Atmospheric
Measurement
Techniques

Radiocarbon analysis of stratospheric CO_2 retrieved from AirCore sampling

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Abstract. Radiocarbon (^{14}C) is an important atmospheric tracer and one of the many used in the understanding of the global carbon budget, which includes the greenhouse gases CO_2 and CH_4. Measurement of radiocarbon in atmospheric CO_2 generally requires the collection of large air samples (a few liters) from which CO_2 is extracted and then the concentration of radiocarbon is determined using accelerator mass spectrometry (AMS). However, the regular collection of air samples from the stratosphere, for example using aircraft and balloons, is prohibitively expensive.

Here we describe radiocarbon measurements in stratospheric CO_2 collected by the AirCore sampling method. AirCore is an innovative atmospheric sampling system, which comprises a long tube descending from a high altitude with one end open and the other closed, and it has been demonstrated to be a reliable, cost-effective sampling system for high-altitude profile (up to ≈ 30 km) measurements of CH_4 and CO_2. In Europe, AirCore measurements have been being performed on a regular basis near Sodankylä (northern Finland) since September 2013. Here we describe the analysis of samples from two such AirCore flights made there in July 2014, for determining the radiocarbon concentration in stratospheric CO_2. The two AirCore profiles were collected on consecutive days. The stratospheric part of the AirCore was divided into six sections, each containing ≈ 35 µg CO_2 (≈ 9.6 µgC), and stored in a stratospheric air subsampler constructed from 1/4 in. coiled stainless steel tubing (≈ 3 m). A small-volume extraction system was constructed that enabled > 99.5 % CO_2 extraction from the stratospheric air samples. Additionally, a new small-volume high-efficiency graphiti-zation system was constructed for graphitization of these extracted CO_2 samples, which were measured at the Groningen AMS facility. Since the stratospheric samples were very similar in mass, reference samples were also prepared in the same mass range for calibration and contamination correction purposes. The results show that the $\Delta^{14}CO_2$ values from tropopause up to about $19(\pm 1)$ km for the sample collected on 15 July was 18 ± 6‰ (samples 1–4), very similar to the current tropospheric value. On the other hand, $\Delta^{14}CO_2$ values from tropopause up to about $18(\pm 1)$ km for the sample collected on 16 July (samples 1–4) showed a large gradient from -62 to 21‰. The next sample in the profile, corresponding to about $18(\pm 1)$–$22(\pm 2)$ km (one sample from each profile), shows slight enrichment of 80 ± 20‰. The last section from both profiles, containing air from the upper stratosphere, was contaminated with pre-fill air.

1 Introduction

The concentration of greenhouse gases (GHG), with carbon dioxide as the most prominent example, has been and still is increasing, predominantly due to emissions from fossil fuel combustion. The consequences in terms of climate change are certainly detrimental (IPCC, 2014a, b) if the rapid increase in GHG concentrations is not regulated and properly accounted for. This creates a necessity for better understanding and quantification of the sources, reservoirs, sinks, and the transport mechanisms involved.

Carbon dioxide is a naturally occurring greenhouse gas produced mainly through respiration by aerobic organisms and decay of organic materials. It is also the product of combustion of any carbon-containing compound. Carbon in carbon dioxide exists in the form of three naturally occurring isotopes, i.e., ^{12}C, ^{13}C, and ^{14}C. Radiocarbon (^{14}C) is the only naturally occurring radioactive isotope of carbon (half-life, $t_{1/2} = 5730 \pm 40$ years), which is continuously produced through the reaction of thermalized neutrons from cosmic radiations with ^{14}N in the upper atmosphere (Lingenfelter, 1963; Masarik and Beer, 1999). The produced ^{14}C combines with oxygen to produce $^{14}CO_2$, which forms a trace component of atmospheric CO_2 (presently $^{14}CO_2/^{12}CO_2 \approx 1.2 \times 10^{-10}$ %). $^{14}CO_2$ is an important atmospheric tracer, which helps in the understanding of the levels of anthropogenic emissions from fossil fuels. This is due to the fact that fossil fuel, and thus also CO_2 from combusting it, is virtually radiocarbon-free. This CO_2 from fossil fuel dilutes the atmospheric $^{14}CO_2$ concentration upon release.

The concentration of CO_2 in the atmosphere has had an observed annual rise in recent years of ≈ 2 ppm year^{-1} (Hartmann et al., 2013; Dlugokencky and Tans, 2016). This rise in the concentration of CO_2 due to the burning of fossil fuels is at present the main cause for the decrease in the radiocarbon concentration in atmospheric CO_2. Aircraft sampling of atmospheric CO_2 is regularly performed at various altitudes, but unfortunately air samples are only collected up to the upper troposphere/lower stratosphere (Sweeney et al., 2015; Machida et al., 2008; Brenninkmeijer et al., 2007, 1995). Although balloon-based sampling has been demonstrated as a method for collecting stratospheric air for measurements of radiocarbon in stratospheric CO_2 (Kanu et al., 2016; Ashenfelter et al., 1972; Nakamura et al., 1992, 1994; Hagemann et al., 1959), this method of sampling is extremely expensive and difficult to sustain for longer periods. Here we describe the use of the AirCore sampling method (Karion et al., 2010) as a viable and affordable alternative for sampling stratospheric air for the measurements of radiocarbon in stratospheric CO_2. As AirCore forms only a modest payload (~ 3.6 kg), it can be flown with a small-size balloon, thus saving considerably on launching costs and infrastructure. The stratospheric part of the AirCore can be divided into several isobaric sub-segments, thus allowing the determination of radiocarbon at different altitude ranges. Although the sample sizes obtained through AirCore sampling are small (only ~ 50 mL, $\sim 10 \mu gC$), they are just enough for performing quantitative radiocarbon measurements at our accelerator mass spectrometry (AMS) facility.

1.1   Sampling

Regular AirCore profiles of CO_2, CH_4, and CO have been made near Sodankylä (in northern Finland, 67.4° N, 26.6° E) since September 2013 (Chen et al., 2016). Normally, the air contained in an AirCore is not stored. We have, however,
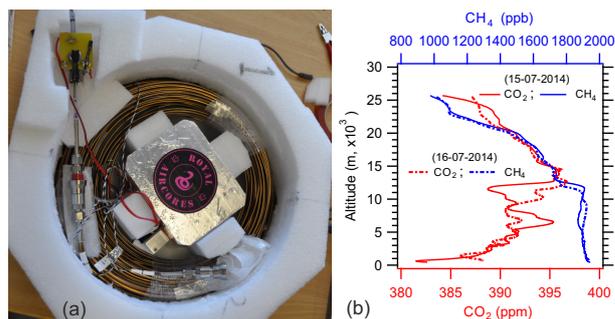
Figure 1. (a) Picture of an AirCore, used during the sampling campaign at Sodankylä, constructed from long thin walled stainless steel tubing (≈ 100 m long, wall thickness of 0.254 mm). **(b)** Corrected vertical concentration profiles of CO_2 (red) and CH_4 (blue) retrieved through AirCore samplings performed on 15 July 2014 (solid line) and 16 July 2014 (dashed line) at Sodankylä. Note the different scale span for CO_2 and CH_4.

