

regions may be or may become important source regions of CH_2Cl_2 and warrant further study.

4 Conclusions

Results from CARIBIC flights spanning a significant part of the world provide evidence that CH_2Cl_2 has increased in the atmosphere since our measurements began in 1998, consistent with the increase observed at a remote surface site, MHD. A summary of the increase seen in each region is provided in Table 2. An increase of between 38 % (Atlantic routes) to 69 % (India monsoon route) was observed, corresponding to an increase of between $\sim$ 7–9 ppt in cleaner air masses, such as those encountered on flights to South Africa and across the North and Central Atlantic and $\sim$ 12–15 ppt in air masses over industrial regions such as Europe and India. This increase was seen in the average CH_2Cl_2 observations for each region, as well as in an increase in high-concentration "pollution" events (e.g. Figs. 4 and 8). The increase is most likely a result of increasing industrial use of CH_2Cl_2, such as its use as a feedstock for the production of HFC-32.

Our results show that CH_2Cl_2 emissions from the Indian subcontinent have increased two- to fourfold in a decade (1998–2008). The annual emissions from the Indian region in 2008, at $\sim$ 20 Gg, are similar to those estimated for the USA in 2005. Other Asian regions may also prove to be emitting large quantities of CH_2Cl_2: from a limited data set we suggest that Southeast Asia may be an important source region. However, there are few in situ data available for this region and further investigations are warranted.

Increases in CH_2Cl_2 in UT air masses with the potential to enter the TTL can also be observed in the CARIBIC database. Whilst CH_2Cl_2 is only a minor contributor to stratospheric ozone depletion, many other chlorocarbons have stable (e.g. CH_3Cl, see Umezawa et al., 2014) or decreasing (e.g. CFCs, CH_3CCl_3) atmospheric abundances. As our data suggest that CH_2Cl_2 may still be increasing in the atmosphere its relative importance may increase if this trend continues.

The Supplement related to this article is available online at doi:10.5194/acp-15-1939-2015-supplement.

Acknowledgements. The authors would like to thank the CARIBIC team and associated partner institutions, Lufthansa Airlines, Lufthansa Technik and Fraport for their work and support that has led to the success of CARIBIC over many years. In particular we thank Andreas Zahn and colleagues for the O_3 data, Dieter Scharffe for the CO data and Peter van Velthoven for the back-trajectory information. Thanks to Claus Koeppel, Dieter Scharffe, Stefan Weber and Martin Körner for facilitating the operations of the container and TRAC samplers before, during and after flights. Early CARIBIC samples were partly analysed at UEA by Georgina Sturrock. J. Laube acknowledges the support of a NERC fellowship (no. NE/I021918/1). The data available in the Supplementary Information would not be possible without the staff at the Cape Grim station and at CSIRO GASLAB Aspendale collecting and maintaining the Cape Grim air archive and preparing the UEA flask and sub-samples. S. Montzka acknowledges the technical assistance of C. Siso, B. Hall, and B. Miller in making NOAA flask measurements at MHD and other sites, and support, in part, by NOAA Climate Program Office's AC4 Program. We also acknowledge CSIRO and the Bureau of Meteorology for funding these activities.

The service charges for this open-access publication have been covered by the Max Planck Society.

Edited by: N. Harris

References

Bin Babar, Z. and Shareefdeen, Z.: Management and control of air emissions from electronic industries, Clean Tech. Envir., 16, 69–77, doi:10.1007/s10098-013-0594-6, 2014.

Baker, A. K., Slemr, F., and Brenninkmeijer, C. A. M.: Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft, Atmos. Meas. Tech., 3, 311–321, doi:10.5194/amt-3-311-2010, 2010.

Baker, A. K., Schuck, T. J., Slemr, F., van Velthoven, P., Zahn, A., and Brenninkmeijer, C. A. M.: Characterization of non-methane hydrocarbons in Asian summer monsoon outflow observed by the CARIBIC aircraft, Atmos. Chem. Phys., 11, 503–518, doi:10.5194/acp-11-503-2011, 2011.

Baker, A. K., Schuck, T. J., Brenninkmeijer, C. A. M., Rauthe-Schöch, A., Slemr, F., Van Velthoven, P. F. J., and Lelieveld, J.: Estimating the contribution of monsoon-related biogenic production to methane emissions from South Asia using CARIBIC observations, Geophys. Res. Lett., 39, L10813, doi:10.1029/2012GL051756, 2012.

