



## 1 Mean age of stratospheric air derived from AirCore observa- 2 tions

3 Andreas Engel<sup>1</sup>, Harald Bönisch<sup>1,2</sup>, Markus Ullrich<sup>1</sup>, Robert Sitals<sup>1</sup>, Olivier Membrive<sup>3</sup>, Fran-  
4 cois Danis<sup>3</sup> and Cyril Crevoisier<sup>3</sup>

5 <sup>1</sup> Institute for Atmospheric and Environmental Science, Goethe University Frankfurt, Frank-  
6 furt, Germany

7 <sup>2</sup> now at Karlsruhe Institute of Technology, KIT, Karlsruhe, Germany.

8 <sup>3</sup> Laboratoire de Météorologie Dynamique (LMD/IPSL), CNRS, Ecole polytechnique, Uni-  
9 versité Paris-Saclay, Palaiseau, France

10 *Correspondence to:* A.Engel, an.engel@iau.uni-frankfurt.de

### 11 **Abstract.**

12 Mean age of stratospheric air can be derived from observations of sufficiently long lived trace  
13 gases with approximately linear trends in the troposphere. Mean age can serve as a tracer to  
14 investigate stratospheric transport and long term changes in the strength of the overturning  
15 Brewer-Dobson circulation of the stratosphere. For this purpose, a low-cost method is required  
16 in order to allow for regular observations up to altitudes of about 30 km. Despite the desired  
17 low costs, high precision and accuracy are required in order to allow determination of mean  
18 age. We present balloon borne AirCore observations from two mid latitude sites: Timmins in  
19 Ontario/Canada and Lindenberg in Germany. During the Timmins campaign five AirCores  
20 sampled air in parallel from a large stratospheric balloon and were analysed for CO<sub>2</sub>, CH<sub>4</sub> and  
21 partly CO. We show that there is good agreement between the different AirCores (better than  
22 0.1%) especially when vertical gradients are small. The measurements from Lindenberg were  
23 performed using small low-cost balloons and yielded very comparable results. We have used  
24 the observations to extend our long term data set of mean age observations at Northern Hemi-  
25 sphere mid latitudes. The time series now covers more than 40 years and shows a small, statis-  
26 tically not significant positive trend of  $0.15 \pm 0.18$  years/decade. This trend is slightly smaller  
27 than the previous estimate of  $0.24 \pm 0.22$  years/decade which was based on observations up to  
28 the year 2006. These observations are still in contrast to strong negative trends of mean age as  
29 derived from some model calculations.



## 1 **1 Introduction**

2 Mean age of stratospheric air is the average time it takes for the atmosphere to transport air  
3 from the tropospheric source region to a given place in the stratosphere. The concept of mean  
4 age was first developed by Kida (1983) and has since been refined and discussed in several high  
5 quality reviews (Hall and Plumb, 1994; Waugh and Hall, 2002). In brief, the concept divides an  
6 air parcels into irreducible fluid elements which are irreversibly mixed during transport in the  
7 stratosphere. Each such fluid element has a separate transport time and transport path associated  
8 to it. The distribution of the statistical probability associated with the different transit times is  
9 called the age spectrum and represents a probability density function (pdf) for individual transit  
10 times to this air parcel. The first moment of the age spectrum is called the mean age of air.  
11 While the age spectrum cannot be measured, mean age can be derived from observations of  
12 inert trace gases under certain conditions. In case of an inert tracer with a perfectly linear trend  
13 in the atmosphere, the time lag between the occurrence of a given mixing ratio of a tracer in the  
14 troposphere and the occurrence of the same mixing ratio at some place in the stratosphere would  
15 be the mean age of air. The two tracers which have been used most widely for this purpose are  
16 CO<sub>2</sub> and SF<sub>6</sub>. Neither of these gases increases completely linearly with time, so the shape of  
17 the age spectrum needs to be taken into account in deriving mean age.

18 Mean age has been identified as a valuable tracer to investigate stratospheric transport time  
19 scales, e.g. by comparing model derived mean age with observations. Long term trends in mean  
20 age have been used to investigate long term changes in the overall overturning circulation of  
21 the stratosphere (Brewer-Dobson circulation, BDC). An increase in the strength of the BDC is  
22 expected from model calculation, which should be reflected in overall shorter transit times, thus  
23 also lower mean age values.