collected the stratospheric part of the AirCore samples for several selected AirCore flights using a stratospheric air sub-sampler described elsewhere (Mrozek et al., 2016). Briefly, the AirCore that has been flown in Sodankylä is constructed from two pieces of stainless steel tubing with an outer diameter of 0.64 cm (1/4 in. and ~ 40 m long) and 0.32 cm (1/8 in. and ~ 60 m long), respectively. The wall thickness for both pieces is 0.025 cm (0.01 in.). The estimated volume of the AirCore is ~ 1400 mL. The AirCore, before releasing with the help of a balloon, is first filled with a standard dry "fill gas" with known CO_2, CH_4, and CO concentrations ($CO_2 = 386.10 \pm 0.09$ ppm; $CH_4 = 1880 \pm 2$ ppb; CO deliberately spiked to 7972 ± 5 ppb). The fill gas is a compressed air cylinder containing dry ambient air (sampled on 27 June 2013 at Sodankylä, Finland) spiked with carbon monoxide. It should thus contain CO_2 with contemporary levels of radiocarbon. The accurate determination of the radiocarbon content in CO_2 of the fill gas was initially not deemed essential for this work, and has thus not been performed. The AirCore is then released with one end open into atmosphere. As the AirCore travels higher in the atmosphere, the fill gas inside the AirCore is evacuated due to the drop in pressure. During its descent through the atmosphere, the evacuated AirCore equilibrates with the ambient pressure, and therefore the tube gradually fills itself with air from its surroundings. The open end of the AirCore is then closed automatically upon landing, preserving the collected air column until analysis is performed, which is typically within a few hours after the AirCore has landed and is recovered.

Several AirCore profiles were collected at Sodankylä during a campaign in July 2014, out of which two stratospheric air profiles (collected on 15 July and 16 July 2014) were preserved for radiocarbon measurements of stratospheric CO_2 described in this work. Figure 1a shows the picture of an AirCore that was used during the sampling campaign. Since the

AirCore is initially filled with a fill gas before release, there is a small fraction of the fill gas still remaining in the Air-Core that is not evacuated completely. This leftover fraction of fill gas contaminates the air from the highest sampled altitude. Fortunately, the impact on the samples from the highest altitude can be accurately corrected by making use of the CO measurements that have been performed in parallel to CO$_2$ and CH$_4$, and the fact that the fill gas contains about a hundredfold as much CO (7972 $\pm$ 5 ppb) than the natural air. In this way the measured CO is a direct measure of the fill gas fraction. The correction takes advantage of the fact that the CO concentration of stratospheric air is low ($\sim$ 15 ppb or $\sim$ 0.2 % of the CO concentration of the fill air). We derive a good approximation of the percentage of the fill air and the stratospheric air based on the measured CO concentration of the mixture of the stratospheric air and the fill air. Details of the corrections will be given in Chen et al. (2016). These corrected atmospheric profiles of CO$_2$ (red, solid and dashed lines) and CH$_4$ (blue, solid and dashed lines) from the two AirCore samplings are shown in Fig. 1b. The CO$_2$ profile shows the variability in the CO$_2$ concentration throughout the atmosphere, whereas the CH$_4$ concentration is rather constant in the troposphere and drops continuously with increasing altitude in the stratosphere, predominantly due to destruction by oxidation.

The AirCore, containing the vertical atmospheric profile, was connected to a cavity ring-down spectrometer (CRDS, Picarro Inc., CA model: G2401) for simultaneous measurements of the CO$_2$, CH$_4$, and CO concentrations. The sampling end of the AirCore was connected to a standard dry "push gas" line (containing the same CO-spiked fill gas again), and the other end was connected to the CRDS analyzer. The sampled air column inside the AirCore was then gently "pushed" out with the push gas into the CRDS analyzer. The exhaust from the CRDS analyzer was connected to a stratospheric air subsampler (SAS) (Mrozek et al., 2016). The sequence of transfer of the stratospheric air from AirCore into the SAS is also illustrated in Fig. 2a (marked in red) of the following section. The SAS built at the University of Groningen, similar to the one described in Mrozek et al. (2016), comprises a series of six pieces of connected stainless steel tubing (Swagelok, o.d. = 6.35 mm, i.d. = 4.57 mm, $\approx$ 50 mL), with each section measuring 3 m. The tubing sections were joined by three-port two-way valves (Swagelok SS-43GXS4), which allows uninterrupted transfer of the AirCore content into the SAS and subsequent isolation of each section for a desired analysis later. Each section in the SAS thus represented an integrated sample from a determinable altitude range. Each section contained $\approx$ 50 mL stratospheric air (at standard temperature and pressure (STP)), with $\approx$ 35 μg CO$_2$ ($\approx$ 9.6 μgC). CO$_2$ samples from each section of the SAS were later extracted and processed for ^{14}C measurements at the Centre for Isotope Research (CIO), Groningen, using accelerator mass spectrometry (AMS).
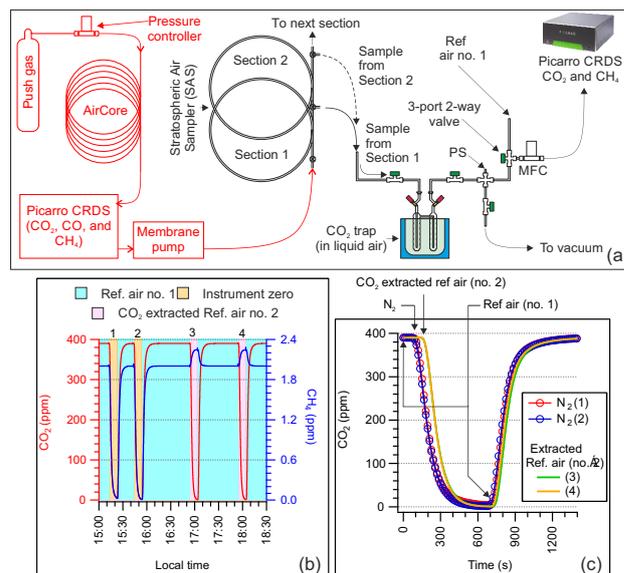
Figure 2. (a) Schematic of the sample transfer procedure from the AirCore into the SAS (marked in red) and the extraction system used for the extraction of CO$_2$ from stratospheric air contained in the SAS. The CO$_2$ trap was submerged in a liquid air bath, which allowed quantitative freezing of CO$_2$ and avoided co-freezing of CH$_4$ and O$_2$. Using a CRDS analyzer (Picarro G2301), the concentration of CH$_4$ in the CO$_2$-extracted air was determined. The components indicated with abbreviations are as follows: MFC, mass flow controller; PS, pressure sensor. (b) An example time series showing a control sampler filled consecutively with N$_2$ (instrument zero, first two shown with an orange background) and reference air (no. 2, CO$_2$-extracted, last two shown with a pink background) to evaluate the extraction efficiency at a flow rate of 3 sccm. Reference air (no. 1) is directed through the Picarro analyzer when the extraction system is being made ready for the next extraction (shown with a cyan background). (c) Superimposed CO$_2$ signal during the introduction of the zero gas (N$_2$) and the CO$_2$-extracted reference air (no. 2) showing a near-100 % extraction efficiency.

