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

E. C. Leedham Elvidge[1], D. E. Oram[2], J. C. Laube[2], A. K. Baker[1], S. A. Montzka[3], 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 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)

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Abstract

Dichloromethane, CH_2Cl_2, is a short-lived chlorocarbon of predominantly anthropogenic origin. Increasing industrial usage and associated emissions resulted in an increasing atmospheric burden throughout the 1900s. Atmospheric abundance peaked around 1990 and was followed by a decline in the early part of the 21st century. Despite the importance of ongoing monitoring and reporting of atmospheric CH_2Cl_2 (it is a regulated toxic air pollutant and a contributor to stratospheric ozone depletion) 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 traversed 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 ∼ 7–9 ppt in background air to ∼ 12–15 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 3–15 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 %) industrial origin. Its main applications include use in paint strippers, degreasers and solvents; in foam production and blowing applications; and as an agricultural fumigant (Montzka et al., 2011b). The most recent estimation (Simmonds et al., 2006) for its natural component suggests it is comprised of a 10 % combined biomass burning and marine source. 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 (Simmonds et al., 2006).

Long-term trends in atmospheric CH_2Cl_2 have been observed since measurements began in the 1970s. 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 (±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). 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 manuscript and are included in Table 2) 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

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Arctic, observed a decline of around -4% (-1.8 ppt) per year (Gautrois et al., 2003). An in-depth discussion of many of the observations during this period can be found in Simmonds et al. (2006).

Short-lived chlorocarbons, including CH_2Cl_2, contribute to stratospheric chlorine and its cycling with stratospheric ozone. 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. At 10–12 km, the contribution of very short-lived chlorocarbons to total atmospheric chlorine is dominated by CH_2Cl_2 and $CHCl_3$. Whilst $CHCl_3$ is of predominantly natural origin, CH_2Cl_2 has a mainly anthropogenic source and so is susceptible to changes in industrial emissions. Montzka et al. (2011b) reported increasing CH_2Cl_2 concentrations in recent years, with 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 $CHCl_3$, 7 % 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 Supplement) whose time series of CH_2Cl_2 between 1995 to 2009 shows increasing atmospheric concentrations in recent years. CH_2Cl_2 is also of concern as it is also a toxic air pollutant and carcinogen and, as such, is regulated by national and EU law. Altogether, an improved understanding of the recent changes in atmospheric CH_2Cl_2 is desirable. For this reason we present and discuss measurements of air samples obtained by the CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) observatory.

2 Methods

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 12 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 14 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).

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 (V.G./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

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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),

5   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 for small changes in instrument response.

10   The V.G. Autospec system was used from the start of analysis at UEA in June 1998 until December 1999. It was then replaced by a second system consisting of an Agilent 6890 GC and 5973 quadrupole MS. With this system pre-concentration was achieved using a commercial, fully automated, 3-stage pre-concentrator (Entech Instruments, model 7100). This system was used throughout the rest of CARIBIC1 and CARIBIC2.

15   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

20   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

25   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

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of the quadrupole analyser is more stable than the Autospec, the working standard is analysed less frequently.

To assist with the transition between the V.G. 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 5 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 5 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 V.G. Autospec value was selected based on the better precision of this instrument.

To provide additional support to the CARIBIC2 dataset, three flights, one per year between 2009–2011, were also analysed on a highly sensitive Waters Autospec magnetic sector GCMS. This system is the direct replacement of the V.G. 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 very similar. 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.

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 Supplementary Material. In Sect. 3.1, CARIBIC data are

compared to the long term CH_2Cl_2 record from Mace Head, Ireland (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. For further information see Montzka et al. (2011a) and http://www.esrl.noaa.gov/gmd/hats/gases/CH2Cl2.html. A compari-

5 son between NOAA and UEA calibration scales is discussed in the Supplement 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, with no apparent offset or change in the relationship between both groups' results over time. Throughout this manuscript we refer to the dry air mole fraction of CH_2Cl_2 as "concentrations" to

10 increase the accessibility and readability of this manuscript.

Analytical precision during CARIBIC1 was 0.9 % for the V.G. 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 cal-

15 culated 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–September 2006, 4.03 % between October 2006–October 2009, 5.54 % between November 2009–October 2012 and 3.3 % in November and December 2012. Average precision for the Autospec system during CARIBIC2 was 0.48 %.

20 The final dataset used in this study is from 1998–2002 and 2005–2012.

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

25 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 accord-

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ing to the method in Zahn & Brenninkmeijer (2003), see also Sect. 3.4. As tropospheric trends in CH_2Cl_2 form the focus of this investigation, stratospherically-influenced samples (which comprised between $\sim$ 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 are 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) are integrated (int.) 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 knmi.nl/samenw/campaign_support/CARIBIC/ or in Scheele et al. (1996). The trajectory model uses 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 1998–2012 CARIBIC flights covered a substantial portion of the global free troposphere (Fig. 1). For the purpose of this investigation several regions were selected. Firstly, a European region within a box spanning 40 to 55° N and −10 to 20° E (Frankfurt Airport = 50.03° N, 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 investi-

gate 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 manuscript mean values prefaced by ± refer to the 1 sigma standard error associated with this average.

