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**GHG analysis of
CARIBIC samples**

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Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft

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Abstract

CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) is a long-term atmospheric measurement program based on the use of a comprehensive scientific instrument package aboard a passenger aircraft.

In addition to real time measurements, whole air sampling is performed regularly at cruising altitude in the upper troposphere and the extra-tropical UT/LS region. Air samples are analysed for greenhouse gases, NMHCs, halocarbons, and isotopic composition. The routinely performed greenhouse gas analysis comprises gas chromatography measurements of CO₂, CH₄, N₂O and SF₆.

The sampling procedure, the GC system used for greenhouse gas analysis and its performance are described. Comparisons with other laboratories have shown good agreement of results as has a comparison with results from a CO₂ in-situ analyser that is also part of the CARIBIC instrumentation.

The timeseries of CO₂ obtained from the collection of 684 samples at latitudes between 30° N and 56° N on 21 roundtrips out of Germany to different destinations in Asia between November 2005 and October 2008 is shown. A timeshift in the seasonal cycle of about one month was observed between the upper troposphere and the tropopause region.

For two sets of return flights from Germany to the Philippines the relations between the four greenhouse gases CO₂, CH₄, N₂O and SF₆ are discussed in more detail. Distinct seasonal changes in the correlation between CH₄ and CO₂ are observed.

1 Introduction

CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container, www.caribic-atmospheric.com) is one of three existing atmospheric chemistry and composition programs based on the use of passenger aircraft (Brenninkmeijer et al., 2005; IGAC). Such programs provide measurement results for

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atmospheric trace constituents that are used for immediate research purposes and for monitoring, i.e. long-term regular surveying. Specific for these aircraft projects is that large sections of the globe are covered, that background tropospheric air is probed and that, depending on the flight routes, a large fraction of the flight time is spend in the tropopause region and the lowermost stratosphere.

The new CARIBIC system is based on a fully automated instrument package (Brenninkmeijer et al., 2007). Since December 2004 it is deployed monthly aboard a Lufthansa Airbus A340-600 passenger aircraft equipped with an advanced multiprobe inlet system. At cruising altitudes between 8.5 and 12.5 km the CARIBIC aircraft frequently crosses the tropopause at mid-latitudes. In the extra-tropics about 40% of the flight time is spent in the transition layer above the tropopause (ex-TTL) while at lower latitudes the free tropical troposphere is probed.

In addition to real time measurements of aerosols and trace gases the CARIBIC experiment includes sampling of air and aerosols. The air samples allow for the precise measurements of long lived trace gases that are difficult to measure in-flight. The samples are analysed for the main greenhouse gases CH₄, CO₂, N₂O, and SF₆ as well as for various hydrocarbons, halocarbons, and isotope ratios.

For the entire CARIBIC experiment the greenhouse gas measurements are relevant for the interpretation of data because they contain information about influence of the biosphere (CO₂, CH₄, N₂O) and of stratospheric processes (CH₄, N₂O), whereas SF₆ also fulfills the role of a tracer of surface emissions from populated industrialized regions. In addition, SF₆ and CO₂ are tracers that allow estimates of the timing and the extent of large scale transport processes (Bönisch et al., 2008). Besides trace gas concentrations also certain isotope ratios are measured as a further part of the CARIBIC project that can help to identify emission sources.

It is also hoped that the CARIBIC greenhouse gas measurements contribute to global long-term monitoring complementing the information collected by ground-based networks and other aircraft measurements. In order to ensure data quality and compatibility with other global datasets the calibration procedure and comparisons with other

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laboratories that have been performed will be described in detail.

2 Air sampling procedure

For the collection of whole air samples the CARIBIC measurement container houses the air sampling device TRAC (Triggered Retrospective Air Collector) (Brenninkmeijer et al., 2007). The air sampling system consists of a computer unit that controls the sampling of air, a three-stage pumping unit, and two separate sample units, each containing 14 glass cylinders with a volume of 2.67 l each. Six of these identically constructed sample units exist (length: 600 mm, width: 622 mm, height: 360 mm, weight: 49 kg). One set of two units is integrated in the container during the monthly flights while the other pairs are circulating among the partner laboratories for analyses. Inside each sample unit two 16-position valves (Valco) are used to switch between the cylinders with one valve for the inlet side of the cylinders and one for the outlet. Stainless steel tubing is used for connecting the glass cylinders to the valves. The two surplus positions of the valves are short-circuited also using stainless steel tubing. The common inlet line is equipped with a 2 μ m sintered stainless steel filter (Swagelok) to remove particles from the sampled air.

The pumping unit houses two metal bellows pumps (Senior Aerospace Metal Bellows, 28823-7), the first with its two bellows in parallel, the second pump with its two bellows in serial, resulting in a three-stage pumping unit (for more details see Brenninkmeijer et al., 2007). The inlet pressure during a flight is about 200–300 mbar and flow rates of 20–30 l/min (STP) are obtainable.

Prior to pressurization the sample cylinders are flushed with outside air for 300 s. In laboratory experiments the mean time for the total air volume inside the canister to be exchanged has been determined as a function of ambient pressure. It is approximately 30 s, so that during the flushing time the air inside the sample cylinder is exchanged about 10 times. After 300 s of flushing the outlet valve is switched to the next position. The total sampling time is the sum of the time interval between the switching points of

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the outlet and the inlet valve and the time needed to replace the air volume inside the canister during the flushing period. Depending on the flight altitude the resulting total sample collection times range from 30 s to 90 s corresponding to a spatial resolution of about 7 to 21 km.

5 A pressure sensor between the outlet of the pumping system and the sample unit controls the pressure inside the sample cylinder. Once the final pressure of 4.5 bar is reached, the inlet valve is also switched. To prevent sudden overpressure a mechanical pressure release valve is set to open at 5 bar. As the in-flight pressure measurement is the sum of ambient pressure and ram pressure and depends on the ambient temperature, the actual pressure in the lab at the time of analysis will be lower than 4.5 bar. It ranges from 3.5 to 4.2 bar corresponding to a sample volume of about 9 to 11 l (STP).

To avoid sampling of polluted air in the vicinity of airports an upper pressure cutoff of 480 mbar is applied and no samples are taken at higher pressures. The sampling procedure starts as the outside pressure falls below this threshold, it stops as soon as the ambient pressure exceeds this value. The sampling points are evenly distributed over the expected flight time and depending on the flight route samples are taken every 30 to 60 min. In between the sampling periods the pumps are switched off in order to save power and reduce heat production. The intended use as an air sampling system triggered by observed events has not yet been put into practice. In contrast to event triggered sampling such as a sudden rise in CO, regular sampling leads to a distribution of samples that is more representative of the various air masses crossed by the aircraft.

20 One set of monthly flights consists of either two or four flight legs. During the first leg all 28 canisters are pressurized. On the following flight leg(s) half of them are vented, are flushed again and finally are refilled. This procedure ensures that the maximum number of cylinders is filled even in case of changes to the flight schedule or technical failure of the equipment. In 2008 sampling was 100% successful with only one sample out of 308 being missed when the flight destination was reached prior to the scheduled arrival time. In 2006 and 2007 an average duty cycle of 96% was achieved.