Barletta, B., Meinardi, S., Simpson, I. J., Rowland, F. S., Chan, C.-Y., Wang, X., Zou, S., Chan, L. Y., and Blake, D. R.: Ambient halocarbon mixing ratios in 45 Chinese cities, Atmos. Environ., 40, 7706–7719, doi:10.1016/j.atmosenv.2006.08.039, 2006.

Brenninkmeijer, C. A. M., Crutzen, P. J., Fischer, H., Güsten, H., Hans, W., Heinrich, G., Heintzenberg, J., Hermann, M., Immelmann, T., Kersting, D., Maiss, M., Nolle, M., Pitscheider, A., Pohlkamp, H., Scharffe, D., Specht, K., and Wiedensohler, A.: CARIBIC – Civil aircraft for global measurement of trace gases and aerosols in the tropopause region, J. Atmos. Ocean. Tech., 16, 1373–1383, doi:10.1175/1520-0426(1999)016<1373:CCAFGM>2.0.CO;2, 1999.

Brenninkmeijer, C. A. M., Crutzen, P., Boumard, F., Dauer, T., Dix, B., Ebinghaus, R., Filippi, D., Fischer, H., Franke, H., Frieß, U., Heintzenberg, J., Helleis, F., Hermann, M., Kock, H. H., Koeppel, C., Lelieveld, J., Leuenberger, M., Martinsson, B. G., Miemczyk, S., Moret, H. P., Nguyen, H. N., Nyfeler, P., Oram, D., O'Sullivan, D., Penkett, S., Platt, U., Pupek, M., Ramonet, M., Randa, B., Reichelt, M., Rhee, T. S., Rohwer, J., Rosenfeld, K.,

Scharffe, D., Schlager, H., Schumann, U., Slemr, F., Sprung, D., Stock, P., Thaler, R., Valentino, F., van Velthoven, P., Waibel, A., Wandel, A., Waschitschek, K., Wiedensohler, A., Xueref-Remy, I., Zahn, A., Zech, U., and Ziereis, H.: Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system, Atmos. Chem. Phys., 7, 4953–4976, doi:10.5194/acp-7-4953-2007, 2007.

Cox, M. L., Sturrock, G. A., Fraser, P. J., Siems, S. T., Krummer, P. B., and O'Doherty, S.: Regional sources of methyl chloride, chloroform and dichloromethane identified from AGAGE observations at Cape Grim, Tasmania, 1998–2000, J. Atmos. Chem., 45, 79–99, doi:10.1023/A:1024022320985, 2003.

Cox, R. A., Derwent, R. G., and Eggleton, E. J.: Photochemical oxidation of halocarbons in the troposphere, Atmos. Environ., 10, 305–308, doi:10.1016/0004-6981(76)90170-0, 1976.

Daikin: World's first commercialization of air conditioning equipment using next-generation refrigerant HFC-32 by Daikin, available at: http://www.daikin.com/press/2012/120927/index.html (last access: 11 April 2014), 2012.

Dalvi, M., Beig, G., Patil, U., Kaginalkar, A., Sharma, C., and Mitra, A. P.: A GIS based methodology for gridding of large-scale emission inventories: Application to carbon-monoxide emissions over Indian region, Atmos. Environ., 40, 2995–3007, doi:10.1016/j.atmosenv.2006.01.013, 2006.

Dickerson, R. R., Andreae, M. O., Campos, T., Mayol-Bracero, O. L., Neusuess, C., and Streets, D. G.: Analysis of black carbon and carbon monoxide observed over the Indian Ocean: Implications for emissions and photochemistry, J. Geophys. Res., 107, 8017, doi:10.1029/2001JD000501, 2002.

European Chlorinated Solvent Association (E.C.S.A.): White Paper - methylene chloride, available at: http://www.eurochlor.org/media/12847/5-1-2-1_white_paper_methylene_chloride.pdf (last access: 30 August 2014), 2007.

Fortems-Cheiney, A., Chevallier, F., Pison, I., Bousquet, P., Szopa, S., Deeter, M. N., and Clerbaux, C.: Ten years of CO emissions as seen from Measurements of Pollution in the Troposphere (MOPITT), J. Geophys. Res., 116, D05304, doi:10.1029/2010JD014416, 2011.