1.2 Extraction

Following the sample collection and subsequent transfer into the SAS at Sodankylä, the SAS was brought back to Groningen for subsequent processing and measurement. CO$_2$ from the air samples in the SAS was extracted using an extraction system (total volume $\approx$ 20 mL) as shown in Fig. 2a. The detachable CO$_2$ trap, made from Pyrex, has two flow-through freezing tubes submerged in a liquid air bath. Each section of the SAS is individually connected to the extraction system. The extraction system is first evacuated for approximately an hour and then the air from the SAS is slowly expanded, during which the CO$_2$ trap is submerged in liquid air. During this expansion of sample in the extraction system, a reference air (no. 1) is directed into the connected CRDS analyzer (Picarro G2301) through a three-port two-way valve. Once the pressure in the extraction system stabilized, the air from the

extraction unit is directed into the CRDS analyzer to determine the CH$_4$ and the remaining CO$_2$ concentration in the extracted air. A flow rate of 3 sccm (standard cubic centimeters per minute), using a mass flow controller (π MFC-LP P2A, MKS), was used for complete extraction of CO$_2$ and simultaneous determination of CH$_4$ in the CO$_2$-extracted air. The extraction procedure was optimized by extractions performed with a reference-air-filled (no. 2) "control" sampler ($\approx$ 50 mL), similar to the SAS. The extraction efficiency was verified by comparison of the change in CO$_2$ signal with introduction of nitrogen (as zero-gas) and CO$_2$-extracted reference air into the CRDS analyzer from the control sampler. The process of optimization is shown in Fig. 2b and c. A time series plot showing consecutive introduction of a zero gas (N$_2$, first two drops in the CO$_2$ and CH$_4$ signal; orange background) followed by CO$_2$-extracted reference air (no. 2, last two drops in the CO$_2$ signal; pink background) is shown in Fig. 2b. In between the consecutive measurements of N$_2$ (1 and 2) and CO$_2$-extracted reference air (3 and 4), reference air (no. 1) was measured, shown with a cyan background. Figure 2c shows the superimposed CO$_2$ signals during introduction of the zero gas (N$_2$) and CO$_2$-extracted reference air (no. 2) from the control sampler into the CRDS analyzer. This method yielded an extraction efficiency > 99.5 %, which was also confirmed from the pressure of CO$_2$ in the CO$_2$ trap measured during the graphitization step discussed in the next section. Although the control loop was filled with N$_2$ and reference air (no. 2) with very similar pressure, the superimposed CO$_2$ signals, in Fig. 2c, show a small difference in the total running time of N$_2$ and CO$_2$-extracted reference air (no. 2). This is due to the fact that the reference air (no. 2) was cooled with liquid air during extraction, which led to a pressure drop, and thus a reduction of the total volume of air going through the CRDS analyzer, before reaching the minimum differential pressure between the extraction system side and the CRDS analyzer side that the (MFC) could handle. As soon as the pressure in the extraction unit attained the minimum pressure ($\approx$ 200 mbar), reference air (no. 1) was then directed into the CRDS analyzer and the extraction system was slowly evacuated while the CO$_2$ trap was still submerged in the liquid air bath. Following the complete evacuation of air from the extraction unit, the CO$_2$ trap was disconnected and immediately taken for graphitization, described in the next section.

The use of liquid air, during the extraction of CO$_2$ from air, prevented the co-freezing of CH$_4$ (and of oxygen). A flow rate of 3 sccm ensured efficient removal of CO$_2$, while allowing simultaneous determination of the CH$_4$ concentration. The concentration of methane in the CO$_2$-extracted reference air (no. 2) as determined by the CRDS was 2242.8 $\pm$ 0.3 ppb (error in the mean, $n = 37$), which was in close agreement with the methane concentration as determined by gas chromatography (GC) (2242.1 $\pm$ 2 ppb) from a whole air sample directly from the cylinder. The slightly higher concentration values observed for methane in CO$_2$-extracted air is most

likely the production of CH$_4$ from the metal–metal friction during the operation of the stainless steel valves, in the sampler, the extraction system, and the control sampler (Higaki et al., 2006). This appearance of "additional" CH$_4$ was attributed to the production from the operation of the stainless steel valves and not to surface degassing, as the production of CH$_4$ from a given valve did not disappear nor decrease upon repetitive turning while the valve is constantly flushed with dry nitrogen. During the extraction of CO$_2$ from the SAS, control extractions were also performed with reference air (no. 2), and all extracted CO$_2$ samples were processed and measured by the AMS.

1.3 Graphitization and AMS analysis

The AMS facility at CIO is a 2.3 MeV Tandetron built by High Voltage Engineering Europa (Gottdang et al., 1995). As the source of our present AMS facility is not yet capable of using gaseous CO$_2$, the CO$_2$ samples are reduced to elemental carbon, which is commonly referred to as graphite in the radiocarbon community. At the CIO, Groningen, the reduction of CO$_2$ ($\sim$ 1–2 mgC – regular sample size) is carried out at 600 °C in the presence of H$_2$ ($\sim$ 2.5 × partial pressure of CO$_2$) and Fe powder (Alfa Aesar, 325 mesh, 2 mg) (Aerts-Bijma et al., 1997). A new graphitization system and procedure was developed later for the preparation of small samples ($\sim$ 10–25 µgC), which featured the use of Fe in the form of a porous pellet (de Rooij et al., 2010) instead of powder, as in the case of regular samples. For the graphitization of the CO$_2$ samples extracted from AirCore stratospheric air samples, we modified and optimized the preparation method of de Rooij et al. (2010). A new low-volume graphitization reactor, as shown in Fig. 3, was designed in-house for the conversion of CO$_2$ into elemental carbon. This graphitization setup comprised two sections: (1) the reactor region (marked in the blue box) and (2) the mass determination region (marked in the red box). The graphitization setup was connected to a common vacuum line to which four other graphitization units were also connected. A turbo pumping station (Edwards, TS75W1001) was used to evacuate the graphitization unit.

The reactor region comprised the stainless steel reactor manifold, a reaction tube, a water trap tube, and a pressure transducer (Measurement Specialties (Europe), Ltd., model: 13A-050A). The reaction tube (o.d. = 6 mm, i.d. = 3 mm, length = 58 mm) and the water-trap tube (6 mm × 3 mm × 30 mm) connected on the manifold were constructed from fused silica. The total volume of the reactor thus achieved was $\approx$ 1.5 mL. We used magnesium perchlorate (Mg(ClO$_4$)$_2$) in the water-trap tube to remove water produced during the reduction of CO$_2$ (Santos et al., 2007a) instead of using Peltier-cooled water traps that are in use for larger samples. We observed that the Peltier-cooled water traps retarded/prohibited the reduction reaction for samples below 50 µgC. Although the reduction reaction is much