3.1 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 in the boundary layer air samples from Mace Head whereas the CARIBIC data show greater variability. This variability in the CARIBIC data is mainly as a result of the fact that these samples represent a wide variety of air masses sampled over a large area (Fig. 2c). 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 previous studies have observed seasonality in data collected by aircraft at an average altitude of 4 km (Miller et al., 2012) we do not see a strong seasonal pattern at 10–12 km in our more sporadic dataset. 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. As seen in Fig. 2a, only a small number of NOAA samples were collected in the first few years of the dataset. Due to this small sample size, biases, for example the influence of seasonality, could be introduced. This adds an additional, unquantified uncertainty to these averages. 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). Both CARIBIC and NOAA data show relatively stable concentrations in the first few years of the dataset followed by steadily increasing concentrations from around 2004 seen on top of the seasonal cycle. The mean CH_2Cl_2 concentration (sample number, $n = 16$) for the first four years of the CARIBIC dataset (1998 to 2001) was compared to the mean CH_2Cl_2 concentration ($n = 49$) for the last four years (2009 to 2012). Mean values were 24.9 ($\pm$1.1) ppt and 38.6 ($\pm$1.2) ppt respectively, an increase of 13.7 ($\pm$1.6) ppt or 55 % between these periods. The increase is consistent with that seen at Mace Head where CH_2Cl_2 increased from 32.1 ($\pm$1.6) ppt to 45.7 ($\pm$0.7) ppt ($n = 15$ and 88 respectively), an increase of 13.6 ($\pm$1.7) ppt. Annual mean values are higher at Mace Head (Fig. 2c). As NOAA and UEA calibration scales compare well (Supplement) this is likely to be as a result of the NOAA samples having been collected at a lower altitude than the CARIBIC samples. NOAA data from Cape Grim (Supplement), representative of clean SH air masses, also show an increase in CH_2Cl_2 concentrations over time, although the Cape Grim trend will not be discussed further here. A summary of descriptive statistics for each region, alongside comparative data from the literature, is provided in Table 2. Measurements in the NH at flight altitudes similar to CARIBIC were made by Simpson et al. (2011). They reported an average of 35.8 ppt over Canada and Greenland in 2008, a value similar to our mean of 36.2 ± 2.9 ppt during this year.

3.2 Africa

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 difference between mean values above and below 30° N has increased over time, from 5.9 ppt in 2000 and 11.5 ppt in 2009–2011. 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.

Mean tropospheric values measured in years for which data are available are shown in Fig. 3b, separated into samples taken above and below 30° N. A statistically significant (Mann-Whitney Rank Sums Test, $p < 0.001$) increase in CH_2Cl_2 is seen between samples collected in 1998–2001 and those collected in 2009–2011. As the northern (above 30° N) segment of the flight route crosses Europe the increase seen over time, 12.5 (±1.8) ppt or 58 %, is similar to that discussed in Sect. 3.1. The increase is slightly lower at latitudes < 30° N, a 44 % increase in CH_2Cl_2, 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 dataset (Fig. 2), suggest that concentrations continue to increase into the 2010s.

Despite the importance of biomass burning with respect to atmospheric trace gases 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 communications, 2014).

3.3 India

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., 2012, 2011; 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.

During 2008, the ASM was a particular focus of CARIBIC with flights to India occurring before, during and after the ASM. For this reason we will 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 ∼ 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 ∼ 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 ∼ 25–40° 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

5 (Fig. 4e). Exceedingly high CH_2Cl_2 levels were observed towards lower latitudes for one of the 2011 flights. These high values are in contrast with the lower concentrations seen at low latitudes during flights over Africa (Sect. 3.2) and to Central America (Sect. 3.4). As with the high values in 2008 (Fig. 4c), analysis of back trajectories indicate these air masses originated from a low altitude over India and Southeast Asia.

10 This region is discussed further in Sect. 3.5.

Increases were calculated for the period between 1998–2000 and 2008, not including 2011–2012 due to the small sample size and large variability. Between 1998–2000 and 2008 CH_2Cl_2 increased by 14.9 (±1.4) ppt (69 %) in the monsoon period and 10.3 (±1.3) ppt (51 %) in the non-monsoon months (Table 2). Measurements of air

15 masses from the Indian and south Asian region were made by Scheeren et al. (2003a, 2002) 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 ~ 20–22 ppt.

20 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. This makes the ASM an ideal case study for calculating emission estimates using the CARIBIC dataset. As the majority of CH_2Cl_2 emissions are indus-

25 trial we assume 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 ab-

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sence of seasonality based on their analysis of data on the global industrial data us of CH$_2$Cl. Previous analyses of meteorological parameters during 2008 (Rauthe-Schöch et al., 2014; 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$_2$Cl$_2$ were measured and which were collected $< 40°$ N (Baker et al., 2011; Schuck et al., 2010) in July–September 2008, a total of 35 samples.

Emission estimates are usually calculated using emission or enhancement 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. Equation (1) shows the calculation of an emission estimate for CH$_2$Cl$_2$, $E_{CH_2C_2}$, from a known emission of CO, E_{CO}, and an emission ratio. In this case, we use the slope of the linear regression from the correlation between CH$_2$Cl$_2$ and CO as our emission ratio, rather than a ratio based on our observed "excess" monsoon concentrations relative to a background mixing ratio, as discussed in Andreae and Merlet (2001) and Le Canut et al. (1996).