Gautrois, M., Brauers, T., Koppmann, R., Rohrer, F., Stein, O., and Rudolph, J.: Seasonal variability and trends of volatile organic compounds in the lower polar troposphere, J. Geophys. Res., 108, 4393, doi:10.1029/2002JD002765, 2003.

Gentner, D. R., Miller, A. M., and Goldstein, A. H.: Seasonal variability in anthropogenic halocarbon emissions, Env. Sci. Tech., 44, 5377–5382, doi:10.1021/es1005362, 2010.

Hall, B. D., Engel, A., Mühle, J., Elkins, J. W., Artuso, F., Atlas, E., Aydin, M., Blake, D., Brunke, E.-G., Chiavarini, S., Fraser, P. J., Happell, J., Krummel, P. B., Levin, I., Loewenstein, M., Maione, M., Montzka, S. A., O'Doherty, S., Reimann, S., Rhoderick, G., Saltzman, E. S., Scheel, H. E., Steele, L. P., Vollmer, M. K., Weiss, R. F., Worthy, D., and Yokouchi, Y.: Results from the International Halocarbons in Air Comparison Experiment (IHALACE), Atmos. Meas. Tech., 7, 469–490, doi:10.5194/amt-7-469-2014, 2014.

IHS: Chlorinated methanes, available at: http://www.ihs.com/products/chemical/planning/ceh/chlorinatedmethanes.aspx, last access: 13 May 2014.

JRC & PBL (European Commission Joint Research Centre, JRC, and the Netherlands Environmental Assessment Agency, PBL): Emission Database for Global Atmospheric Research (EDGAR), release version 4.0, available at: http://edgar.jrc.ec.europa.eu/, 2009.

Koppmann, R., Johnen, F. J., Plass-Dulmer, C., and Rudolph, J.: Distribution of methyl chloride, dichloromethane, trichloroethene and tetrachloroethene over the North and South Atlantic, J. Geophys. Res., 98, 517–526, doi:10.1029/93JD01864, 1993.

Kowalska, J. and Gierczak, T.: Qualitative and quantitative analyses of the halogenated volatile organic compounds emitted from the office equipment items, Indoor Built Environ., 22, 920–931, doi:10.1177/1420326X12458299, 2012.

Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Worton, D. R., Sturges, W. T., Grunow, K., and Schmidt, U.: Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics – a case study, Atmos. Chem. Phys., 8, 7325–7334, doi:10.5194/acp-8-7325-2008, 2008.

Laube, J. C., Martinerie, P., Witrant, E., Blunier, T., Schwander, J., Brenninkmeijer, C. A. M., Schuck, T. J., Bolder, M., Röckmann, T., van der Veen, C., Bönisch, H., Engel, A., Mills, G. P., Newland, M. J., Oram, D. E., Reeves, C. E., and Sturges, W. T.: Accelerating growth of HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane) in the atmosphere, Atmos. Chem. Phys., 10, 5903–5910, doi:10.5194/acp-10-5903-2010, 2010.

Law, K. S., Sturges, W. T., Blake, D. R., Blake, N. J., Burkholder, J. B., Butler, J. H., Cox, R. A., Haynes, P. H., Ko, M. K. W., Kreher, K., Mari, C., Pfeilsticker, K., Plane, J. M. C., Salawitch, R. J., Schiller, C., Sinnhuber, B.-M., von Glasow, R., Warwick, N. J., Weubbles, D. J., Yvon-Lewis, S. A., Butz, A., Considine, D. B., Dorf, M., Froidevaux, L., Kovalenko, L. J., Livesey, N. J., Nassar, R., Sioris, C. E., and Weisenstein, D. K.: Chapter 2. Halogenated Very Short-Lived Substances, in: Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project Report No. 50, World Meteorological Organization, Geneva, Switzerland, 2007.

Majumdar, D. and Srivastava, A.: Volatile organic compound emissions from municipal solid waste disposal sites: A case study of Mumbai, India, JAPCA J. Air Waste Ma., 62, 398–407, doi:10.1080/10473289.2012.655405, 2012.

McCulloch, A.: Determination of comparative HCFC and HFC emission profiles for the foam and refrigeration sectors until 2015. Part 3: Total emissions and global atmospheric concentrations, Marbury Technical Consulting and University of Bristol, 2004.

McCulloch, A. and Midgley, P. M.: The production and global distribution of emissions of trichloroethene, tetrachloroethene and dichloromethane over the period 1988–1992, Atmos. Environ., 30, 601–608, doi:10.1016/1352-2310(09)50032-5, 1996.