more efficient and faster with the use of $Mg(ClO_4)_2$, care must be taken to avoid any $Mg(ClO_4)_2$ particles entering the heated section of the reactor tube, which mostly happened due to electrostatic repulsion produced through the operator. It seems likely that one of the thermal decomposition products of $Mg(ClO_4)_2$ (Devlin and Herley, 1986) poisons the catalytic properties of Fe, and thus significantly slows down or even prohibits the reduction reaction. Before the actual graphitization, $Mg(ClO_4)_2$ in the water trap was heated to 100 °C while evacuating the system. This released a significant amount of water, making the trap even more efficient during graphitization. Iron pellets (≈ 1.4 mg, 1.3 mm diameter, ≈ 0.4 mm thick) were prepared by pressing Fe powder (Alfa Aesar, 325 mesh) at 300 N (de Rooij et al., 2010). The reactor temperature was set at 500 °C, and hydrogen equivalent to ≈ 2.2 times the CO_2 partial pressure (at STP) was used. Hydrogen is introduced into the reactor through the vacuum line, while the CO_2 in the reactor is frozen in the water trap with liquid N_2. While introducing hydrogen in the reactor, the valve connecting the common vacuum line and the pump is closed. The reaction temperature and hydrogen pressure were optimized for minimum CH_4 production, thereby minimizing the loss of sample during the graphitization process. To optimize the reaction condition, we continuously monitored the production of CH_4 in the reactor during test graphitizations with a residual gas analyzer (Extorr, XT100) connected to the manifold through a 25 µm (i.d.) GC capillary column. This manifold was identical to the one used for sample preparation, except for the additional port to connect the GC capillary column (not shown in Fig. 3). The reaction time for CO_2 samples < 50 µgC was typically less than 20 min with reaction efficiency better than 95 %. The reaction progress was determined by monitoring the change of pressure inside the reactor using the pressure transducer (no. 1) connected on the manifold.

The reactor region in the setup is connected to the mass determination region with a known volume. This known volume was used for the determination of the mass of the reference gases as well as of the stratosphere CO_2 samples. As contamination is a serious concern for radiocarbon measurements of ultra-small samples by AMS, it requires quantitative determination of the accumulated contaminants over the whole preparation process. Contamination of two types pose a threat to radiocarbon determination in ultra-small samples: (1) modern carbon contamination (MCC, containing contemporary levels of radiocarbon) and (2) dead carbon contamination (DCC, originating from fossil materials with no radiocarbon). MCC and DCC affect samples differently, depending on the age and mass of the sample (Paul et al., 2016; Brown and Southon, 1997; Santos et al., 2007b; de Rooij et al., 2010). Very small samples such as those in the present work (≤ 10 µgC) are severely affected by both MCC and DCC. Hence, for such small samples determination of the accumulated contaminating carbon is essential. To determine the mass of accumulated contaminating carbon in a
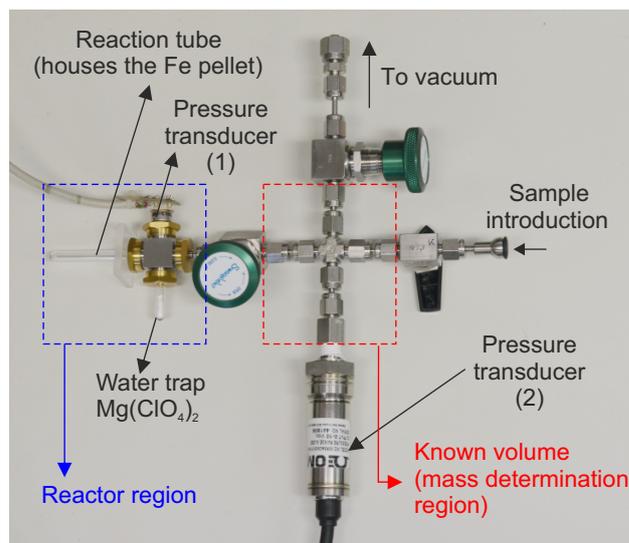
Figure 3. Newly designed reactor (≈ 1.5 mL, blue box) for preparation of ultra-small samples (3–50 µgC) for AMS measurements. Each section of the stratospheric air subsampler contains ≈ 35 µg CO_2 sample that is reduced to graphite (≈ 9.6 µgC) on porous iron pellets at 500 °C in the presence of hydrogen ($\approx 2.2 \times$ partial pressure of CO_2). The mass determination section, comprising a known volume, is used to determine the mass of the reference materials and the samples based on pressure measured at pressure transducer (no. 2). Pressure transducer (no. 1) is used to monitor the progress of the graphitization reaction.

sample, reference materials (with masses similar to that of the sample) containing varying levels of radiocarbon are also prepared following identical preparation steps. The extent to which the reference materials deviate from the consensus value provides a direct measure of the accumulated contaminating carbon. With this information, correction of the radiocarbon values is possible (de Rooij et al., 2010; Santos et al., 2007b; Brown and Southon, 1997). This correction to the reference samples is also applied to the stratospheric samples to remove the deviations arising from contamination, assuming that all samples accumulate similar contaminations following similar preparation steps. As the relative influence of MCC and DCC depends critically on the mass of the samples, an accurate determination of the sample mass is essential.

Following completion of the graphitization reaction, the graphitized iron pellets were pressed on AMS aluminum holders, so-called "targets". Since these pellets are too small and the amount of material is not sufficient to fill the hole of the targets, a clean unused iron pellet was first dropped into the target hole on top of which the graphitized pellet was placed. This procedure with two pellets allowed stable measurements, as the pressed target surface was much smoother this way (excessive fracturing of the pressed surface was observed with only one pellet). Each target is measured for 40 min in the AMS and the data are analyzed offline.