24 The experimental data base of mean age observations for the verification of such changes is  
25 sparse. It relies mainly on very sporadic balloon borne observations of CO<sub>2</sub> and SF<sub>6</sub> dating back  
26 to 1975 (Engel et al., 2009) and on satellite observations of SF<sub>6</sub> (Stiller et al., 2012; Haenel et  
27 al., 2015). The balloon borne observations used in Engel et al. (2009) were taken in a region  
28 between 24 and 35 km where the vertical gradient in mean age at Northern Hemisphere mid  
29 latitudes was found to be very small, leading to little variability in this region. The balloon data  
30 was limited to a total of 28 flights and showed a positive trend of 0.24 years per decade for this  
31 region, which was however estimated to be non-significant. Satellite observations of SF<sub>6</sub> used  
32 in Stiller et al. (2012) and Haenel et al. (2015) were limited to the lifetime of the Envisat satellite



1 of about 10 years. They show an uneven distribution of trends with positive trends in the middle  
2 stratosphere of the northern Hemisphere but negative trends in the Southern Hemisphere. Mod-  
3 elling work by Garny et al. (2014) showed that mixing has a strong influence on mean age and  
4 that enhanced mixing leads to higher mean ages in large parts of the stratosphere (“aging by  
5 mixing”). Ploeger et al. (2015) then showed that trends in mean age are to a large degree also  
6 influenced by trends in mixing and not only in residual transport. Overall, it has become clear  
7 that the interpretation of changes in mean age as changes in residual circulation is inadequate,  
8 but rather that it represents a combination of changes in mixing and in residual transport.

9 The experimental investigation of changes in mean age of stratospheric air is to a large degree  
10 restricted by the availability of observations. The balloon borne data set presented in Engel et  
11 al. (2009) relies to a large part on samples collected in the stratosphere using large and heavy  
12 cryogenic whole air samplers. These instruments require large and expensive balloons to carry  
13 them to altitudes above 25 km. The use of these large balloons involves a large operational team  
14 and is very expensive. The uncontrolled parachute descent of such large payloads after the  
15 flights further presents a large operational constraint due to safety regulations. These safety  
16 regulations make it virtually impossible to fly such large payloads in densely populated areas  
17 as Central Europe. Due to these operational constraints and in order to create a larger and more  
18 representative data base, an easy to launch and cheap technique to allow for the measurement  
19 of age tracers would be required. AirCore, a new technique to sample air which has been sug-  
20 gested by Karion et al. (2010) may provide such an opportunity. In brief, this technique relies  
21 on collecting air in a previously evacuated, long stainless steel tube. When deploying AirCore  
22 on a balloon, the tube, which is open on one side and closed on the other side, is filled with a  
23 fill gas (FG) which has different chemical characteristics from the ambient air to be sampled.  
24 The tube is emptied during ascent of the balloon due to the decreasing pressure with altitude.  
25 Upon descent of the balloon, ambient air is pushed into the AirCore. Due to the length of the  
26 tube and the laminar flow during the collection, the air is only partially mixed and the infor-  
27 mation on the vertical distribution is retained for a while before eventually being mixed due to  
28 molecular diffusion. After collection, the sampled air can then be analysed by pushing it out of  
29 the tube with a push gas (PG), which must again be well distinguishable from ambient air.

30 A very light weight AirCore developed at University Frankfurt for deployment on small, cheap  
31 and easy to launch balloons as used for launching of e.g. ozone sondes is presented in section  
32 2 together with the analytical set-up for measurements of the AirCore and the data retrieval. In  
33 section 3 we present observations from two mid latitude campaigns, the first one in Timmins,



1 Ontario in 2015 and the second one in Lindenberg, Germany in 2016. Results from a first test  
2 campaign in Timmins, Ontario in 2014 have been published in Membrive et al. (2016). Due to  
3 technical problems the results from the campaign in 2014 cannot be used to derive mean age.  
4 The mean ages calculated from the observations in 2015 and 2016 are presented in section 4  
5 together with and an updated long term evolution of mean age. Summary and conclusions are  
6 given in section 5.

## 7 **2 University Frankfurt AirCore**

8 The AirCore used by University of Frankfurt was developed under two main aspects. The first  
9 aspect is that the instrument should be sufficiently light to allow for flights under simple bal-  
10 loons at mid latitudes in Europe. The second aspect is that the AirCore should be optimised to  
11 allow measurements at high altitudes with an optimal resolution. The AirCore is currently used  
12 for measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO.