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After returning from the last flight leg the container is removed from the aircraft. The sample units are de-installed and the pressurized samples circulate through up to five European labs for measurements of greenhouse gases, non-methane hydrocarbon, halocarbons as well as for measurements of the isotopic composition ($^{18}\text{O}(\text{CO}_2)$, $^{13}\text{C}(\text{CO}_2)$ (Assonov et al., 2009), $\text{D}(\text{H}_2)$, $^{13}(\text{CH}_4)$ (Rhee et al., 2004)).

3 Characterization of the greenhouse gas GC system

The greenhouse gas analysis comprises measurements of CH_4 , CO_2 , N_2O , and SF_6 using a HP 6890 gas chromatograph equipped with a flame ionization detector (FID) for measuring CH_4 and CO_2 and an electronic capture detector (ECD) for N_2O and SF_6 . This system was initially designed and installed by D. Worthy (Env. Canada), however, details have been modified since. Figure 1 shows a simplified schematic of the GC sampling system at the beginning of a measurement cycle.

The system has been designed to enable the automated measurement of a sequence of 28 samples. For the analysis of CARIBIC samples the two sample units and a working standard are connected to the system via an 8-position selector valve that controls the sampling source. All valve switching is automated.

One single measurement cycle runs for 12 min. Loading of the sample and its passage through the system are controlled by four valves. Two valves are operated synchronously to simultaneously load the sample loops for the two channels. They are therefore both labelled valve 1 and are treated as one valve in this description. Valve 2 is controlling the flow from the sample loop towards the ECD, valve 5 towards the FID channel. When a cycle begins, the Porapak column of the ECD-channel is still being flushed backwards with the carrier gas Ar/CH_4 . Backflushing stops after 0.2 min, this is the time step shown in Fig. 1.

Loading of a sample starts after 0.5 min. The two sample loops are connected in serial with the smaller 10 ml loop for the FID channel upstream. The ECD sample loop has a volume of 15 ml. A pressure of 4 psi is applied for 0.5 min for loading the sample

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loops, afterwards another 30 s are allowed for pressure equilibration. 1.5 min after the start of a cycle valve 1 is switched and the respective carrier gas starts flowing through each sample loop. Backflushing, which is controlled by the switching of valve 2, starts after 8.3 min and lasts for 3.7 min.

5 Valve 5 controls the flow towards the FID. While CH_4 is detected directly, CO_2 is converted to CH_4 using a nickel catalyst as methanizer. In the beginning the methanizer is bypassed and CH_4 from the sample is directly detected by the FID. After 3.9 min valve 5 is switched and the flow is then passing through the methanizer. CO_2 from the sample is converted to CH_4 which can be detected by the FID. After 7.5 min valve 5 is
10 switched back to its initial position. The efficiency of the methanizer is monitored by comparing the ratio of CH_4 and CO_2 mixing ratios and peak areas. It has been above 96% for all samples analysed.

Both channels are equipped with packed polymer columns. The FID channel is equipped with a Porapak Q 3/4" column (10 ft, 100/120 mesh), N_2 (5.0) is used as carrier gas at a constant flow rate of 50 ml/min. The FID is kept at 220°C and it is
15 operated at a flow of H_2 of 80 ml/min that is directed via the methanizer and a flow of synthetic air of 250 ml/min.

On the ECD channel two columns in serial are needed for the separation of N_2O and SF_6 . A Porapak Q 1/8" (6 ft, 80/100 mesh) column and a HayeSep Q 1/8" (6 ft, 80/100 mesh) column are used. The ECD is operated at a temperature of 390°C
20 with Ar/CH_4 (5%) as carrier gas at a flow rate of 90 ml/min and an anode flow rate of 3 ml/min. All three columns are kept in a single oven at a constant temperature of 50°C. Figure 2 shows typical examples of the chromatograms for a working standard. At an oven temperature of 50°C the retention times are 1.93 min for CH_4 , 3.25 min for CO_2 ,
25 4.33 min for N_2O , and 5.52 min for SF_6 .

During the analysis of CARIBIC samples four consecutive injections per sample are made, the results of which are averaged. The precision of the data points is calculated from the standard deviation of those four injections. In between samples three injections from a running standard gas are made. This also starts and ends a series of

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measurements so that each sample analysis is bracketed by a series of measurement of the running standard. The analysis of a complete set of 28 samples takes approximately 48 h during which slow ambient pressure and temperature changes occur. This has an influence on the sensitivity of the detectors, especially on that of the ECD. The procedure of alternating measurements of the running standard and samples allows to correct for these drifts.

For the calculation of mixing ratios peak heights and areas are determined using the numerical integration routine of the Agilent Chemstation software (Rev.A.10.01) that is controlling the GC. Both, peak area and peak height are evaluated separately and only if both resulting mixing ratios agree, thus proving an undistorted peak shape, the mixing ratio of a sample is taken to be the average of both numbers. The typical precision obtained on the system is 0.17% for CH₄, 0.08% for CO₂, 0.15% for N₂O, and 1.5% for SF₆.

3.1 Standard gases and calibration

The calibration of the greenhouse gas analysis presently relies on three NOAA CMDL standards. Table 1 shows their mixing ratios of CH₄ (adjusted CMDL83 scale (Dlugokencky et al., 2005)), CO₂ (WMO-X2007 scale), N₂O (NOAA 2006 scale (Hall et al., 2007)), and of SF₆ (NOAA 2006 scale (Hall et al., 2007)). To keep up with increasing CO₂ and SF₆ levels two new standards are being purchased from NOAA ESRL that will be included in the calibration routine from 2009 on.

Table 1 also shows the results of the calibration of all four working standards. KOMP1 was filled on top of the institute's building in Mainz, Germany, in September 2005. It has been used as running standard for the sample measurements as described above until December 2007. Presently SIL194 is used for that purpose. SIL194 and SIL195 have been filled at the Schauinsland observatory in southern Germany (1205 m a.s.l.) (Schmidt et al., 2003) in September 2005, SIL196 in November 2005. All working standards have been prepared using Drierite (CaSO₄) as drying agent.

The working standard that is used as running standard for the analysis of CARIBIC

whole air samples is calibrated against the NOAA standards monthly the day before the monthly analysis of samples. The two working standards that are not used in the monthly measurements are also calibrated regularly to check their stability, but this is done less frequently, about once every three months.

5 In Table 1 the number of calibration runs performed up to now is given in brackets for each standard. For SIL196 this includes one measurement performed at the Max Planck Institute for Biogeochemistry in Jena (Germany). The numbers given are the arithmetic means of all measurements. No drift within the precision of the system as given above has been observed in the greenhouse gas mixing ratios.

10 For calibration of the working standards a linear relation between signal and detector response is assumed for both, the FID and the ECD. Although ECDs are known to be non-linear, within the range of mixing ratios that is covered by the standards the assumption of a linear behaviour is well approximating the observed response of the detector. The slope of the response line as determined in the separate calibration run
15 is taken into account for the actual sample analysis.