McCulloch, A., Aucott, M. L., Graedel, E., Kleinman, G., Midgley, P. M., and Li, Y.-F.: Industrial emissions of trichloroethene, tetrachloroethene and dichloromethane: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8417–8427, doi:10.1029/1999JD900011, 1999.

Miller, J. B., Lehman, S. J., Montzka, S. A., Sweeney, C., Miller, B. R., Karion, A., Wolak, C., Dlugokencky, E. J., Southon, J., Turnbull, J. C., and Tans, P. P.: Linking emissions of fossil fuel CO_2 and other anthropogenic trace gases using atmospheric $^{14}CO_2$, J. Geophys. Res., 117, D08302, doi:10.1029/2011JD017048, 2012.

Millet, D. B., Atlas, E. L., Blake, D. R., Blake, N. J., Diskin, G. S., Holloway, J. S., Hudman, R. C., Meinardi, S., Ryerson, T. B., and Sachse, G. W.: Halocarbon emissions from the United States and Mexico and their global warming potential, Env. Sci. Tech., 43, 1055–1060, doi:10.1021/es802146j, 2009.

Montzka, S. A., Krol, M., Blugokencky, E., Hall, B., Jöckel, P., and Lelieveld, J.: Small interannual variability of global atmospheric hydroxyl, Science, 331, 67–69, doi:10.1126/science.1197640, 2011a.

Montzka, S. A., Reimann, S., Engel, A., Kruger, K., O'Doherty, S., Sturges, W. T., Blake, D., Dorf, M., Fraser, P., Friodevaux, L., Jucks, K., Kreher, K., Kurylo, M. J., Miller, J., Neilson, O.-J., Orkin, V. L., Prinn, R. G., Rhew, R., Santee, M. L., Stohl, A., and Verdonik, D.: Chapter 1. Ozone-Depleting Substances (ODSs) and Related Chemicals, in: WMO Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, World Meteorological Organization, Geneva, Switzerland, 2011b.

NRDC (National Resources Defense Council): Cooling India with less warming: The business case for phasing down HFCs in room and vehicle air conditioners available at: http://www.nrdc.org/international/india/files/air-conditioner-efficiency-IP.pdf (last access: 11 April 14), 2013.

O'Doherty, S., Rigby, M., Mühle, J., Ivy, D. J., Miller, B. R., Young, D., Simmonds, P. G., Reimann, S., Vollmer, M. K., Krummel, P. B., Fraser, P. J., Steele, L. P., Dunse, B., Salameh, P. K., Harth, C. M., Arnold, T., Weiss, R. F., Kim, J., Park, S., Li, S., Lunder, C., Hermansen, O., Schmidbauer, N., Zhou, L. X., Yao, B., Wang, R. H. J., Manning, A. J., and Prinn, R. G.: Global emissions of HFC-143a (CH_3CF_3) and HFC-32 (CH_2F_2) from in situ and air archive atmospheric observations, Atmos. Chem. Phys., 14, 9249–9258, doi:10.5194/acp-14-9249-2014, 2014.

Olivier, J. G. J., Bloos, J. P. J., Berdowski, J. J. M., Visschedijk, A. J. H., and Bouwman, A. F.: A 1990 global emission inventory of anthropogenic sources of carbon monoxide on $1° \times 1°$ developed in the framework of EDGAR/GEIA, Chemosphere – Global Change Science, 1, 1–17, doi:10.1016/S1465-9972(99)00019-7, 1999.

Palmer, P. I., Jacob, D. J., Mickley, L. J., Blake, D. R., Sachse, G. W., Fuelberg, H. E., and Kiley, C. M.: Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data, J. Geophys. Res.-Atmos., 108, 4753, doi:10.1029/2003JD003591, 2003.

Randel, W. J. and Park, M.: Deep convective influence on the Asian summer monsoon anticyclone and associated tracer variability observed with Atmospheric Infrared Sounder (AIRS), J. Geophys. Res., 111, D12314, 2006.

Ramanathan, R., Anand, R., Jain, A., and Rao, J. M.: Process for the production of difluoromethane, United States Patent no. US 6,723,887 B2, 2004.

Rauthe-Schöch, A., Baker, A. K., Schuck, T., Brenninkmeijer, C. A. M., Zahn, A., Herrmann, M., Stratmann, G., Ziereis, H., and van Velthoven, P.: Pollution transport from the South Asian Monsoon anticyclone, Atmos. Chem. Phys. Discuss., submitted, 2015.