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 the sources of CO and CH$_2$Cl$_2$ differ, as CO has a larger relative source from biofuel burning (Dickerson et al., 2002), CO still provides the best option for emission estimates in this region. Other, anthropogenic, compounds have their own limitations. Emission estimates are available for SF$_6$ but it does not correlate well with CH$_2$Cl$_2$, possibly as it has large point sources and is not as widely and evenly distributed as sources of CH$_2$Cl$_2$, CO and many other trace gases. For other compounds, e.g. HFC-32 (Sect. 3.6) or C$_2$Cl$_4$, Indian emission estimates are not available. On the scale of a regional emission estimate, CO and CH$_2$Cl$_2$ 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. Comparisons between CO and anthropogenic chlorocarbons, including CH$_2$Cl$_2$,

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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).

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 $\Delta CH_2Cl_2/\Delta CO$ value from our sample set ($n = 35$) to the $\Delta CH_2Cl_2/\Delta CO$ value obtained from a smaller dataset based on the method used in Baker et al. (2011). Baker et al., when performing emission estimates for the same CARIBIC 2008 monsoon dataset, minimised the influence of variability with respect to processing or other transport effects by selecting a dataset 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 $\Delta CH_2Cl_2/\Delta CO$ and r value. The $\Delta CH_2Cl_2/\Delta CO$ and r values for our dataset are shown in Table 3 and for the Baker et al. subset are 4.39×10^{-4} (age corrected slope) and $r = 0.67$. This suggests that the correlation observed in our dataset (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.

$$E_{CH_2Cl_2} = E_{CO} \times \left(\frac{\Delta CH_2Cl_2}{\Delta CO} \right) \tag{1}$$

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 as previous studies on both the CARIBIC dataset (Rauthe-Schöch et al., 2014; Baker et al., 2011) and independent studies from the same region (Scheeren et al., 2002) have shown that air within the monsoon anticyclone is isolated and mixing in of background air is minimal. One can compare our $\Delta CH_2Cl_2/\Delta CO$ value with those from previous studies (Table 3). Our ratio is within $\sim 20\%$ of the ratio calculated for a ground-based station nearer to emission sources (Gentner et al., 2010). This is an excellent agreement considering that the (lower) Gentner et al. ratio is from 2005 data whereas our ratio is from 2008 and the ratio is increasing over time (changes to the ratio over time are discussed further below). 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 variations in transport time lead to variations in the degree of mixing, and in the bootstrapping error analysis of the $\Delta CH_2Cl_2/\Delta CO$ 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, changes to CO are likely to have occurred during this time and so we age-correct our emission ratios with respect to CO using Eq. (2), a method used by both Baker et al. (2011) and Scheeren et al. (2002). Here, the emission ratio at time 0, ER, 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. Both k_{CO} at $2.1 \times 10^{-13}\,cm^3\,molec^{-1}\,s^{-1}$ and $\langle[OH]\rangle$ at $2.48 \times 10^6\,molec\,cm^{-3}$ are taken from Baker et al. (2011, and refs. within) and $k_{CH_2Cl_2}$ at $1.1 \times 10^{-13}\,cm^3\,molec^{-1}\,s^{-1}$ from Villenave et al. (1997). This procedure leads to a correction in our emission ratio for the 2008 monsoon season of around -8%.

$$ER_0 = ER_t e^{(k_{CO} - k_{CH_2Cl_2})\langle[OH]\rangle \Delta t} \tag{2}$$

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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 and (2) uncertainties associated with using a slope calculated from a discrete set of samples to calculate a regional emission

5 estimate. The errors associated with (1) are small compared to those associated with (2) and so we use (2) to set bounds on our emission estimates. To investigate possible variations in $\Delta CH_2Cl_2/\Delta CO$ a bootstrapping procedure was applied. Using the Wood (2003) procedure we resampled, with replacement, our CH_2Cl_2 and CO datasets 10 000 times, each time calculating $\Delta CH_2Cl_2/\Delta CO$. The output from the resampling

10 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

15 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, Maldives, Nepal and Pakistan. EDGAR emissions are provided per year and are split into categories

20 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 emissions were split

25 into two categories: (1) biomass burning related emissions and (2) all other, mainly anthropogenic, emissions. Category (2) was assumed to remain constant throughout the year and the annual emissions provided by EDGAR for CO sources within this category were divided equally between all months. Category (1) emissions were corrected for the effect of the monsoon using the GFED data and the method in Baker

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et al. (2012). 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 $\pm 50\,\%$ (Olivier et al., 1999), hopefully 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 this error remains constant throughout the EDGAR database.

The CH_2Cl_2 vs. CO correlation within the monsoon ($<40^\circ$ N, July–September 2008) can be seen in Fig. 5a. The 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 3 includes $\Delta CH_2Cl_2/\Delta CO$ values from this study as well as a range of published values from a variety of sources, including; biomass burning (Simmonds et al., 2006; Rudolph et al., 1995), urban emissions (Gentner et al., 2010) and aircraft data (Scheeren et al., 2002). Whilst the Simmonds et al. (2006) ratio, observed at the remote Cape Grim site, is extremely low, the rest of the ratios show a consistent increase over time due to increased emissions of CH_2Cl_2.