3.2 The effect of water vapour

Sampling aboard the CARIBIC aircraft takes place at altitudes between 7 km and 12.5 km (with ~96% of the samples being collected at the cruising altitude range of 8.5 km to 12.5 km). As water vapour levels at these altitudes are generally low, no drying agent is used. (Butenhoff and Khalil, 2002) pointed out that if drying is not applied
20 neither prior to pressurization of air samples nor prior to their analysis the possibility of water vapour condensation inside the sample canister needs to be taken into account.

The saturation pressure of water at a laboratory temperature of 21°C is 24.87 mbar (Wexler, 1976). Assuming a pressure of 4000 mbar inside a sample canister and a
25 laboratory temperature of 21°C, even an exceptionally high water vapour content of a sample of 5000 ppm corresponds to a relative humidity in the sample of ~80% (vapor pressure of ~20 mbar) (Wexler, 1976; Buck, 1981) which is still below saturation.

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Water vapor is detected by two instruments in the CARIBIC container, namely a two-channel photo-acoustic laser spectrometer and a chilled mirror frost point hygrometer. The water probe of the inlet contains two separate orifices, one facing flight direction (total water) and one pointing perpendicular (water vapor only), so that gaseous and condensed water can be distinguished (Brenninkmeijer et al., 2007). The actual water content of a sample can be estimated from integrating the continuously measured total water content (the sum of gaseous water and cloud water) of the ambient air over the sampling time. For about 96% of the samples the water content is below 500 ppm, corresponding to roughly 8% relative humidity in the laboratory. Only for about 2% of the samples the water content exceeds 1000 ppm. As the relative humidity thus is well below 100% for all samples only the volumetric correction

$$x_{\text{dry}} = x_{\text{measured}} \cdot (1 + x_{\text{H}_2\text{O}}) \quad (1)$$

needs to be taken into account to obtain dry mixing ratios x_{dry} from the measured ones x_{measured} with $x_{\text{H}_2\text{O}}$ being the mole fraction of water in the sample. This correction factor is applied to all results of the greenhouse gas analysis.

With ~96% samples containing less than 500 ppm of water the correction factor $1+x_{\text{H}_2\text{O}}$ is usually below the average relative error of the measured greenhouse gas mixing ratios that can be determined with an average precision ranging from 0.08% (CO_2) to 1.5% (SF_6).

To experimentally verify the absence of a significant water vapor effect test measurements with a drying tube were performed for 14 samples from a flight from Frankfurt to Chennai (India) that took place in April 2008. The GC-analysis was repeated for a set of 14 samples with a drying tube containing $\text{Mg}(\text{ClO}_4)_2$. From the integration of the continuously measured total water content of the ambient air the water content of these samples was calculated to be 70.13 ppm on average, ranging from 7.2 ppm to 225.3 ppm. The measurements with and without the drying tube agreed within their $1-\sigma$ error bars for all samples and for all species measured and no systematic difference or bias was observed.

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The maximum water content of the re-measured samples was 225.3 ppm. This corresponds to a correction of the greenhouse gas mixing ratio of 0.02%. Taking the average precision of 0.08% that can be achieved in the measurement of CO₂ a water content of a sample of 800 ppm was needed to be able to detect the difference in the CO₂ mixing ration that is caused by the volume effect of water in the sample cylinder. As the precision for the measurement of CH₄ (0.17%), N₂ (0.15%), and SF₆ (1.5%) is not as good as for CO₂, even higher water vapor contents of the samples were necessary for a measurable difference.

3.3 Intercomparison with other laboratories

Whole air samples from the CARIBIC experiment were also analysed for greenhouse gases using gas chromatography in other laboratories, namely in Heidelberg and in Jena.

In 2006 altogether 55 samples from three flights were analysed for CH₄ and CO₂ at the Institute for Environmental Physics (IUP) Heidelberg (Germany) as well as on the CARIBIC greenhouse gas system. The CO₂ mixing ratio in the samples varied between 376 ppm and 387 ppm, the CH₄ mixing ratio varied between 1687 ppb and 1911 ppb. For CH₄ a slope of the correlation line of 0.98 ± 0.02 ppb/ppb with $r^2 = 0.97$ was found. No systematic difference of the results of the two analyses was observed. For CO₂ the slope was 0.89 ± 0.05 ppm/ppm with $r^2 = 0.86$. There seemed to be better agreement for higher CO₂ values than for lower ones, but due to the large scatter of the data with a maximum difference between the two analyses of 1.9 ppm no definite conclusion could be drawn.

The data quality of the CARIBIC greenhouse gas analysis has been improved since then by optimising gas flows and temperatures of the GC system as well as details of the calibration procedure. A more recent comparison of 14 samples from one flight with the Max Planck Institute for Biogeochemistry in Jena (Germany) took place in November 2008. In Jena all 14 samples were analysed for CH₄, CO₂, N₂O and SF₆ on a similar GC system but with higher precision (Jordan and Brand, 2001). Also one of

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the CARIBIC working standards (SIL 196) was analysed on this GC system for all four greenhouse gases and in addition was analysed with a LoFlo system (Da Costa and Steele, 1997) for CO₂. The results of the GC measurements in Jena are included in the mean values given for standard SIL196 in Table 1. For all four greenhouse gases the measurements on the two different greenhouse gas systems agreed within their 1- σ error bars.

The sample measurements in Jena were performed ten weeks after the analysis in Mainz. During that time the samples were circulating through four different laboratories for hydrocarbon, halocarbon and isotope analyses. After returning to Mainz successive to the measurement in Jena 12 of the 14 samples still had enough pressure left in the canisters to allow for another greenhouse gas analysis. Repeating the greenhouse gas measurements in Mainz after ten weeks showed good agreement within the error bars with the first measurement directly after the flight with exception of two samples that showed an increased mixing ratio of CO₂ after ten weeks.

In general the agreement between the results obtained in Jena and those obtained in Mainz before was good. Correlating the measured mixing ratios resulted in correlation parameters r^2 of 0.997 for CH₄ (1774–1883 ppb), 0.959 for CO₂ (379–385 ppm), 0.987 for N₂O (315–323 ppb), and 0.653 for SF₆ (6.48–6.77 ppt). The weaker correlation for SF₆ reflects the larger scatter in the data obtained on the CARIBIC GC system with the absolute error ranging from 0.04 ppt to 0.08 ppt (corresponding to a relative error of 0.7–1.3%). All line fitting was done using the least orthogonal distance method (Cantrell, 2008).

For three of the samples the CO₂ measurements in Jena resulted in somewhat higher mixing ratios than the measurements in Mainz immediately after the flight. The difference was 0.51, 0.58, and 0.71 ppm, while the uncertainty of the Mainz measurement was only 0.19, 0.28, and 0.24 ppm. Repeating the analysis in Mainz after ten weeks gave a significantly enhanced CO₂ value for two of those samples and the results of the repeated measurement agreed well with the results from Jena. It is plausible that an increase of CO₂ has occurred during the long storage and travelling

time of the samples.

Looking at the absolute difference of the mixing ratios measured on the two different GC systems as a function of the mixing ratio as determined in Mainz no significant dependence of the deviation on the mixing ratio could be observed for CO₂, N₂O, and SF₆. With exception of CH₄ for which a slope of (0.06±0.02) ppb/ppb has been found the slopes of the absolute difference as a function of the mixing ratio were compatible with zero.