### 13 **2.1 Overall concept**

14 As explained above, the University Frankfurt AirCore is designed to provide optimum resolu-  
15 tion in the stratosphere while keeping the weight sufficiently low for use under a small balloon.  
16 The vertical resolution, which can be achieved by AirCore measurements, will generally de-  
17 pend on the geometry of the AirCore itself, on the effective volume of the analyser deployed  
18 and on the storage time between collection of the sample and the analysis. The target of our  
19 AirCore is to derive mean age from CO<sub>2</sub>. As the loss of CH<sub>4</sub> in the stratosphere results in the  
20 production of CO<sub>2</sub>, CH<sub>4</sub> needs to be measured simultaneously. We therefore decided to use a  
21 Picarro G2401 analyser for this, which is able to measure CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O with a tem-  
22 poral resolution of about 2-3 seconds and very high precision, which is better than 0.01% for  
23 CO<sub>2</sub> and 0.05% for CH<sub>4</sub> over a 5 sec period under typical ambient conditions.

24 Molecular Diffusion is described by Fick's first law of diffusion, which states that the diffusive  
25 flux  $J$  is proportional to the concentration gradient  $\frac{\partial c}{\partial x}$  and the Diffusion-constant  $D$ .

$$26 \quad J = -D \times \frac{\partial c}{\partial x}$$

27 The same amount of air stored in a short tube with large inner diameter will be stretched out  
28 over a much shorter distance than in a narrow and longer tube. The diffusive flux is thus lower



1 when using a longer and thinner tube. As the amount of sample collected by AirCore is propor-  
2 tional to the ambient pressure, very little air is collected at high altitudes. In order to minimize  
3 loss of vertical resolution with altitude, it is thus desirable to have thin and long tubes for the  
4 storage of stratospheric air. On the other hand, the absolute amount of air collected by the Air-  
5 Core is limited by the total volume of the tube, which is low for tubing with small inner diam-  
6 eter. We have therefore decided to construct an AirCore from different diameter tubes in such  
7 a way that the high altitude air is stored in the thin diameter tubing part of the AirCore while  
8 the overall volume is provided by wider diameter tubing in which the lower altitude air will  
9 eventually be stored. The AirCore operated at University Frankfurt is thus composed of 20 m  
10 of 8mm O.D. tubing, and 40 m each of 4 and 2 mm outer diameter tubing. The thinnest walled  
11 tubing we could identify were 0.2 mm wall thickness for 8 mm and 4 mm outer diameter tube.  
12 A 2 mm outer diameter tube with an 0.12 mm wall thickness is available. The volume per  
13 weight is highest for the large outer diameter tubing. All tubings were custom produced for the  
14 production of our AirCores. The tubes are joined by light weight adaptors allowing to solder  
15 the tubes together. As suggested in Karion et al. (2010), all tubes were silanized prior to solder-  
16 ing them together. The AirCore is closed during flight on the 2 mm side, while the 8 mm O.D.  
17 tube is the open ended side of AirCore. The calculated weight of the AirCore based on the  
18 specifications of the tubes is 1.4 kg for the 100 m long tube. The final weight of the tube was,  
19 however, slightly higher due to the wall thickness being on the high side of the specified toler-  
20 ance. An automated closure valve (Chen et al., 2017) is added on the closed side and a sample  
21 dryer is mounted on the open end. The drier is based on  $\text{Mg}(\text{ClO}_4)_2$  filled in a  $\frac{1}{2}$ " O.D. tube of  
22 50 mm length containing a total of  $4\text{cm}^3$  of  $\text{Mg}(\text{ClO}_4)_2$ . The AirCore is mounted in a Styrofoam  
23 box for thermal insulation and mechanical protection. As the temperature of the AirCore during  
24 the collection determines the amount of air, which can be sampled, we monitor this temperature  
25 with a minimum of three temperature sensors. The automatic closure valve (Chen et al., 2017)  
26 closes the AirCore after landing. This valve is controlled by a light weight electronics package  
27 which also includes the data logger for the temperature sensors and was developed at University  
28 Groningen (Chen et al., 2017). The overall weight of the AirCore in flight mode and using the  
29 University Groningen electronics package and closure valve is about 2.5 kg including a protec-  
30 tive housing.