Using this ratio 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 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 $515 \pm 22\,Gg\,yr^{-1}$ 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 $4\,\%$ of the global total. These estimates are discussed further in Sect. 3.6.

CH$_2$Cl$_2$ 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$_2$Cl$_2$ 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 datasets for comparison with the 2008 dataset (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$_2$Cl$_2$ 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 200. Our emission estimates suggest that emissions have increased from a range of 3–15 Gg in the late 1990s to around 16–25 Gg in 2008. A significant increase is seen over time, even with the inclusion of a rigorous bootstrapping analysis in our predicted range of emission estimates.

3.4 North and central Atlantic

The final flight route with the temporal resolution needed for identifying CH$_2$Cl$_2$ trends is across the Atlantic to Central 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 dataset (2001–2002). The latitudinal gradient increases over time and can be seen in the binned mean values for 2009–2011. However, it is still less pronounced than the latitudinal gradients observed en route to Africa or India. A slight decrease in CH_2Cl_2 is observed from north to south or moving west across the Atlantic away from Europe, although the number of samples taken to the west and south are less that to the north and east.

Average values for tropospheric samples taken within each year (Fig. 6c) show an increase in time, as discussed in previous sections. The increase between the 2000–2002 and 2009–2011 periods (the latter chosen to match with the years covered in previous sections) was from 23.2 (± 0.4) ppt to 32.0 (± 0.6) ppt, an increase of 8.8 (± 0.7) ppt or 38 %. The magnitude of this increase is smaller than that observed for Europe and India and closer to that observed for the southern section of the flights to Africa. This is most likely due to the influence of cleaner air masses over the Atlantic and Central America. Similarly low concentrations were seen over the Suriname rainforest in 1998 by Scheeren et al. (2003b) who reported a mean concentration of 16.3 ± 4.4 ppt at similar altitudes to CARIBIC (Table 2).

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. A detailed discussion of O_3 as a chemical marker for the structure of the UTLS was provided in 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).

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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 two-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 400–500 ppbv O_3 ($n = 4$ for each two year period) the median CH_2Cl_2 value increased from 11.0 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. For example, interception of a couple of samples with low CH_2Cl_2 concentrations reduced the mean 2009–2010 value to below that seen in 2001–2002.

3.5   Vertical profiles 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 and Sturges, 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 (~ 12 km) and 380 K (~ 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 in recent years can be seen. Because of this skew, median values and the range (min-max) are quoted 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. 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. A clear increase in both average and maximum CH_2Cl_2 concentrations can be observed in

the CARIBIC dataset. 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 15.3–17.2 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

5 fact that (1) their measurements were taken a few years earlier than CARIBIC; (2) their measurements were taken at a higher altitude; (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 pe-

10 riod (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

15 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. 8d 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 indus-

20 trial solvent emissions have also increased. Studies in China have shown exceedingly high ground level concentrations of CH_2Cl_2. For example, a 2001 study in 45 different Chinese cities by Barletta et al. (2006) saw an urban average of 226 ppt 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

25 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 R140A, a direct replacement for HCFC-22. It is estimated that about 95.9 % 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 rate of increase 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 dataset (Sect. 3.3 and Fig. 4e). A shift in the main consumers and emitters of HFCs is supported by the O'Doherty et al. (2014) study who found that the inter-hemispheric gradient has declined over time, driven by decreasing NH emissions and/or increasing SH emissions. A comparison of recent HFC-32 global emission estimates is made by O'Doherty et al. (2014, and refs. within). Their comparison suggests 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 also be contributing to the increasing atmospheric concentrations. Industrial sources include use in office (plastic) materials

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and electronics (Bin Babar and Shareefdeen, 2014; Kowalska and Gierczak, 2012), the production and use of which is increasing in developing nations such as India and those in south east Asia. A CH_2Cl_2 source from municipal waste disposal (Majumdar and Srivastava, 2012) may be of particular importance for India where mismanage-

5   ment 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

10   that India might be an important source of industrial CH_2Cl_2 emissions, as seen in the CARIBIC dataset. We estimated 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). However, these are small percentages of the 515 Gg yr^{-1} estimates by the WMO as average annual global emissions

15   (Montzka et al., 2011b) and it is likely that other regions also 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

20   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. 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

25   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 must be linked to 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 ~ 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 dataset we suggest that Southeast Asia may be an important source region. However, there is little 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.

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

| Region | Temporal data coverage | | Number of tropospheric samples ([*]) |
	Annual	Monthly	
Europe	Data collected 1998–2002 and 2005–2012	All months covered	123
	Min. coverage: $n = 1$ in 1999		
	Max. coverage: $n = 16$ in both 2009 and 2011		
Africa	2000, 2009–2011. Individual flights:	Mainly NH winter	140
	2000	May, Jul, Dec	32
	2009	Mar, Oct	47
	2010	Nov, Dec	22
	2011	Jan, Feb, Mar	39
India	Data collected 1998–2001, 2008, 2011 and 2012.		295
	The summer monsoon (Jul, Aug, Sep) was sampled in 1998, 1999, 2000 and 2008. In other years samples were only taken outside of the monsoon season.		
	Monsoon	Jul, Aug, Sep	105
	Non-monsoon	Rest of year	190
North and Central Atlantic	Data collected 2001–2002, 2007, 2009–2012	All months covered	282 (108)
Tropics	All data within ±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. Where stratospheric data are used (flights across the North and Central Atlantic and in the tropics) the number of stratospheric samples is shown in brackets.