The mean value of the difference was 1.63 ppb for CH₄, 0.09 ppm for CO₂ and it was 0.009 ppb for N₂O. These values are below the average absolute error of the Mainz analysis (1.86 ppb for CH₄, 0.21 ppm for CO₂, 0.36 ppb for N₂O for the compared samples). While the measurements of SF₆ of the working standard agreed very well (Jena: (5.983±0.005) ppt, Mainz: (5.96±0.09) ppt) a systematic offset of about 0.14 ppt was found for the air samples. The measurement in Mainz resulted SF₆ mixing ratios from 6.48–6.77 ppt, whereas values obtained in Jena were systematically lower, ranging from 6.35–6.62 ppt. This may be mainly due to the linear extrapolation of the ECD-response that is done for the CARIBIC GC system, since the currently used laboratory standards only cover the range of 3.82–4.78 ppt (cf. Table 1). While for the analyses of the working standards all three NOAA laboratory standards are used, the air sample analysis relies on only one working standard being measured simultaneously with the samples. Although the slope of the calibration line as determined prior to the sample analysis is considered when calculating a sample's SF₆ mixing ratio, this results basically in a one point calibration which is less accurate. With the detector response being known to be non-linear, the extrapolation introduces a systematic error that increases with the SF₆ mixing ratio.

This issue will be investigated further as soon as the range covered by the laboratory standards has been extended to current atmospheric levels of SF₆. The new standards will allow for a better characterization of the ECD response curve thus leading to a more accurate determination of the SF₆ mixing ratio.

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The instrument package of the CARIBIC container also includes a non-dispersive infrared device for in-situ measurements of CO₂ operated by Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Paris, France. The instrument is based on the Li-6262 (LI-COR) analyser that has been modified to comply with the requirements of operation onboard an aircraft (Gibert et al., 2009). It is calibrated in flight with two standards that are calibrated at LSCE using a LoFlo CO₂ analyser (Da Costa and Steele, 1997).

For five series of flights the standards used for the in-situ instrument were additionally calibrated for comparison at MPIC Mainz using the CARIBIC greenhouse gas GC system following the procedure as described above. Figure 3 shows the difference of the analyses as a function of the absolute CO₂ mixing ratio as determined at MPIC. With exception of one standard very good agreement is observed and no systematic difference with the absolute mixing ratio is observed.

Figure 4 compares the results from the laboratory analysis of the air samples to the in-situ measurement for one flight from Frankfurt to Guangzhou (November 2007). Shown are the flight altitude and the CO₂ mixing ratio as a function of time. The in-situ data is shown as measured (grey dots) and also integrated over the sampling time for each individual whole air sample (open symbols). Five samples fall into calibration periods of the in-situ instrument so that no integral can be calculated. As the air sampled by the in-situ instrument is dried, the data from the whole air samples has been corrected for the water content of the sample as described above.

The absolute difference between the sample analysis and the integrated in-situ data ranges from 0.03 ppm to 0.3 ppm with an average difference of 0.12 ppm. Considering an absolute error for CO₂ of 0.20 ppm for the GC measurements for this flight and a precision of 0.18 ppm for the in-situ instrument during this flight the overall agreement is very good. A more detailed comparison of the continuous CO₂ data and the whole air sample analysis including all flights is in preparation.

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4 Results

4.1 Timeseries of CO₂

From May 2005 until October 2008, 993 samples have been collected on flights to South America, North America, and Asia. As an example of greenhouse gas results from the CARIBIC experiment. Figure 5 shows time series of CO₂ measured from the whole air samples on flights to Asia. Plotted are monthly mean values with the error bars indicating the standard deviation of one month's measurements. The timeseries includes all CARIBIC flights to the Philippines via China (21 roundtrips) and to India (12 roundtrips, sampling on 7 roundtrips) between November 2005 and October 2008.

As the CARIBIC aircraft frequently crosses the tropopause, the data set is divided into two subsets. The partitioning is based on the levels of SF₆, N₂O, and O₃, and in addition considers potential vorticity from the ECMWF model (van Velthoven, 2009). The top panel shows the data from the extra-tropical tropopause transition layer and the lowermost stratosphere, the bottom panel shows data from the upper troposphere. In total 684 samples have been collected on these flights that were analysed for CO₂, of which 443 were collected in the free troposphere, and 241 were collected in the tropopause region and the lowermost stratosphere.

A harmonic polynomial has been fitted to the data taking into account the standard deviation of each point:

$$f(t) = a_1 + a_2 \cdot t + a_3 \cdot t^2 + a_4 \cdot \sin(2\pi t/12) + a_5 \cdot \cos(2\pi t/12) + a_6 \cdot \sin(4\pi t/12) + a_7 \cdot \cos(4\pi t/12), \quad (2)$$

t being the time in months since January 2005. The resulting fit coefficients and χ^2 values are listed in Table 2. Both subsets show a similar linear increase of $a_2=0.35\pm 0.07$ ppm/month (troposphere) and $a_2=0.21\pm 0.08$ ppm/month (stratosphere). Negative values of the parameter a_3 indicate a deceleration of the CO₂ increase. However, considering the large error of the coefficients a_3 and taking into

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account the large values of the reduced χ^2 , no reliable conclusion on the long-term trend in the CO₂ mixing ratio can be drawn. Longer time series are needed to address this question.

Between the two regimes a time shift in the seasonal cycle of about one month is observed. While the minimum CO₂ mixing ratio in the troposphere is observed in September it is seen in the stratosphere in October. The maximum mixing ratio is observed in May in the troposphere and in June above the tropopause. Using the fit coefficients from Table 2, the CO₂ mixing ratios have been detrended by subtracting the quadratic part of Eq. (2) and a mean seasonal cycle was calculated for both datasets. In the troposphere the difference of the mixing ratio between the winter maximum and the subsequent summer minimum in the detrended mean seasonal cycle is ~6 ppm. Above the tropopause the expected weakening of the amplitude of the seasonal cycle is observed and the difference is ~2.5 ppm.

4.2 Spatial distribution and variability of samples

As during the flights to Asia in August and in September 2008 only one sample was collected that can be attributed to the stratosphere, no standard deviation can be calculated for these months. In general, the number of stratospheric samples is lower in summer due to the higher altitude of the tropopause. In addition, for all seasons the geographical distribution of the so-called stratospheric samples has a strong bias towards more northern latitudes, where the tropopause is lower in all seasons. On the flights to Asia ~66% of all samples are collected north of 30° N, the most northern sampling point being at 56.05° N. While ~50% of the tropospheric samples fall into that latitude band this applies for ~96% of the samples from above the tropopause. Thus, the distribution of the samples among stratosphere and troposphere has a bias with regard to season and geography that has to be taken into account when interpreting data.