The concentration of CO_2 in stratospheric air, as observed in the two collected AirCore profiles (shown in Fig. 1), was between 387 and 397 ppm corresponding to 9.51–9.76 µgC in each section of the SAS. Since the mass of CO_2 from each section of the SAS was quite constant, reference samples and CO_2 samples from reference air (no. 2, from control loop) were prepared in the same mass range as the samples, a prerequisite for contamination correction. For correcting the ^{14}C in CO_2 measurements of the stratospheric air samples and CO_2 from reference air (no. 2), a set of three different reference materials was prepared with ^{14}C levels relevant for the present measurements. This set comprised ANU sucrose ($\Delta^{14}C = 506.1$‰, IAEA C6), HOxII ($\Delta^{14}C = 340.6$‰, SRM 4990C), GS51 ($\Delta^{14}C$ Activity $= 88$‰, local reference material prepared from cane sugar acquired in November 2002). Furthermore, a background material, Rommenhöller CO_2 (virtually free of ^{14}C) was also used. In addition to these reference samples, CO_2 (~ 2 mgC) was extracted from reference air no. 2 for the determination of its ^{14}C activity ($\Delta^{14}C = 12 \pm 4$‰). All the ^{14}C activities shown in this paper are reported as $\Delta^{14}C$ (‰) (Mook and van der Plicht, 1999), which indicates the enrichment/depletion in $^{14}C / C$ of CO_2 with respect to the preindustrial level of 0‰. The HOxII measurements were used to calibrate all the other ^{14}C activities. The two other reference materials, IAEA C6 and GS51, were used to verify the reliability of the correction. Unlike the reference materials, which were directly graphitized from CO_2, the CO_2 samples extracted from reference air (no. 2) were treated following preparation steps identical to the CO_2 samples from stratospheric air. Figure 4 shows a summary of all the corrected ^{14}C activities of the reference materials and CO_2 from reference air (no. 2) relative to HOxII standards. The corrections due to MCC and DCC contamination ranged from ~ -12‰ for reference air no. 2, via ~ -35‰ for GS-51, to ~ -60‰ for ANU. The correction values for reference air no. 2 and GS-51 are the most relevant for the actual stratospheric samples. The corrected ^{14}C activities determined for the reference samples and reference air are in good agreement with their consensus values and the measured value respectively, although some individual outliers occur and GS51 is systematically lower than its established value (by 27 ± 7‰). On the other hand, the reference air no. 2, which is the only one that is also CO_2 extracted from air just like the samples, agrees very well. The error bars associated with each data point correspond to the measurement uncertainties of which the poor counting statistics (~ 2000 counts, $1/\sqrt{2000} = 22$‰) comprise the largest fraction. The reported activities in Fig. 4 are the averages of all measurements ($\pm$ standard error in the mean).
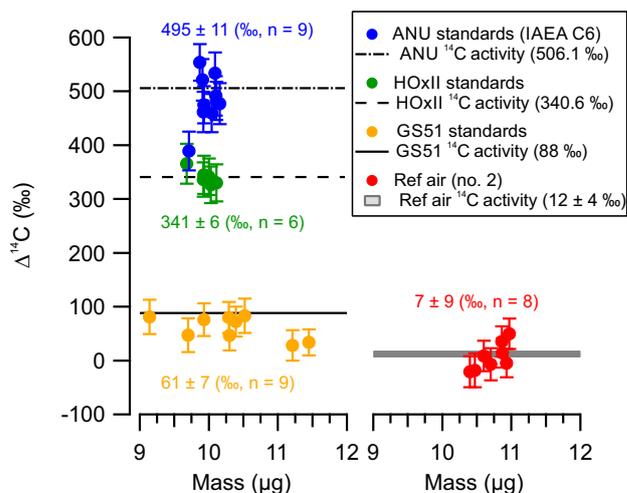
Figure 4. A summary of the derived ^{14}C activities (in $\Delta^{14}C$, ‰) of the reference materials and CO_2 extracted from reference air (no. 2) relative to HOxII. All the reference samples were prepared following identical preparation steps.

2 Results

The air samples stored in the SAS represented an integrated sample corresponding to an altitude range, the extent of which depended on the ambient pressure at the altitude where the sample was collected. The section of the AirCore profile that is transferred into the SAS can be determined based on the time it required for the sample to flow from the AirCore through the CRDS analyzer into the SAS. The concentration of CH_4 in the CO_2-extracted air, in each SAS section, was used to verify the correctness of the determined altitude based on timing. The decrease in the concentration of CH_4 in the stratosphere with increasing altitude is continuous and steep, making CH_4 a suitable proxy for the altitude check. However, due to the production of CH_4 from stainless steel surfaces as mentioned previously, the CH_4 signal might be corrupted in an unpredictable manner and to an unknown extent. Therefore, both timing and CH_4 information are used to determine the altitude range, and the degree of similarity between them is a good measure of reliability. Figure 5a and b show the results of the altitude determination from the two stratospheric AirCore samples collected on 15 and 16 July 2014. The blue circles show the AirCore CH_4 profile, the black solid line shows the AirCore profile corrected for fill gas, and the red solid line shows the predicted CH_4 concentration in each section of the SAS, based on the AirCore profile and the recorded sampling time and flow rate. Figure 5c and d show the correlation between the CH_4 concentration as predicted based on timing, shown in panel a and b, and concentrations measured by the CRDS analyzer during extraction. For most samples, the predicted CH_4 concentration was in good agreement with the concentration measured by the

CRDS analyzer during extraction. The largest deviation was observed for the sample representing the upper stratosphere (i.e. SAS section no. 6, marked with a red arrow in Fig. 5c and d) due to contamination from leftover fill gas, which contains compressed dry ambient air (sampled at Sodankylä, Finland) spiked with carbon monoxide. This influence from the fill gas above 24 km causes the difference between the measured and the corrected vertical CH$_4$ profiles of the atmosphere shown in Fig. 5a and b. The predicted CH$_4$ values for the SAS are of course based on the measured profile. The predicted value for the SAS above ~ 22 km for 15 July 2016 (Fig. 5c) and 16 July 2016 (Fig. 5d) is approximately 150 and 165 ppb lower than the measured value, respectively. The AirCore profiles, shown in Fig. 5, were obtained as the air from the AirCore moved through the CRDS analyzer into the sampler. During this transfer, behind the analyzer there is a small additional mixing of samples through diffusion that is not captured in the presented AirCore profile data. While diffusion in principle has affected all the samples to some extent, the ones near the upper stratosphere are affected the most due to the large difference in the CH$_4$ concentration of the sample and the fill gas. This extra contamination of upper stratospheric air (SAS section no. 6) with the leftover fill gas in the AirCore, due to diffusion, is predominantly the cause of the large observed deviation.

As timing is our primary parameter for altitude calculation, reliable knowledge of the timing during the filling of the SAS is crucial, i.e., the time when the valves at both ends of the SAS were closed during the filling process. Timing also includes here the accurate knowledge of the flow rate at which the sample from the AirCore is transferred into the SAS. A timing problem was observed in the dataset shown in Fig. 5b, which could have been caused by any of the previously mentioned reasons. By introducing a best fit timing offset of -33 s, we moved the whole predicted profile slightly upwards, and then the resultant predicted altitude range showed a good agreement with the measured concentrations, as seen in Fig. 5d. Control of the SAS filling process should, however, be improved, which is a topic for future research.

Figure 6a shows the CO$_2$ concentrations retrieved from the two AirCore samples described in this paper (orange triangles for 15 July 2014 and cyan circles for 16 July 2014) and the respective corrected AirCore profile (red line for 15 July 2014 and blue line for 16 July 2014). Figure 6b shows the measured radiocarbon concentration in the extracted CO$_2$ samples, with orange triangles representing samples from 15 July 2014 and cyan circles representing samples from 16 July 2014. The present Δ^{14}C value for tropospheric CO$_2$ is $\approx 20\,‰$ (Levin et al., 2013; Graven, 2015; Hua et al., 2013). The uncertainties in the Δ^{14}C values, shown in Fig. 6b, are about $\pm 30\,‰$, entirely caused by counting statistics. The sample from the upper stratosphere of the AirCore sampled on 16 July (sample 6) was lost during the graphitization process due to a leak in the reactor. As mentioned in the previ-
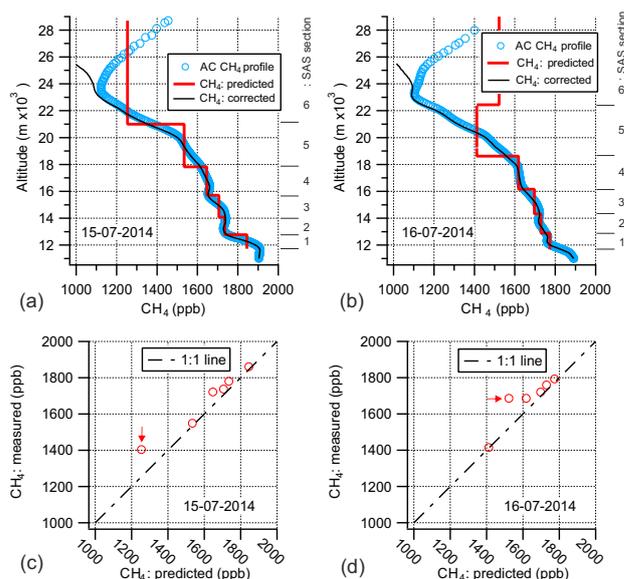
Figure 5. (a) AirCore (AC) CH$_4$ profile (shown with blue open circles), the corrected AirCore profile (shown with a solid black line), and calculated CH$_4$ concentration for each section of the SAS for the samples collected on 15 July 2014. **(b)** The same for the samples collected on 16 July 2014. **(c, d)** Correlation between the calculated CH$_4$ concentration and the CH$_4$ concentration as measured by the CRDS analyzer while extracting the CO$_2$ from the samples. The measured CH$_4$ concentration values, for both profiles, are in good agreement with the calculated CH$_4$ concentrations for all samples, except for the ones (indicated by arrows) corresponding to the upper stratosphere, which are contaminated with leftover fill gas.