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	Values[a]/ppt
This paper		
Europe		
CARIBIC data	1998–2001	$\bar{x} = 24.9 \pm 1.1$, $n = 16$
	2009–2012	$\bar{x} = 38.6 \pm 1.2$, $n = 49$
	Increase	13.7 ± 1.6
Mace Head NOAA data	1998–2001	$\bar{x} = 32.1 \pm 1.6$, $n = 15$
	2009–2012	$\bar{x} = 45.7 \pm 0.7$, $n = 88$
	Increase	13.6 ± 1.7
Africa		
Above 30° N	2000	$\bar{x} = 21.7 \pm 0.8$, $n = 3$
	2009–2011	$\bar{x} = 34.2 \pm 1.6$, $n = 23$
	Increase	12.5 ± 1.8
Below 30° N	2000	$\bar{x} = 15.8 \pm 0.6$, $n = 29$
	2009–2011	$\bar{x} = 22.7 \pm 0.6$, $n = 85$
	Increase	6.9 ± 0.8
India		
Summer monsoon (Jul–Sep)	1998–2000	$\bar{x} = 21.5 \pm 0.5$, $n = 56$
	2008	$\bar{x} = 36.4 \pm 1.3$, $n = 50$
	Increase	14.9 ± 1.4
Non-monsoon months	1998–2000	$\bar{x} = 20.1 \pm 0.5$, $n = 81$
	2008	$\bar{x} = 30.4 \pm 1.2$, $n = 62$
	Increase	10.3 ± 1.3
North and Central Atlantic	2000–2002	$\bar{x} = 23.2 \; (\pm 0.4)$, $n = 89$
	2009–2011	$\bar{x} = 32.0 \; (\pm 0.6)$, $n = 180$
	Increase	$8.8 \; (\pm 0.7)$
Other aircraft studies		
TTL (Schauffler et al., 1993)	1991–1992	$\bar{x} = 14.9$, $\sigma = 1.1$, $n = 12$
Suriname rainforest (Scheeren et al., 2003b)	1998	
< 2 km altitude		$\bar{x} = 26.0 \pm 2.9$, $\tilde{x} = 26.2$, $n = 42$
3–7 km altitude		$\bar{x} = 16.4 \pm 0.3$, $\tilde{x} = 16.4$, $n = 12$
7–12 km altitude		$\bar{x} = 16.3 \pm 4.4$, $\tilde{x} = 17.5$, $n = 26$
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., 2003a)	2001	$\bar{x} = 23$, $\sigma = 3$
Canada & Greenland, up to 12 km alt. (Simpson et al., 2011)	2008	$\bar{x} = 35.8 \pm 2.9$
Tropics (0 ± 25°), 345–350 K θ band (HIPPO, Wofsy et al., 2012)	2009–2011	$\bar{x} = 26.3$, $R = 15.87$–49.83, $n = 20$
Ground-based		
Atlantic cruise 45° N–30° S (Koppmann et al., 1993)	1989	
SH		$\bar{x} = 18 \pm 4$
NH		$\bar{x} = 36 \pm 6$ ppt
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	
Background		$\bar{x} = 28$, $\sigma = 4$
Urban		$\bar{x} = 226$, $\sigma = 232$

[a] $\bar{x}$ = mean, $\tilde{x}$ = median, σ = standard deviation, R = range and n = number of samples. For our study ± refers to the standard error.

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Table 3. A comparison of enhancement ratios from this study (airmass age corrected) and existing literature.

Source	$\Delta CH_2Cl_2/\Delta CO/mol\,mol^{-1}$
India, summer monsoon period (this study)	
1998	1.00×10^{-4}, $r = 0.69$
1999	1.58×10^{-4}, $r = 0.53$
2000	2.49×10^{-4}, $r = 0.86$
2008	4.00×10^{-4}, $r = 0.62$
Other studies[a]	
Biomass burning, Africa savanna, 1991[b]	2.48×10^{-5} (error = 26 %), $r = 0.65$
Wildfires, Cape Grim, 1998–2004[c]	< 1–6×10^{-7}
Asian pollution outflow, Bay of Bengal, 1999[d]	4.4×10^{-5} ($\pm 4.7 \times 10^{-5}$), $r = 0.39$
Urban, California, 2005[e]	3.10×10^{-4} $\pm 3.0 \times 10^{-5}$, $r = 0.58$–0.66
Urban, USA, 2004[f]	2.39×10^{-4} (1.78×10^{-4}–2.9×10^{-4}), $r = 0.56$–0.83
Urban, Mexico, 2006[f]	1.93×10^{-4} (1.09×10^{-4}–2.92×10^{-4}), $r = 0.43$–0.81