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All samples collected on the flights to Asia were collected in the northern hemisphere within 14.39° N and 56.05° N. From the detrended data a mean seasonal cycle was calculated for all tropospheric samples in five latitudinal bands of 10° width. Figure 6 shows the mean seasonal cycle of the CO₂ mixing ratio for all tropospheric samples (top panel) and for the four latitudinal bands from 10° to 50°. The interval 50°–60° has been omitted due to the small number of samples. The error bars indicate the standard deviation of one month's mean value. Also shown is a harmonic polynomial fit to the detrended mean cycle (solid lines) and the corresponding 1- σ confidence bands (dotted lines). For fitting the polynomial the data points have been weighted with the inverse of the squared standard deviation. With the 1- σ -confidence bands of all latitudinal intervals overlapping, no significant latitudinal gradient in the amplitude of the seasonal cycle can be observed. For the stratospheric data the detrended timeseries can be fitted for the latitude bands 30°–40°, 40°–50°, and 50°–60°. Again, the confidence bands for the different bands overlap, so that no gradient can be concluded from the data.

For latitudes south of 30° N a decrease in the amplitude of the seasonal cycle in the troposphere has been observed from 6 ppm at 30°–25° N to 3 ppm at the equator by the JAL collaboration analysing CO₂ flask data from 1993–2007 (Matsueda et al., 2008). The amplitude of (6±2) ppm derived for (35±5)° from the 2005–2008 CARIBIC measurements is consistent with that result. The absence of a latitudinal gradient in the CARIBIC CO₂ data may to some extent result from the timeseries up to now only spanning three years. With longer timeseries the quality of the harmonic polynomial fit would improve and allow conclusions on the gradient.

Despite the different latitudinal distribution of the samples there is no systematic difference observed in the CO₂ time series for tropospheric and stratospheric samples, that can be attributed to result from a bias due to sampling location. Thus the timeseries of the two regimes averaged over the entire latitudinal range of 10°–60° may be compared e.g. with respect to the timeshift. In contrast, the latitudinal distribution of the sampling locations needed to be considered when looking at CO₂ data measured

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closer towards the equator as the gradient of the seasonal amplitude becomes steeper at low latitudes (Matsueda et al., 2008). It would also become relevant when looking at data with a steeper latitudinal gradient already at higher latitudes.

The procedure of regular sampling during a flight at cruising altitude as opposed to sampling triggered by certain events, is supposed to ensure representativeness of the samples and exclude biases. Thus the question arises how representative the CARIBIC samples are for background air. The following statistics includes all samples that were analysed for greenhouse gases, 849 samples in total. This includes 28 flights into or in the southern hemisphere.

First, the data set was again divided into purely tropospheric samples and those that have experienced stratospheric influence. The latter ones usually contain air from the extra-tropical transition layer, very few from the lowermost stratosphere. For each monthly roundtrip the median CO₂ mixing ratio was calculated for the stratospheric and the tropospheric subset and for each sample the deviation of the measured CO₂ mixing ratio from that monthly median. Figure 7 shows the distribution of the deviation from the monthly median for the tropospheric (a) and the stratospheric (b) sample subset. Referring to the deviation from the monthly median for each sample ensures that seasonal variations and the continuous rise of CO₂ do not affect the distribution.

If sampling in pollution plumes frequently happened, a considerable number of samples should contain high amounts of CO₂, whereas sampling of only background air should result in a near Gaussian distribution when ignoring spatial variations. As during the CARIBIC flights air is sampled in different locations, spatial variations of the CO₂ mixing ratio will result in the distribution deviating from a Gaussian.

Averaging the difference from the monthly median over all samples the standard deviation is $\sigma \sim 1.5$ ppm for both distributions. In the troposphere $\sim 94.3\%$ of the samples are within an interval of ± 3 ppm from the median, 1.9% are more than 3 ppm lower than the median, and 3.8% are more than 3 ppm higher. In the stratospheric data subset that contains 307 out of 849 samples $\sim 91.1\%$ of the samples are within ± 3 ppm around the monthly median, 7.6% are more than 3 ppm lower and 1.3% (4 samples) are more

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than 3 ppm higher than the median value. Comparing with the monthly mean mixing ratio results in similar values, indicating that the mean value is not strongly influenced by extreme values such as plumes.

Although the percentage of samples that fall within the $\pm 2\sigma$ interval is close to what is expected for a Gaussian (94.4%), the distribution deviates from a normal distribution as it is not symmetric. In addition, $\sim 77\%$ (troposphere) and $\sim 73\%$ (stratosphere) of the samples fall into the ± 1.5 ppm interval around the median which is a higher percentage than expected for a normal distribution (68.3% falling into the $\pm 1\sigma$ interval). The low number of samples with CO_2 mixing ratios significantly above the median implies that the influence of plumes on the distribution is low and the CARIBIC air samples do represent background air for both, the troposphere and the extra-tropical tropopause transition layer.

With a longer sampling time the probability of sampling air from pollution plumes would increase but the sample would contain a mixture of plume air and background air. For studies of plumes the initially intended triggered operation of the air sampler is preferable. The current mode of taking samples evenly distributed over the flight time yields a better representation of the atmospheric background greenhouse gas concentrations.

4.3 Flights Frankfurt \leftrightarrow Guangzhou \leftrightarrow Manila

Figure 8 shows an overview of the greenhouse gas results for a roundtrip from Frankfurt (Germany) to Manila (Phillippines) and back via Guangzhou (China) that took place in February 2008. The top panel shows the altitude of the aircraft as a function of time. Markers along the altitude profile show where air samples have been collected. Also included is the timeseries of potential vorticity (PV) in PV-units ($\text{PVU} \hat{=} 10^{-6} \text{ km}^2 \text{ kg}^{-1} \text{ s}^{-1}$) as a measure of stratospheric air. High values of PV indicating stratospheric air have been encountered on the long-distance flight between Frankfurt and Guangzhou. In the tropics the tropopause is higher so that during the two short flight legs between Guangzhou and Manila PV is always low.

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The middle and bottom panels display the timeseries of CH₄ and CO₂ (middle) and of N₂O and SF₆ (bottom). Throughout all four flights a positive correlation of CH₄, CO₂, N₂O, and SF₆ is observed whereby flight phases in stratospheric air indicated by high PV values coincide with lower values of CH₄ and CO₂, as well as of N₂O and SF₆.

CH₄ and N₂O both have mainly biogenic sources. CH₄ is mainly removed from the atmosphere by reaction with the OH radical (Dlugokencky et al., 1994). N₂O is stable in the troposphere and thus relatively well mixed and gets removed in the stratosphere because of photochemical destruction (Ko et al., 1991), showing a strong gradient across the tropopause. SF₆ is only emitted from anthropogenic sources. It has a very long lifetime and its atmospheric levels increase continuously due to growing emission rates (Maiss and Levin, 1994; Gloor et al., 2007). During the CARIBIC flights the lowest mixing ratios of N₂O and SF₆ are encountered in winter since then the tropopause height is lower and the CARIBIC aircraft with its cruising altitude being independent of season penetrates deeper into the stratosphere.

A positive correlation between CH₄ and CO₂ is typically seen at northern mid-latitudes during CARIBIC flights in boreal winter. Since in winter photosynthetic activity is low and less CO₂ is taken up by the biosphere, atmospheric CO₂ levels increase. The air encountered in winter above the tropopause is already aged and still preserves the lower CO₂ concentration of the preceding summer.