ous section, during the extraction and graphitization of the stratospheric samples, CO$_2$ from reference air (no. 2) was also extracted, graphitized, and measured. AMS measurements of the eight CO$_2$ samples extracted from reference air (no. 2, $\approx 10\,\mu$gC each), after contamination corrections, yielded a mean Δ^{14}C value of $7 \pm 9\,‰$, which is in close agreement with the directly measured value of a 2 mgC sample extracted from reference air (no. 2) that yielded a Δ^{14}C value of $12 \pm 4\,‰$. This gives confidence in the contamination corrections applied.

The two CO$_2$ profiles shown in Fig. 6a are very similar, with slight differences near the tropopause (11–12 km, ≈ 4 ppm). The Δ^{14}C values in Fig. 6b corresponding to the SAS sections 1–4, for the sample collected on 15 July, are very similar ($18 \pm 6\,‰$). However, the Δ^{14}C values in Fig. 6b corresponding to the SAS sections 1–4, for the sample collected on 16 July, show a large gradient (from -62 to $+21\,‰$). The Δ^{14}C values corresponding to SAS sections 3, 4, and 5 are very similar in the two presented profiles. The Δ^{14}C values corresponding to SAS section 5, in both profiles, show some enrichment in ^{14}CO$_2$ due to constant production of radiocarbon in the stratosphere. In Fig. 6b, the Δ^{14}C value drops for the last sample (collected on 15 July 2014), which confirms the contamination of stratospheric
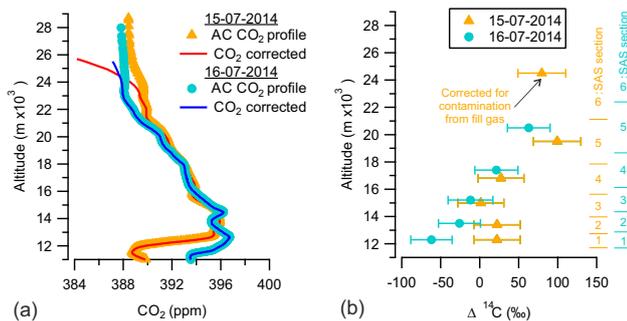
Figure 6. (a) AirCore (AC) CO_2 profiles (orange triangles for 15 July 2014 and cyan circles for 16 July 2014) and their corresponding corrected AirCore CO_2 profiles (red line for 15 July 2014 and blue line for 16 July 2014). **(b)** The $\Delta^{14}C$ values (‰, orange triangles representing samples from 15 July 2014 and cyan circles representing samples from 16 July 2014) in each section of the SAS. The last CO_2 sample extracted from the AirCore sampled on 16 July 2014 was lost. The uncertainties in the $\Delta^{14}C$ values correspond to measurement uncertainties arising from limited counting statistics.

CO_2 (enriched in ^{14}C) with the CO_2 from fill gas (natural levels of ^{14}C, although the exact $\Delta^{14}C$ value is not known), as mentioned previously. The extent of contamination in the last sample from the fill gas was determined from the CO profile, since the concentration of CO in the stratosphere is low and fairly constant (≈ 15 ppb), whereas the concentration of CO in the fill gas is high and known (7972 ppb). This leads to a small correction (from 73 to 80‰) for contamination with $\sim 11\%$ fill gas, for which we assumed a $\Delta^{14}C$ value of 20‰. Since the contamination by the fill gas was only $\sim 11\%$, the exact $\Delta^{14}C$ value of the fill gas is not very important: even assuming a $\pm 20‰$ uncertainty in its value would only lead to an extra uncertainty of $\pm 2.5‰$ in the corrected value, which is negligible compared to the $\pm 30‰$ uncertainty in the value due to limited counting statistics. In future campaigns the $\Delta^{14}C$ of CO_2 in the fill gas will still be determined.

The three $\Delta^{14}C$ values observed for the lower altitude samples for the 16 July 2014 profile (Fig. 5b), especially the sample close to the tropopause (11–13 km), have ^{14}C values that are, in part, significantly lower than present-day tropospheric air. The occurrence of a polluted air mass causing this can be ruled out due to the absence of a simultaneous rise of CO at such altitudes. The most probable explanation is thus contamination somewhere in the SAS sampling or extraction process.

The results for these very first datasets are, due to both limited counting statistics and various other uncertainties (in timing and other issues such as possible sample contamination), not accurate enough to deduce any transport processes in the atmosphere; rather, these results are a proof of principle, showing that the AirCore sampling for radiocarbon determination in stratospheric air is feasible. As the sampling

method is relatively cheap, regular sample collections (e.g., every 2 months) are affordable; an AirCore sampling program for ^{14}C measurements with improved precision in the future has a great potential for leading to better understanding of the ^{14}C budget and the transport mechanisms involved.

3 Conclusions and outlook

The results presented in this paper show that AirCore sampling is, in principle, a viable sampling method for the purpose of radiocarbon measurements in stratospheric CO_2. In this proof of principle experiment we achieved a measurement uncertainty of $\sim \pm 30‰$, mostly limited by the AMS counting statistics. The $^{14}CO_2$ content in the stratosphere (up to $\sim 19 \pm 1$ km) from the sample collected on 15 July 2014 seems very well mixed, with $\Delta^{14}C$ values of $\sim 18 \pm 6‰$ being very close to the present-day troposphere. However, the sample collected on 16 July 2014 shows a very large $\Delta^{14}C$ gradient from the tropopause to $\sim 18 \pm 1$ km. The exact reason for the large negative values near the tropopause on 16 July 2014 is not known to us, but contaminations could be a likely reason. Samples from higher than 18 km are likely to be slightly enriched in $^{14}CO_2$ ($\sim 80 \pm 20‰$), as expected in these higher latitudes as the production of ^{14}C is predominant in the stratosphere (Masarik and Beer, 1999).