## 31 **2.2 Estimated vertical resolution**

32 The vertical resolution of the derived mixing ratio profiles is influenced by sampling, storing  
33 and measurements procedures. The principal procedure to estimate vertical resolution has been



1 outlined by Karion et al. (2010). Resolution is lost due to molecular diffusion during the storage  
2 of the sampled air in the AirCore and due to mixing during the sampling and analysis process.  
3 Molecular diffusion can be calculated using Fick's law. The mixing process is essentially in-  
4 fluenced by two parameters: (i) Taylor dispersion during the collection and analysis of the sam-  
5 ples and (ii) the effective cell volume of the analyser, which has to be flushed. Mixing processes  
6 are species independent, while the first effect (molecular diffusion during storage) is species  
7 dependent, each species having a different molecular diffusion coefficient. The cell volume of  
8 the analyser is not an intrinsic limitation of the resolution of the AirCore itself, but will be  
9 included in the derived resolution based on the Picarro G2401 analyser used for our analysis.  
10 As molecular diffusion is a function of time and molecule, the resolution of our AirCore is also  
11 a function of time and will deteriorate with time and differ for each molecule. As explained  
12 above, molecular diffusion will lead to more loss of resolution in a wider tube. Therefore, our  
13 AirCore loses resolution much stronger at lower altitudes during storage, where the sampled air  
14 is the wider tube. We have applied the same parameters as described in Karion et al. (2010) to  
15 derive the vertical resolution for our AirCore. Figure 1 compares the vertical resolution of our  
16 AirCore to other AirCore systems (Karion et al., 2010; Membrive et al., 2016). The calculation  
17 is based on the assumption of sampling air down to 1000 hPa. At the upper altitudes, the reso-  
18 lution is dominated in these calculation by the effective volume of the analyser cell, while mo-  
19 lecular diffusion is the dominant term at low altitudes. The overall vertical resolution of the  
20 measurements is better than 1 km below 24 km altitude and increases to about 2.5 km at 30 km  
21 altitude (Fig. 1). For comparison, the HR-AirCore described by Membrive et al. (2016) achieves  
22 a vertical resolution which is better than 300 m below 15 km and better than 500 m below 22  
23 km, however using much longer tubing resulting in a higher weight.

### 24 **2.3 Operation and analytical setup**

25 Before the flight the AirCore is checked for leak tightness and cleanliness. As a first test, a gas  
26 of known concentration is measured either directly or by passing it through the AirCore and the  
27 measurements are compared. As a further test, the AirCore is filled with a gas of known con-  
28 centration and analysed again after a storage time of 24 hours. Only if the CO<sub>2</sub> and CH<sub>4</sub> readings  
29 from both values agree within the uncertainties, the AirCore is considered as clean and leak  
30 tight. It is then filled with a fill gas (FG) of known CO<sub>2</sub>, CH<sub>4</sub> and CO concentration no longer  
31 than 24 hours before flight. Before flight the automatic valve mounted on the inlet side of the  
32 AirCore is opened.



1 The AirCore should be analysed as quickly after the flight as possible as molecular diffusion  
2 decreases the achievable vertical resolution. During the flight in Timmins, Ontario, this oc-  
3 curred about 4 hours after the ~300 km flight, while the analysis started within an hour after  
4 landing during the flights launched from Lindenberg. In order to achieve this fast analysis, the  
5 analytical setup consisting of a Picarro analyser and a gas control system must be deployed in  
6 the field. For this purpose, we mounted the analytical system in a car when operating from  
7 Timmins and inside our laboratory bus during flights from Lindenberg. The setup also included  
8 a battery-operated inverter allowing to run the Picarro for up to 6 hours, thus also allowing to  
9 keep the instrument heated and under constant flow while driving to the predicted landing area.  
10 We use the same gas as Fill Gas (FG) and Push Gas (PG). This gas-mixture contains typical  
11 atmospheric CO<sub>2</sub> values, typical CH<sub>4</sub> values expected around 30 km altitude and significantly  
12 higher CO values than observed either in the troposphere or in the stratosphere. Based on the  
13 CO values, it is thus possible to distinguish between the sampled atmospheric air, the PG and  
14 the FG, which is left in the tube.