Figure 9 displays the correlations between CH₄ and CO₂ for the flight in February 2008 (circles) and for a flight on the same route that was conducted in August 2007 (triangles). While the winter flight exhibits a rather compact positive correlation between the two compounds the summer data look rather different. The relation turns into an anticorrelation that is however less compact. In summer CO₂ tropospheric levels decrease strongly due to uptake of CO₂ by vegetation and oceans. At the same time CH₄ declines less or may even slightly increase like it was observed during the CARIBIC flight in August. During this flight CH₄ tends to be higher than during the flight in February and the positive correlation observed in winter is lost. This reflects enhanced emissions of CH₄ from rice paddies, wetlands and landfills and enhanced

convective transport into the upper troposphere.

While CH₄ is still lower at higher PV values (closed symbols in Fig. 9) this is now different for CO₂. The tropopause region and lowermost stratosphere still contains air that has been transported across the tropopause earlier which resulted in the observed shift in the seasonal cycle. Therefore this region preserves the still elevated CO₂ mixing ratios of early summer. High PV now coincides with higher CO₂ while this was reversed in winter. In contrast, the positive correlation remains for N₂O and SF₆. Still, lower N₂O and SF₆ values coincide with high values of PV.

5 Summary and conclusions

The CARIBIC air sampling system and the greenhouse gas analysis of air samples have been reliably working since 2005. Very good results have been obtained in comparisons of the sample analysis with other laboratories and no systematic differences were encountered for CH₄, CO₂, and N₂O. The issue of a possible systematic offset in the CARIBIC SF₆ data set will be resolved in the near future by extending the range of mixing ratios covered by the primary standards.

The monthly operation of the CARIBIC system enables detailed systematic observations of greenhouse gases in the upper troposphere and lowermost stratosphere. The measurement results imply that the samples collected are representative of background air of the upper troposphere at mid-latitudes and in the tropics and of the extra-tropical UT/LS region.

The seasonal cycle of CO₂ has been analysed separately for the upper troposphere and the tropopause region. A time shift of about one month due to transport across the tropopause has been found. In addition to this delay the amplitude of the seasonal cycle is weakened from 6 ppm in the upper troposphere to 2.5 ppm in the tropopause region. Between 30° N and 56° N no variation of the amplitude of the seasonal cycle has been found, however, the possibilities of statistical analysis are limited due to the current restriction of the data set to three years.

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Two example flights from Germany to East Asia discussed as examples show a distinct positive correlation between CH₄ and CO₂ in boreal winter that switches into an anticorrelation reflecting the seasonal changes in atmospheric CO₂ and CH₄ levels.

CARIBIC is continuing the monthly flights of its instrument container including the collection of air samples providing a continuously growing data set. Longer timeseries will allow for more detailed statistical analyses in the future. In addition, we hope the repeated simultaneous accurate measurements will provide useful data for comparisons of several species at the same time while at present model evaluations are made species by species mostly independently.

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Table 1. Mixing ratios of CH₄, CO₂, N₂O, and SF₆ of NOAA standards and working standards. For the working standards the error is calculated from the standard deviation of the mean of several independent calibration runs (number of runs given in brackets). For SIL196 one measurement performed at the Max Planck Institute for Biogeochemistry in Jena is included.

	CH ₄ [ppb]	CO ₂ [ppm]	N ₂ O [ppb]	SF ₆ [ppt]
CA 04450	1797.92	367.65	316.00	4.77
CA 06883	1684.13	373.17	304.80	3.82
CA 06890	1887.30	382.95	325.60	4.78
KOMP1 (<i>n</i> =13)	1866.51±0.27	378.78±0.05	319.93±0.07	6.11±0.01
SIL194 (<i>n</i> =7)	1866.53±0.42	384.42±0.08	322.89±0.17	6.29±0.02
SIL195 (<i>n</i> =5)	1890.99±0.48	380.99±0.06	324.06±0.17	6.08±0.02
SIL196 (<i>n</i> =4)	1843.68±0.10	374.86±0.06	320.28± 0.09	5.97±0.01

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Table 2. Coefficients a_1 to a_7 that result from fitting function 2 to the CO₂ timeseries shown in Fig. 5.

	troposphere	stratosphere
a_1	376.30±0.82	377.23±1.07
a_2	0.35±0.07	0.21±0.08
a_3	-0.003±0.001	-0.001±0.001
a_4	2.64±0.25	0.58±0.20
a_5	0.08±0.38	-0.97±0.35
a_6	-0.69±0.30	-0.25±0.31
a_7	0.084±0.34	0.43±0.25
reduced χ^2	1.54	3.17

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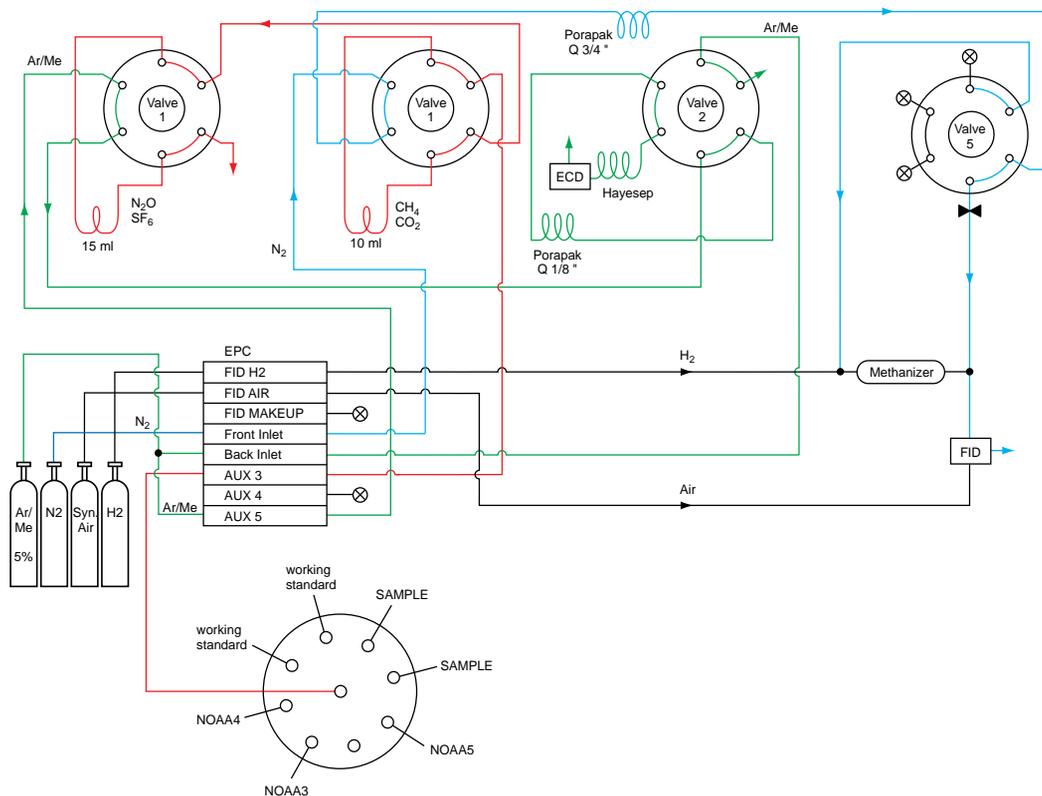


Fig. 1. Schematic layout of the GC-system for the detection of greenhouse gases at the beginning of a measurement cycle. Valves 1 have already switched to their position for loading the sampling loops, valve 2 is in the position for directing the carrier gas flow through the columns of the ECD channel, and the flow throw valve 5 is directed to the methanizer.