[a] Described by: emission source, location, year of study.
[b] Rudolph et al. (1995).
[c] Simmonds et al. (2006).
[d] Scheeren et al. (2002).
[e] Gentner et al. (2010).
[f] Millet et al. (2009).
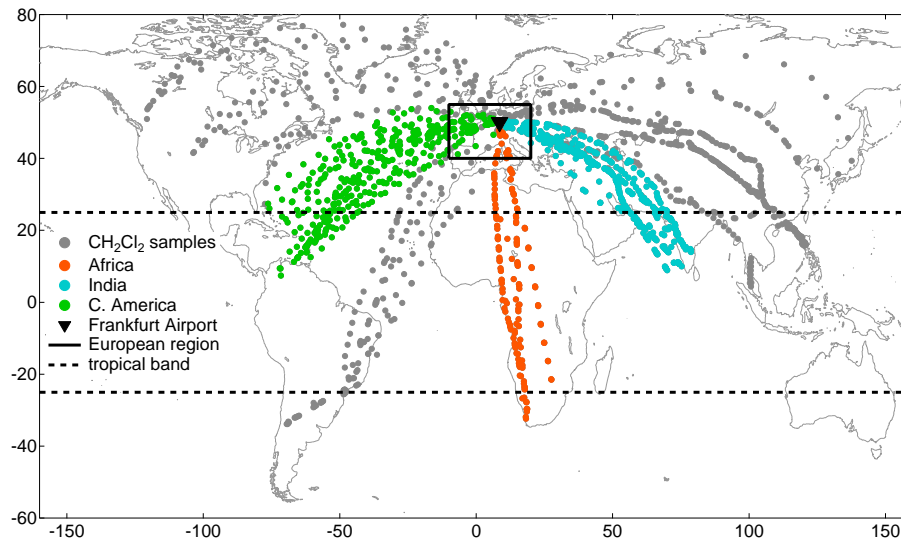
Figure 1. CARIBIC whole air samples analysed for CH_2Cl_2 between 1998–2002 and 2005–2012. Flight routes used in this study are highlighted, see inset legend.
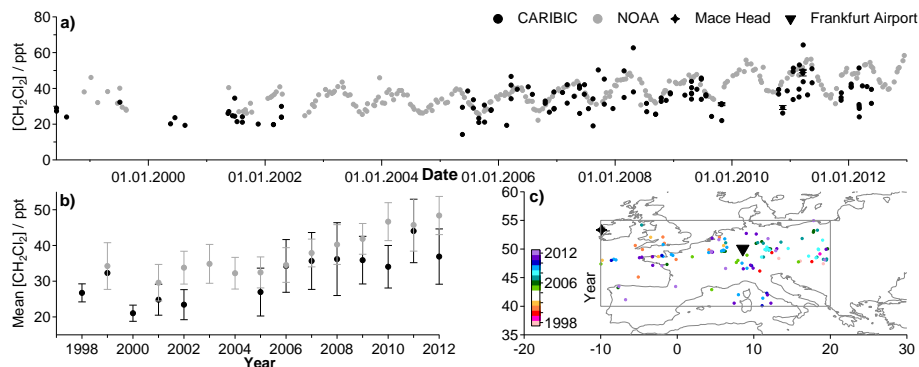
Figure 2. (a) European CH_2Cl_2 time series from June 1998 to December 2012. Error bars given for combined value based on multiple measurements, see Sect. 2. **(b)** Annual mean CH_2Cl_2 values for all CARIBIC and NOAA Mace Head data, error bars are 1σ. **(c)** Geographical distribution of CARIBIC samples coloured by year (see inset colour bar) within a box spanning 40–55° N and –10–20° E and in relation to Frankfurt Airport (CARIBIC2 base) and NOAA sampling site at Mace Head.
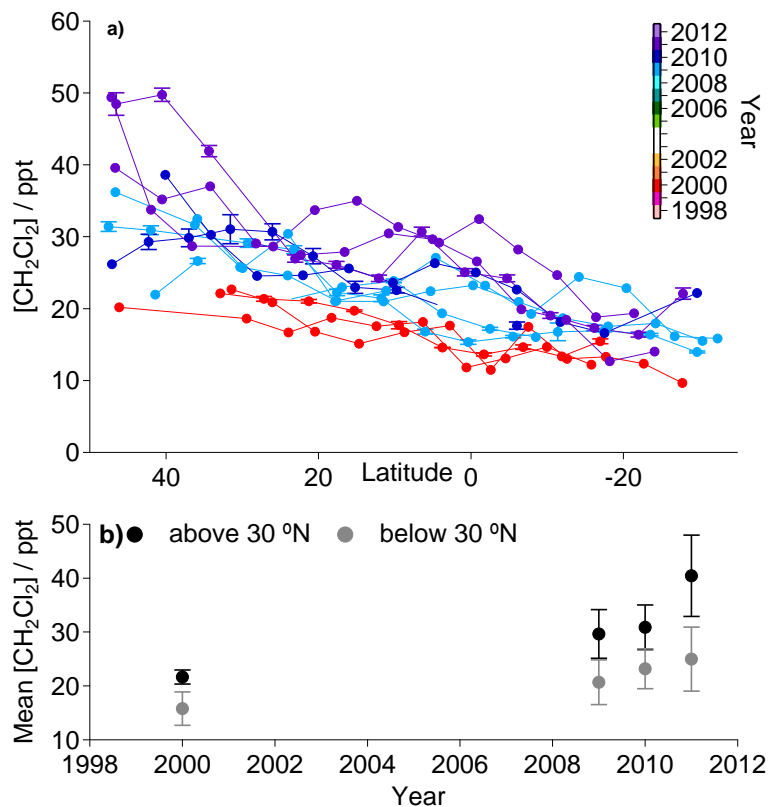
Figure 3. (a) Latitudinal distributions of CH_2Cl_2 observed during flights to South Africa, colour = year (see inset colour bar). Error bars given for combined value based on multiple measurements, see Sect. 2. **(b)** Annual mean tropospheric CH_2Cl_2 values for data shown in panel a, split into above and below 30° N, error bars are 1σ.