Since the sampling technique is relatively cheap, it is feasible to couple an AirCore SAS sampling program to a regular AirCore launch program, such as the one that is regularly being carried out at Sodankylä, Finland, throughout the year. The stratospheric samples required for radiocarbon measurements could always be taken from any AirCore sampling and need not have to be part of dedicated campaigns with special protocols, as long as the sample size obtained is adequate for AMS measurements. As indicated by the results in Fig. 5, one of the major challenges we faced in this work is the altitude determination for each section of the SAS. In that respect, it would help if we could avoid the contamination of the CH_4 signal due to the production of CH_4 from stainless steel valves and connectors. Replacing every stainless steel valve with valves made from polymeric material might be unfeasible, but some sections can certainly be modified in future versions. For example, currently the extraction system is completely constructed from stainless steel components, which in future can be completely replaced with glass components. This would partially reduce the extent of contamination of stratospheric air with CH_4 produced as a result of metal–metal friction. The other important source of uncertainty in the projection of altitude is the accurate knowledge of the timing, based on which the altitude is calculated. Future experiments would require careful laboratory record-keeping for more accurate altitude determination. Through these experiments we also learned that the samples that were collected at the top of profiles are contaminated with the fill gas; therefore collecting an air column from a slightly lower

altitude range would introduce less contamination. The Δ^{14}C values for the contaminated samples (last sections of SAS) can also be corrected if the extent of contamination is well defined, which would require a careful characterization of the sample transfer process, from the AirCore to the SAS, or accurate measurements of CO$_2$ and CH$_4$ concentrations for these same air samples. Thus it is certainly critical to treat the stratospheric samples very carefully, and rigorous testing of the sampling process is needed to rule out leakages, potential contaminations arising from memory effects of the sampler wall and the extent of sample profile integrity as the sample from the AirCore is moved into the SAS through the CRDS analyzer. Additionally, the graphitization process also requires careful monitoring since incomplete reduction would result in a lower sample mass than expected in addition to isotopic fractionation and thus a less accurate contamination correction based on reference materials (that are then relatively larger in mass). Therefore it is important to have very consistent reaction efficiencies. It is also important that the mass of the reference material, used for correction, closely matches that of the samples.

Difficulties with altitude determination and possibilities of various contamination sources notwithstanding, we successfully demonstrated a new method of stratospheric ^{14}C sampling, for which we have successfully dealt with small ($\sim 10\,\mu$gC) samples. This is thanks to our small and efficient extraction system with near-100 % extraction efficiency. With the installation of the newly designed small volume graphitization reactor, we also achieved reaction efficiencies better than 95 % for samples as small as $\sim 10\,\mu$gC. The ^{14}C ion counts can be increased further (~ 2–2.5 times) with the use of smaller Fe pellets (< 1 mg) due to the increase in the number density of the carbon atoms in the sputtered volume of the AMS target. This would improve the counting statistics (from ~ 30 to below 20‰) and thus the AMS measurement uncertainties. Alternatively, the use of a state-of-the-art AMS facility with a gas ionization source (Ruff et al., 2010, 2007) would lead to less contamination (thanks to the avoidance of the graphitization step) and a considerably higher number of accumulated counts (thanks to the higher efficiency) and thus a higher precision, even with such small samples. Such a new AMS system will be installed in Groningen in the course of 2017.

4 Data availability

The datasets are available upon request from the authors.

References

Aerts-Bijma, A. T., Meijer, H. A. J., and van der Plicht, J.: AMS sample handling in Groningen, Nucl. Instrum. Methods Phys. Res., Sect. B, 123, 221–225, 1997.

Ashenfelter, T. E., Gray, J., Sowl, R. E., Svendsen, M., and Telegadas, K.: A Lightweight Molecular Sieve Sampler for Measuring Stratospheric Carbon-14, J. Geophys. Res., 77, 412–419, doi:10.1029/JC077i003p00412, 1972.

Brenninkmeijer, C. A. M., Lowe, D. C., Manning, M. R., Sparks, R. J., and vanVelthoven, P. F. J.: The ^{13}C, ^{14}C and ^{18}O isotopic composition of CO, CH$_4$, and CO$_2$ in the higher southern latitudes lower stratosphere, J. Geophys. Res.-Atmos., 100, 26163–26172, doi:10.1029/95jd02528, 1995.

Brenninkmeijer, C. A. M., Crutzen, P., Boumard, F., Dauer, T., Dix, B., Ebinghaus, R., Filippi, D., Fischer, H., Franke, H., Frieß, U., Heintzenberg, J., Helleis, F., Hermann, M., Kock, H. H., Koeppel, C., Lelieveld, J., Leuenberger, M., Martinsson, B. G., Miemczyk, S., Moret, H. P., Nguyen, H. N., Nyfeler, P., Oram, D., O'Sullivan, D., Penkett, S., Platt, U., Pupek, M., Ramonet, M., Randa, B., Reichelt, M., Rhee, T. S., Rohwer, J., Rosenfeld, K., Scharffe, D., Schlager, H., Schumann, U., Slemr, F., Sprung, D., Stock, P., Thaler, R., Valentino, F., van Velthoven, P., Waibel, A., Wandel, A., Waschitschek, K., Wiedensohler, A., Xueref-Remy, I., Zahn, A., Zech, U., and Ziereis, H.: Civil Aircraft for the regular investigation of the atmosphere based on an instrumented container: The new CARIBIC system, Atmos. Chem. Phys., 7, 4953–4976, doi:10.5194/acp-7-4953-2007, 2007.

Brown, T. A. and Southon, J. R.: Corrections for contamination background in AMS C-14 measurements, Nucl. Instrum. Methods Phys. Res., Sect. B, 123, 208–213, doi:10.1016/s0168-583x(96)00676-3, 1997.

Chen, H., Kivi, R., Heikkinen, P., Kers, B., de Vreis, M., Hatakka, J., Laurila, T., Sweeney, C., and Tans, P.: High-latitude balloon observations of CO$_2$/CH$_4$/CO using AirCore: evaluation of Sodankylä TCCON retrievals, in preparation, 2016.

de Rooij, M., van der Plicht, J., and Meijer, H. A. J.: Porous iron pellets for AMS ^{14}C analysis of small samples down to ultramicroscale size (10–25 μgC), Nucl. Instrum. Methods Phys. Res., Sect. B, 268, 947–951, doi:10.1016/j.nimb.2009.10.071, 2010.

Devlin, D. J. and Herley, P. J.: Thermal decomposition and dehydration of magnesium perchlorate hexahydrate, Thermochim. Acta, 104, 159–178, doi:10.1016/0040-6031(86)85195-4, 1986.

Dlugokencky, E. and Tans, P.: Trends in Atmospheric Carbon Dioxide, www.esrl.noaa.gov/gmd/ccgg/trends/, last access: September 2016.

Gottdang, A., Mous, D. W., and van der Plicht, J.: The HVEE C-14 system at Groningen., Radiocarbon, 37, 649–656, 1995.

Graven, H. D.: Impact of fossil fuel emissions on atmospheric radiocarbon and various applications of radiocarbon over this century, P. Natl. Acad. Sci. USA, 112, 9542–9545, doi:10.1073/pnas.1504467112, 2015.