Roberts, G., Wooster, M. J., and Lagoudakis, E.: Annual and diurnal african biomass burning temporal dynamics, Biogeosciences, 6, 849–866, doi:10.5194/bg-6-849-2009, 2009.

Rudolph, J., Khedim, A., Koppmann, R., and Bonsang, B.: Field study of the emissions of methyl chloride and other halocarbons from biomass burning in western Africa, J. Atmos. Chem., 22, 67–80, doi:10.1007/BF00708182, 1995.

Scharffe, D., Slemr, F., Brenninkmeijer, C. A. M., and Zahn, A.: Carbon monoxide measurements onboard the CARIBIC passenger aircraft using UV resonance fluorescence, Atmos. Meas. Tech., 5, 1753–1760, doi:10.5194/amt-5-1753-2012, 2012.

Schauffler, S. M., Heidt, L. E., Pollock, W. H., Gilpin, T. M., Vedder, J. F., Solomon, S., Lueb, R. A., and Atlas, E. L.: Measurements of halogenated organic compounds near the tropical tropopause, Geophys. Res. Lett., 20, 2567–2570, doi:10.1029/93GL02840, 1993.

Scheele, M. P., Siegmund, P. C., and Van Velthoven, P. F. J.: Sensitivity of trajectories to data resolution and its dependence on the starting point: in or outside a tropopause fold, Meteorol. Appl., 3, 267–273, doi:10.1002/met.5060030308, 1996.

Scheeren, H., Lelieveld, J., De Gouw, J. A., Van der Veen, C., and Fischer, H.: Methyl chloride and other chlorocarbons in polluted air during INDOEX, J. Geophys. Res., 107, 8015, doi:10.1029/2001JD001121, 2002.

Scheeren, H. A., Lelieveld, J., Roelofs, G. J., Williams, J., Fischer, H., de Reus, M., de Gouw, J. A., Warneke, C., Holzinger, R., Schlager, H., Klüpfel, T., Bolder, M., van der Veen, C., and Lawrence, M.: The impact of monsoon outflow from India and Southeast Asia in the upper troposphere over the eastern Mediterranean, Atmos. Chem. Phys., 3, 1589–1608, doi:10.5194/acp-3-1589-2003, 2003.

Schuck, T. J., Brenninkmeijer, C. A. M., Slemr, F., Xueref-Remy, I., and Zahn, A.: Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft, Atmos. Meas. Tech., 2, 449–464, doi:10.5194/amt-2-449-2009, 2009.

Schuck, T. J., Brenninkmeijer, C. A. M., Baker, A. K., Slemr, F., von Velthoven, P. F. J., and Zahn, A.: Greenhouse gas relationships in the Indian summer monsoon plume measured by the CARIBIC passenger aircraft, Atmos. Chem. Phys., 10, 3965–3984, doi:10.5194/acp-10-3965-2010, 2010.

Simmonds, P. G., Manning, A. J., Cunnold, D. M., McCulloch, A., O'Doherty, S., Derwent, R. G., Krummel, P. B., Fraser, P. J., Dunse, B., Porter, L. W., Wang, R. H. J., Greally, B. R., Miller, B. R., Salameh, P., Weiss, R. F., and Prinn, R. G.: Global trends, seasonal cycles, and European emissions of dichloromethane, trichloroethene, and tetrachloroethene from the AGAGE observations at Mace Head, Ireland, and Cape Grim, Tasmania, J. Geophys. Res., 111, D18304, doi:10.1029/2006JD007082, 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: C1-C10 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.

Sprung, D. and Zahn, A.: Acetone in the upper troposphere/lowermost stratosphere measured by the CARIBIC passenger aircraft: Distribution, seasonal cycle, and variability, J. Geophys. Res., 115, D16301, doi:10.1029/2009JD012099, 2010.

Streets, D. G., Bond, T. C., Carmichael, R., Fernandes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J.-H., and Yarber, K. F.: An inventory of gaseous and

primary aerosol emissions in Asia in the year 2000, J. Geophys. Res., 108, 8809, doi:10.1029/2002JD003093, 2003.

Thouret, V., Cammas, J.-P., Sauvage, B., Athier, G., Zbinden, R., Nédélec, P., Simon, P., and Karcher, F.: Tropopause referenced ozone climatology and inter-annual variability (1994–2003) from the MOZAIC programme, Atmos. Chem. Phys., 6, 1033–1051, doi:10.5194/acp-6-1033-2006, 2006.