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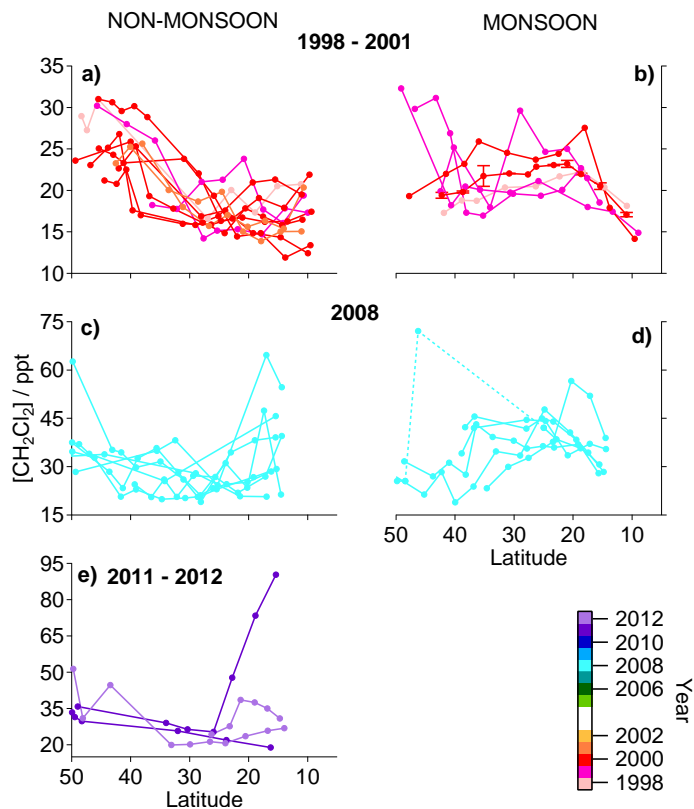
Figure 4. Latitudinal distributions of CH_2Cl_2 observed during flights to India for non-monsoon months on the left and monsoon months (July, August, September) on the right. Colour = year, see inset colour bar. Error bars given for combined value based on multiple measurements, see Sect. 2.