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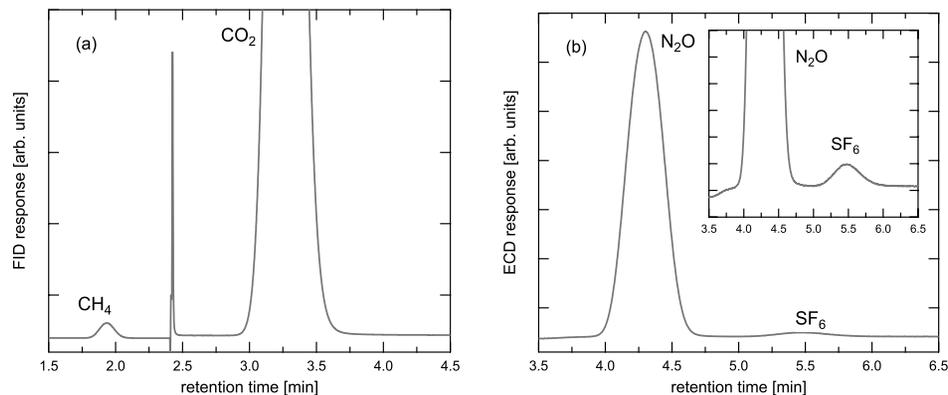


Fig. 2. Examples of gas chromatograms of the working standard obtained with an FID **(a)** and an ECD **(b)**. To detect CO₂ with the FID the gas flow is directed over a methanizer after the CH₄ has passed. The spike in the FID chromatogram at 3.9 min is caused by this valve switching.

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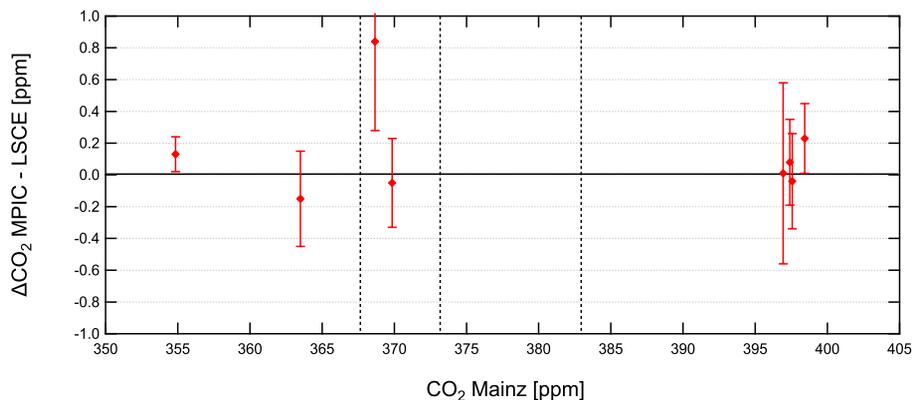


Fig. 3. Absolute difference of the analysis of CO₂ mixing ratios for eight reference gases as a function of the absolute CO₂ mixing ratio as determined at MPIC. The vertical dashed lines indicate the CO₂ mixing ratios contained in the NOAA standards used for calibration at MPIC (cf. Table 1).

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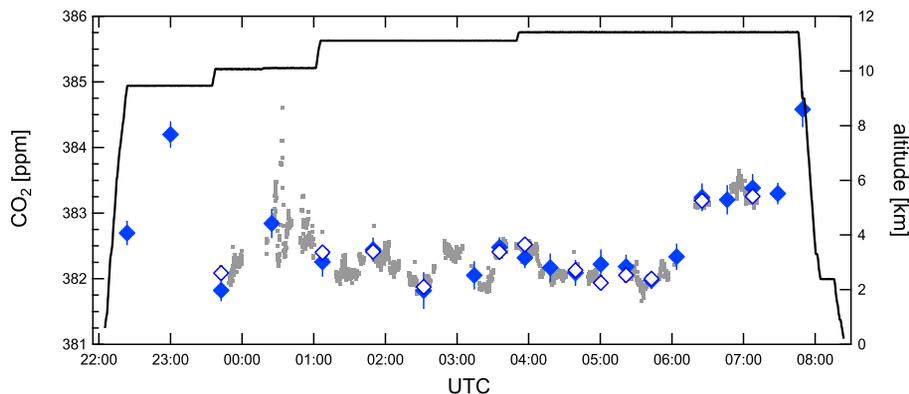


Fig. 4. Altitude (solid line) and timeseries of CO_2 measured in-situ (grey dots) and from wholeair samples (closed symbols) for one CARIBIC flight. Integrals over the sampling times have been calculated from the continuous timeseries (open symbols) unless the sampling time coincided with a calibration gap.

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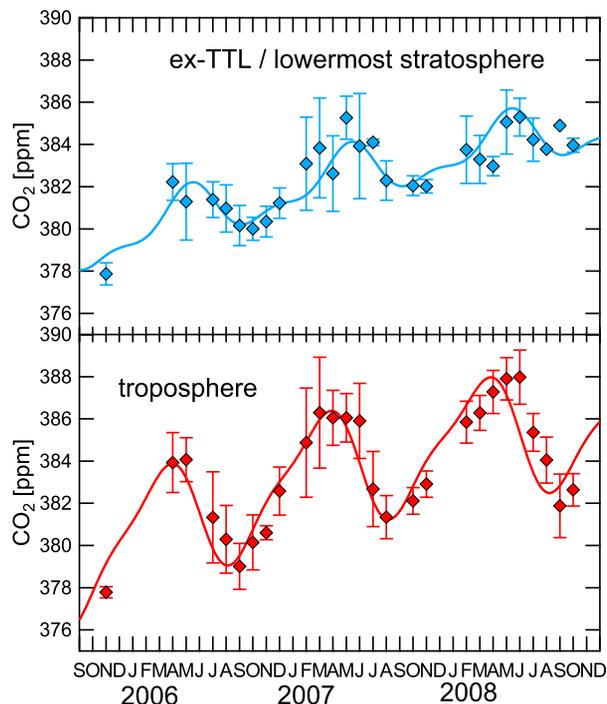


Fig. 5. CO₂-timeseries measured during CARIBIC flights to Asia in the extra-tropical tropopause transition layer and lowermost stratosphere (upper panel) and in the upper troposphere (lower panel). The cycle above the tropopause is delayed by approximately one month. The error bars indicate the standard deviation from the monthly mean. Each month typically 28 samples are collected.