Trudinger, C. M., Etheridge, D. M., Sturrock, G. A., Fraser, P. J., Krummer, P. B., and McCulloch, A.: Atmospheric histories of halocarbons from analysis of Antarctic firn air: Methyl bromide, methyl chloride, chloroform, and dichloromethane, J. Geophys. Res., 109, D22310, doi:10.1029/2004JD004932, 2004.

Umezawa, T., Baker, A. K., Oram, D., Sauvage, C., O'Sullivan, D., Rauthe-Schöch, A., Montzka, S. A., Zahn, A., and Brenninkmeijer, C. A. M.: Methyl chloride in the upper troposphere observed by the CARIBIC passenger aircraft observatory: large-scale distributions and Asian summer monsoon outflow, J. Geophys. Res.-Atmos., 119, 5542–5558, doi:10.1002/2013JD021396, 2014.

UNEP CAP (United Nations Environment Programme Compliance Assistance Programme): Fact Sheet no.26. Alternatives for Carbon Tetrachloride – CCl_4 (CTC) in laboratory and analytical uses, United Nations Environment Programme Compliance Assistance Programme, 2009.

Velders, G. J. M., Fahey, D. W., Daniel, J. S., McFarland, M., and Andersen, S. O.: The large contribution of projected HFC emissions to future climate forcing, PNAS, 106, 10949–10954, doi:10.1073/pnas.0902817106, 2009.

Villenave, E., Orkin, V. L., Huie, R. E., and Kurylo, M. J.: Rate Constant for the reaction of OH radicals with dichloromethane, J. Phys. Chem., 101, 8513–8517, doi:10.1021/jp9721614, 1997.

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.

Warneck, P.: Chemistry of the Natural Atmosphere, Academic Press, London, 1st edition, 1988.

Wisher, A., Oram, D. E., Laube, J. C., Mills, G. P., van Velthoven, P., Zahn, A., and Brenninkmeijer, C. A. M.: Very short-lived bromomethanes measured by the CARIBIC observatory over the North Atlantic, Africa and Southeast Asia during 2009–2013, Atmos. Chem. Phys., 14, 3557–3570, doi:10.5194/acp-14-3557-2014, 2014.

Wofsy, S. C., Daube, B. C., Jimenez, R., Kort, E., Pittman, J. V., Park, S., Commane, R., Xiang, B., Santoni, G., Jacob, D., Fisher, J., Pickett-Heaps, C., Wang, H., Wecht, K., Wang, Q.-Q., Stephens, B. B., Shertz, S., Watt, A. S., Romashkin, P., Campos, T., Haggerty, J., Cooper, W. A., Rogers, D., Beaton, S., Hendershot, R., Elkins, J. W., Fahey, D. W., Gao, R. S., Moore, F., Montzka, S. A., Schwarz, J. P., Perring, A. E., Hurst, D., Miller, B. R., Sweeney, C., Oltmans, S., Nance, D., Hintsa, E., Dutton, G., Watts, L. A., Spackman, J. R., Rosenlof, K. H., Ray, E. A., Hall, B., Zondlo, M. A., Diao, M., Keeling, R., Bent, J., Atlas, E. L., Lueb, R., Mahoney, M. J.: HIPPO Combined Discrete Flask and GC Sample GHG, Halo-, Hydrocarbon Data (R_20121129), available at: http://dx.doi.org/10.3334/CDIAC/hippo_012 (Release 20121129), file HIPPO_noaa_flask_allparams_merge_insitu_20121129 (last access: 6 April 2014), Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA, 2012.

Wood, M.: Resample procedure for bootstrap confidence intervals, available at: http://woodm.myweb.port.ac.uk/programs.htm (last access: 8 April 2014), 2003.

Worton, D. R., Sturges, W. T., Schwander, J., Mulvaney, R., Barnola, J.-M., and Chappellaz, J.: 20th century trends and budget implications of chloroform and related tri-and dihalomethanes inferred from firn air, Atmos. Chem. Phys., 6, 2847–2863, doi:10.5194/acp-6-2847-2006, 2006.

Zahn, A. and Brenninkmeijer, C. A. M.: New Directions: A Chemical Tropopause Defined, Atmos. Environ., 37, 439–440, doi:10.1016/S1352-2310(02)00901-9, 2003.