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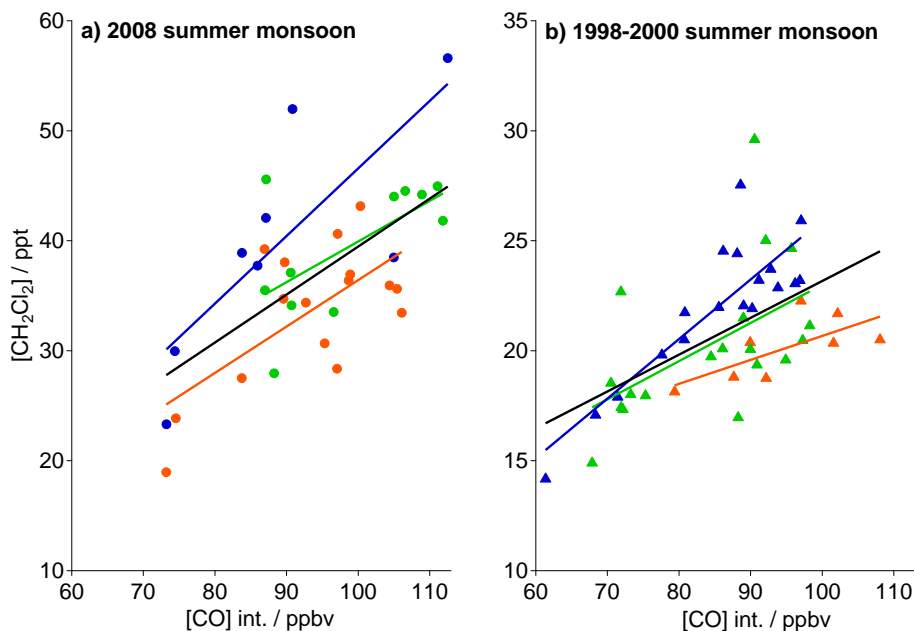
Figure 5. Correlation plots of CH_2Cl_2 and CO for **(a)** the 2008 summer monsoon period (coloured by individual months) and **(b)** the early years of the CARIBIC India dataset (coloured by individual years). Further details in Table 3.
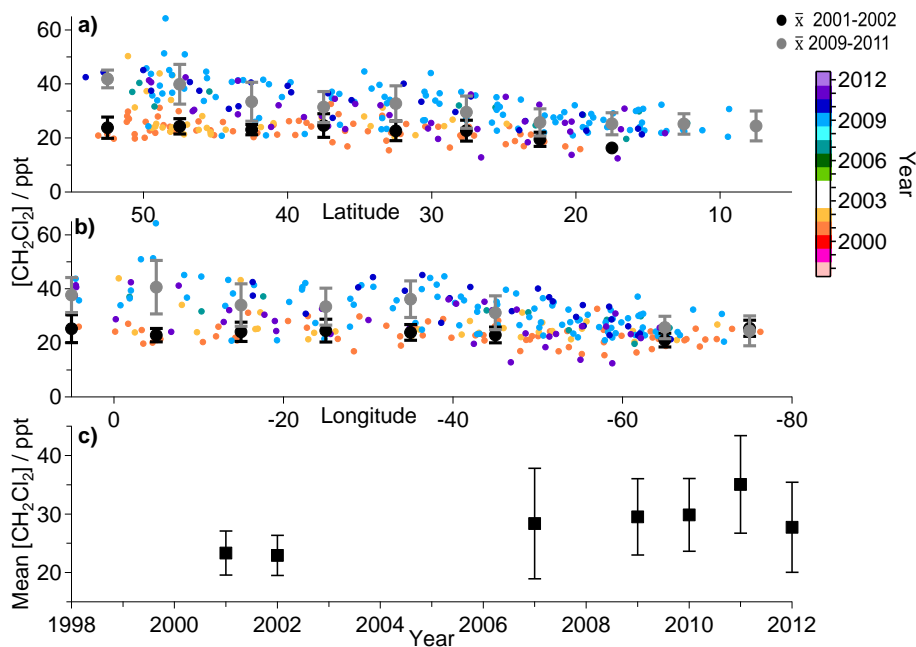
Figure 6. (a) Latitudinal and **(b)** longitudinal distributions of CH_2Cl_2 along flight routes across the North and Central Atlantic to Central America. Colour = year (see inset colour bar). Average, $\bar{x}$, values for 5° latitude and 10° longitude bins are shown for 2001–2002 and 2009–2011 (see Sect. 3.4), error bars are 1σ variation within these bands. **(c)** Annual mean CH_2Cl_2 concentrations for all samples taken along these routes, error bars are 1σ variation.
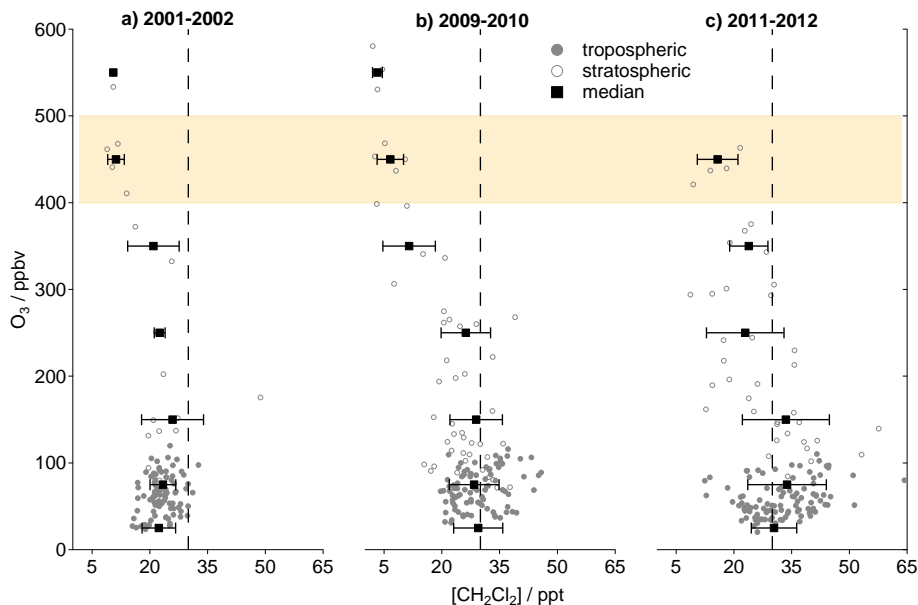
Figure 7. Profiles of CH_2Cl_2 relative to O_3 from samples collected on flights across the North and Central Atlantic to Central America. Median values are for 50 ppb O_3 bins between 0–100 ppbv and 100 ppbv O_3 bins above this, error bars are 1σ. The coloured band highlights the region between 400–500 ppbv O_3 discussed in Sect. 3.4. The dashed line represents 30 ppt CH_2Cl_2 (see Sect. 1), provided as a visual marker to illustrate the shift over time to higher concentrations of CH_2Cl_2.
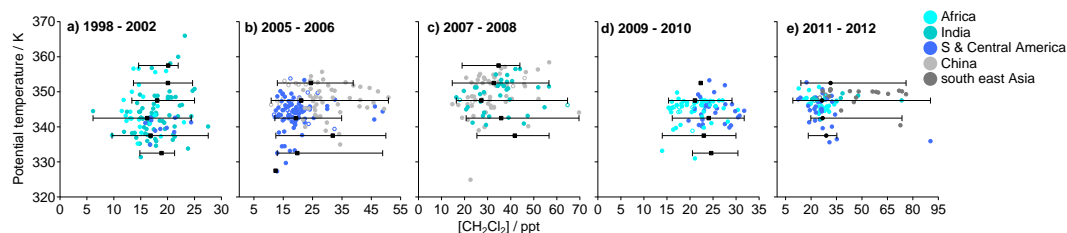
Figure 8. Profiles of CH$_2$Cl$_2$ relative to potential temperature for samples taken within the latitude range 0° ± 25°. Median (error bars are range) values for 5 K bins are overlaid in black (error bars = 1σ). Colour represents flight route, see inset colour bar.