Hagemann, F., Gray, J., Machta, L., and Turkevich, A.: Stratospheric Carbon-14, Carbon dioxide, and Tritium, Science, 130, 542–552, doi:10.1126/science.130.3375.542, 1959.

Hartmann, D. L., Klein Tank, A. M. G., Rusticucci, M., Alexander, L. V., Bronnimann, S., Charabi, Y., Dentener, F. J., Dlugokencky, E. J., Easterling, D. R., Kaplan, A., Soden, B. J., Thorne, P. W., Wild, M., and Zhai, P. M.: Observations: Atmosphere and Surface, in: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, UK and New York, NY, USA, 159–254, 2013.

Higaki, S., Oya, Y., and Makide, Y.: Emission of Methane from Stainless Steel Surface Investigated by Using Tritium as a Radioactive Tracer, Chem. Lett., 35, 292–293, doi:10.1246/cl.2006.292, 2006.

Hua, Q., Barbetti, M., and Rakowski, A. Z.: Atmospheric Radiocarbon for the Period 1950–2010, Radiocarbon, 55, 2059–2072, doi:10.1017/S0033822200048979, 2013.

IPCC: Climate Change 2014: Impacts, Adaptation, and Vulnerability, Part A: Global and Sectoral Aspects, Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Field, C. B., Barros, V. R., Dokken, D. J., Mach, K. J., Mastrandrea, M. D., Bilir, T. E., Chatterjee, M., Ebi, K. L., Estrada, Y. O., Genova, R. C., Girma, B., Kissel, E. S., Levy, A. N., MacCracken, S., Mastrandrea, P. R., and White, L. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 1132 pp., 2014a.

IPCC: Climate Change 2014: Impacts, Adaptation, and Vulnerability, Part B: Regional Aspects, Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Barros, V. R., Field, C. B., Dokken, D. J., Mastrandrea, M. D., Mach, K. J., Bilir, T. E., Chatterjee, M., Ebi, K. L., Estrada, Y. O., Genova, R. C., Girma, B., Kissel, E. S., Levy, A. N., MacCracken, S., Mastrandrea, P. R., and White L. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 688 pp., 2014b.

Kanu, A. M., Comfort, L. L., Guilderson, T. P., Cameron-Smith, P. J., Bergmann, D. J., Atlas, E. L., Schauffler, S., and Boering, K. A.: Measurements and modeling of contemporary radiocarbon in the stratosphere, Geophys. Res. Lett., 43, 1399-1406, doi:10.1002/2015gl066921, 2016.

Karion, A., Sweeney, C., Tans, P., and Newberger, T.: AirCore: An Innovative Atmospheric Sampling System, J. Atmos. Ocean. Tech., 27, 1839–1853, doi:10.1175/2010jtecha1448.1, 2010.

Levin, I., Kromer, B., and Hammer, S.: Atmospheric $\Delta^{14}CO_2$ trend in Western European background air from 2000 to 2012, Tellus B, 65, 20092, doi:10.3402/tellusb.v65i0.20092, 2013.

Lingenfelter, R. E.: Production of Carbon 14 by Cosmic-Ray Neutrons, Rev. Geophys., 1, 35–55, doi:10.1029/RG001i001p00035, 1963.

Machida, T., Matsueda, H., Sawa, Y., Nakagawa, Y., Hirotani, K., Kondo, N., Goto, K., Nakazawa, T., Ishikawa, K., and Ogawa, T.: Worldwide Measurements of Atmospheric CO_2 and Other Trace Gas Species Using Commercial Airlines, J. Atmos. Ocean. Tech., 25, 1744–1754, doi:10.1175/2008jtecha1082.1, 2008.

Masarik, J. and Beer, J.: Simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere, J. Geophys. Res.-Atmos., 104, 12099–12111, doi:10.1029/1998jd200091, 1999.

Mook, W. G. and van der Plicht, J.: Reporting ^{14}C activities and concentrations, Radiocarbon, 41, 227–239, doi:10.1017/S0033822200057106, 1999.

Mrozek, D. J., van der Veen, C., Hofmann, M. E. G., Chen, H., Kivi, R., Heikkinen, P., and Röckmann, T.: Stratospheric Air Sub-sampler (SAS) and its application to analysis of $\Delta^{17}O(CO_2)$ from small air samples collected with an AirCore, Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-124, in review, 2016.

Nakamura, T., Nakazawa, T., Nakai, N., Kitagawa, H., Honda, H., Itoh, T., Machida, T., and Matsumoto, E.: Measurement of ^{14}C Concentrations of Stratospheric CO_2 by Accelerator Mass Spectrometry, Radiocarbon, 34, 745–752, 1992.

Nakamura, T., Nakazawa, T., and Honda, H.: Seasonal variations in ^{14}C concentrations of stratospheric CO_2 measured with accelerator mass spectrometry, Nucl. Instrum. Methods Phys. Res., Sect. B, 92, 413–416, doi:10.1016/0168-583X(94)96045-3, 1994.

Paul, D., Been, H. A., Aerts-Bijma, A. T., and Meijer, H. A. J.: Contamination on AMS sample targets by modern carbon is inevitable, Radiocarbon, 58, 407–418, doi:10.1017/RDC.2016.9, 2016.

Ruff, M., Wacker, L., Gaeggeler, H. W., Suter, M., Synal, H. A., and Szidat, S.: A gas ion source for radiocarbon measurements at 200 kV, Radiocarbon, 49, 307–314, 2007.

Ruff, M., Szidat, S., Gaggeler, H. W., Suter, M., Synal, H. A., and Wacker, L.: Gaseous radiocarbon measurements of small samples, Nucl. Instrum. Methods Phys. Res., Sect. B, 268, 790–794, doi:10.1016/j.nimb.2009.10.032, 2010.

Santos, G. M., Southon, J. R., Druffel-Rodriguez, K. C., Griffin, S., and Mazon, M.: Magnesium perchlorate as an alternative water trap in AMS graphite sample preparation; a report on sample preparation at KCCAMS at the University of California, Irvine, Radiocarbon, 46, 165–173, doi:10.1017/S0033822200039485, 2007a.

Santos, G. M., Southon, J. R., Griffin, S., Beaupre, S. R., and Druffel, E. R. M.: Ultra small-mass AMS ^{14}C sample preparation and analyses at KCCAMS/UCI Facility, Nucl. Instrum. Methods Phys. Res., Sect. B, 259, 293–302, doi:10.1016/j.nimb.2007.01.172, 2007b.

Sweeney, C., Karion, A., Wolter, S., Newberger, T., Guenther, D., Higgs, J. A., Andrews, A. E., Lang, P. M., Neff, D., Dlugokencky, E., Miller, J. B., Montzka, S. A., Miller, B. R., Masarie, K. A., Biraud, S. C., Novelli, P. C., Crotwell, M., Crotwell, A. M., Thoning, K., and Tans, P. P.: Seasonal climatology of CO_2 across North America from aircraft measurements in the NOAA/ESRL Global Greenhouse Gas Reference Network, J. Geophys. Res.-Atmos., 120, 5155–5190, doi:10.1002/2014jd022591, 2015.