15 The gas flow system used for the analysis of AirCore is shown in Figure 2. This system allows  
16 to flush the two lines which are needed to connect the AirCore for the analysis with a standard  
17 gas (Cal Gas) or the push gas used for the analysis (connection and flushing, upper panel in  
18 Figure 2). During the connection all dead volumes of the connectors can be flushed, minimizing  
19 the contamination from ambient air. During the connection the Picarro is flushed with push gas.  
20 The pressure of the PG is regulated to slightly above ambient pressure (typically 1030 hPa) and  
21 the flow through the Picarro is regulated to 40 ml/min. Once all lines are flushed and connected  
22 and the Picarro gives a stable reading of the expected value for the PG, the two-position position  
23 valve can be switched. PG regulated at 1030 hPa is then flushed through the AirCore with a  
24 flow of 40 ml/min. The stratospheric (upper altitude) air is flushed out first. Before stratospheric  
25 air arrives at the Picarro analyser, the standard gas that was used for flushing the connection  
26 lines will arrive first, followed by the remaining FG from the AirCore. The amount of FG left  
27 will depend on the lowest pressure reached during flight and on the temperature of the AirCore  
28 during that phase (see section data retrieval). A typical example of the raw analytical results  
29 from the measurements of two AirCores embarked simultaneously on board the flight from  
30 Timmins in 2015 (see section 3.1) is shown in Figure 3. Figure 4 shows a zoom on the CO  
31 measurements shortly after switching the rotary valve. The PG with its high CO values close to  
32 1.4 ppm is measured. Then the CO values drop due to the lower values of the calibration gas  
33 with which the connection line was flushed. This is then followed by the FG remaining in the  
34 tube. Note that during this flight the amount of FG left was not sufficient for the Picarro to



1 arrive at its expected value of close to 1.4 ppm. After the passing of the peak with high CO  
2 from the FG, the values drop sharply showing much lower CO values. These lower CO values  
3 are expected in the middle stratosphere (Toon et al., 1999;Engel et al., 2006b) due to the pho-  
4 tochemical balance between production of CO from oxidation of CH<sub>4</sub> and the breakdown of  
5 CO due to oxidation with the OH radical. The transition from high CO (remaining FG) to low  
6 CO thus marks the beginning of the sampled air at the upper part of the profile. In a similar  
7 way, the transition from rather low tropospheric CO to high CO marks the time when all the  
8 sampled air has been pushed out of the AirCore and the PG used to push the air out of the  
9 AirCore is seen by the analyser.

## 10 **2.4 Data retrieval**

11 The Picarro analyser will deliver a time series of mixing ratios as a function of measurement  
12 time. The absolute values of the Picarro analyser are transferred to the WMO scale (X2007  
13 scale for CO<sub>2</sub> and X 2004a scale for CH<sub>4</sub>) based on a calibration function derived from absolute  
14 values of 4 gas bottles with a range of CO<sub>2</sub> values between 390 and 416 ppm of CO<sub>2</sub> and 1.07  
15 to 1.91 ppm of CH<sub>4</sub> (only 3 gas bottles). The mixing ratios determined by the Picarro analyser  
16 have to be matched to the altitude at which the air was sampled by the AirCore during the flight.  
17 The basis of this altitude attribution is the ideal gas law and the molar amount sampled at each  
18 altitude during the flight. This matching is achieved in a 4 stage process. First (i) the amount of  
19 remaining Fill Gas is determined, then (ii) the sampling of air based on the ideal gas law is  
20 calculated. In the third step (iii) the start and end times of AirCore in the analyser time series  
21 are determined and finally (iv) the sampling and the analysis can be matched based on the molar  
22 amount.

### 23 **2.4.1 Determination of remaining Fill Gas**

24 In the case of slow vertical displacement of the balloon, pressure equilibrium between the Air-  
25 Core and the surrounding air can be assumed. Under this assumption of an instantaneous pres-  
26 sure equilibrium, the molar amount  $n$  of an ideal gas stored in volume  $V$  at pressure  $p$  and  
27 temperature  $T$  is according to the ideal gas law:

$$28 \quad n = \frac{p \cdot V}{R \cdot T}$$





1 where  $R$  is the general gas constant. The temperature in this aspect is not the ambient tempera-  
2 ture but the temperature of the coil, as we assume an instantaneous equilibrium between tem-  
3 perature of the air inside the AirCore with the coil temperature. In the (i) first step the amount  
4 of FG remaining in the AirCore at the top of the profile is then calculated by searching for the  
5 minimum in  $\frac{p}{T}$ .