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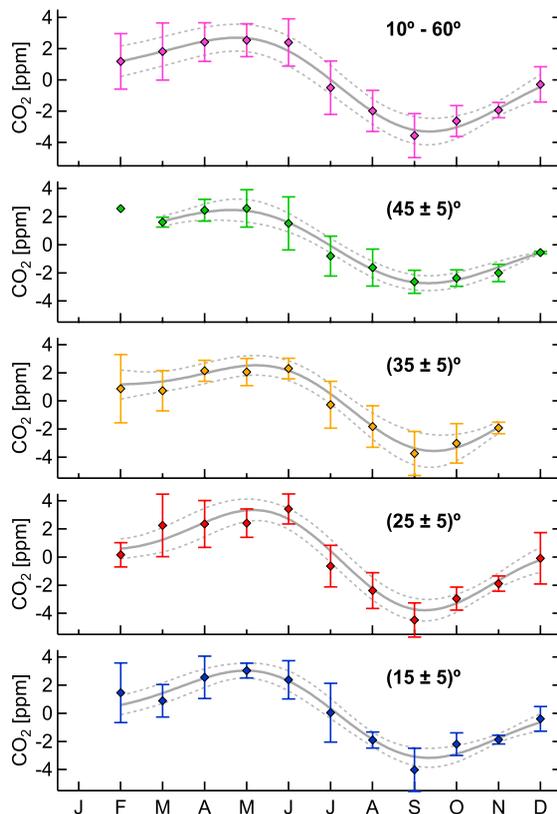


Fig. 6. Seasonal cycle of CO₂ for all tropospheric samples (top panel) and for four latitudinal bands of 10° width. The solid lines are harmonic polynomial fits to the detrended cycle, the dashed lines mark the 1-sigma confidence bands. The error bars indicate the standard deviation of each month's mean value.

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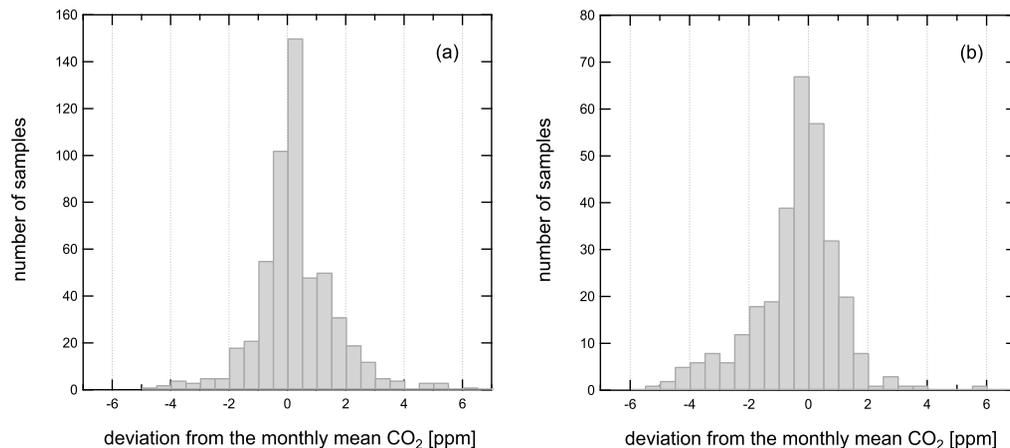


Fig. 7. Distribution of the CO₂ mixing ratio around the monthly median value for samples collected in the upper troposphere **(a)** and above the tropopause **(b)**. Only few samples have mixing ratios exceeding the monthly median by more than 3 ppm, which implies that the samples are largely representative for background air.

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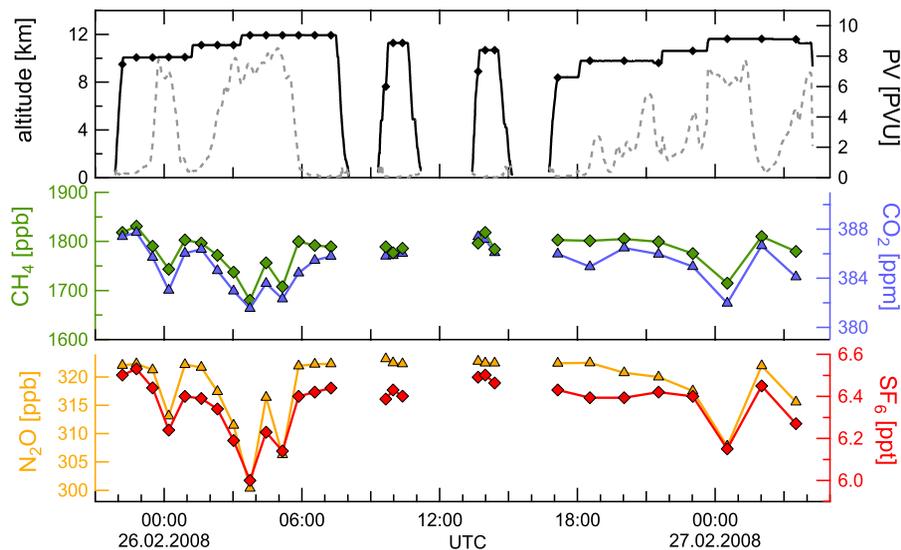


Fig. 8. Overview of CARIBIC flights Frankfurt ↔ Guangzhou ↔ Manila on 25, 26, 27 February 2008. Top panel: Altitude (black solid line) and PV (grey dotted line), middle panel: CH₄ (green diamonds) and CO₂ (blue triangles) mixing ratios, bottom panel: N₂O (orange triangles) and SF₆ mixing ratios (red diamonds).

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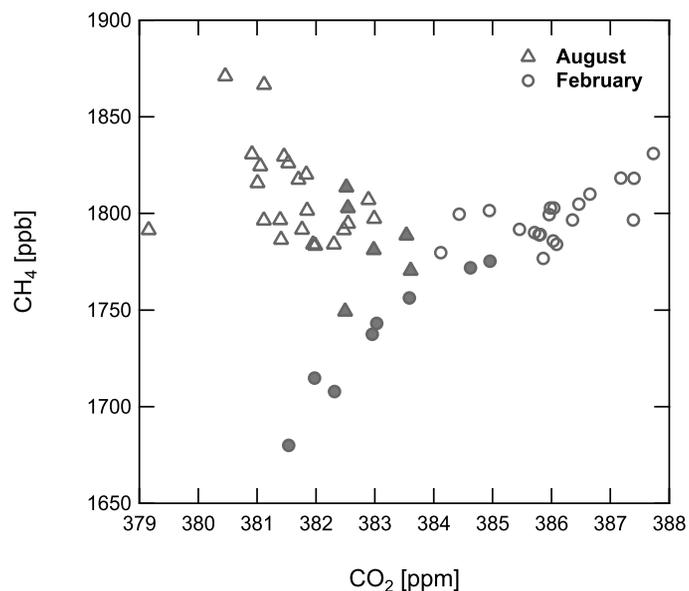


Fig. 9. Correlation between CH₄ and CO₂ for two CARIBIC flights, one in August 2007 (triangles) and one in February 2008 (circles). While in winter a pronounced positive correlation can be observed, this behaviour changes in summer. Samples taken at high PV values >3 PVU are marked by filled symbols, tropospheric samples by open symbols.

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