6 As noted above, the assumptions about pressure equilibrium between air inside the AirCore and  
7 outside air needs to be made in this calculation. While this is certainly a valid assumptions for  
8 a slow descent of the balloon, it will be less valid the faster the descent of the balloon. In the  
9 case of a rubber balloon which will burst while still ascending and then immediately start to  
10 descent the situation is even more difficult, as the pressure inside the AirCore will actually be  
11 higher than the outside pressure during the beginning of the descent, because a non-equilibrium  
12 will exist both for the emptying of the tube during ascent and the re-filling of the tube during  
13 the descent. The size of this non-equilibrium effect will depend on the geometry of the AirCore  
14 but also on the filling of the sample dryer. In particular, this latter may provide a significant  
15 flow restriction if the  $\text{Mg}(\text{ClO}_4)_2$  is packed very densely. The amount of FG left in the AirCore  
16 is thus expected to differ significantly from the equilibrium amount calculated before based on  
17 the minimum in  $\frac{p}{T}$ . We have taken particular care to have a short and loosely packed dryer  
18 providing minimal flow restriction. As the FG used in our case differs significantly in CO val-  
19 ues from ambient air and from the calibration gas used, it is possible to determine the amount  
20 of remaining FG by integrating the CO peak observed during the measurement of the AirCore  
21 (Chen et al., 2017) as illustrated in Figure 4. When switching from the bypass to the measure-  
22 ments mode, the gas inside the Picarro measurement cell is first replaced by the calibration gas,  
23 which was used to flush the transfer line to the AirCore during the connection. The calibration  
24 gas (Cal Gas) is then replaced by the FG which remained in the AirCore and then by ambient  
25 stratospheric air. All of these gases are partially mixed and all of them contain some CO. In  
26 order to separate the amount of CO due to PG and Cal Gas from the signal due to remaining  
27 FG, we performed a measurement in a similar set-up but with our AirCore filled with pure  
28 nitrogen, which contained no detectable amounts of CO. The CO in this set-up is thus not due  
29 to remaining FG and can be used to correct the offset due to PG and Cal Gas when integrating  
30 the CO peak from the remaining FG. Using the known mixing ratio of CO in the FG, the molar  
31 amount of remaining FG can be determined. In the case of the two fast descent profiles from  
32 Lindenberg (see section 3), the pressure of remaining FG was determined to be 17.2 hPa and  
33 7.3 hPa, respectively, while the corresponding pressures derived from the minimum in  $\frac{p}{T}$  was



1 slightly lower at 15.2 hPa and 7 hPa, respectively. The differences are rather small, correspond-  
2 ing to altitude differences of a km or less, as the flow restriction of our AirCore is low due to  
3 the large inner diameter of the 8 mm tube (which carries the largest part of the volume) and the  
4 carefully packed sample dryer. In the following we have therefore only corrected this effect by  
5 adopting the upper sampling pressure during the Lindenberg flights to the value calculated from  
6 the integration of the CO peak of the remaining FG.

#### 7 **2.4.2 Sampling of ambient air with AirCore**

8 In the second step, we determine the amount of moles sampled during every time step of the  
9 balloon trajectory. Again in case of slow descent the assumption of pressure equilibrium be-  
10 tween the tube and the sampled ambient air is justified. Starting at the molar amount determined  
11 during step 1 and adding up over the pressure and coil temperature measured during the descent  
12 of the balloon results in a matrix linking ambient pressure and altitude to sampled molar  
13 amount. In the case of a faster descent, the assumption of pressure equilibrium is not completely  
14 valid, but as shown in section 2.4.1. the effect is small. To a first order this is compensated by  
15 starting the summing at the molar amount determined from integration of the CO peak as de-  
16 scribed in section 2.4.1.

17 The approach of summing up the amount of moles in the AirCore during the flight will take  
18 also into account that air from the AirCore can be lost again, if the pressure of ambient air is  
19 below that of the AirCore, e.g. in case the balloon ascends (which can occur for large strato-  
20 spheric balloons) or if the AirCore heats up after landing without being closed. The procedure  
21 is thus integrated in time until the moment that the AirCore is closed either manually or via an  
22 automatic closure valve.

#### 23 **2.4.3 Matching AirCore and Picarro data**

24 In the third step we determine the starting and ending point in the measurements of the air mass  
25 sampled and stored in the AirCore with the Picarro (see Figure 2). This is achieved by fitting a  
26 Gaussian curve to the CO peak from the remaining FG (see Figure 4). In case that there is so  
27 much FG left that the CO peak reaches a plateau the left and right side of the remaining CO  
28 from FG are fitted separately using only one side of the Gaussian for fitting. The time when the  
29 peak reaches half its height is chosen as the start time. The time derived for the rising CO peak  
30 is then taken as the start time of the FG, the time derived for the descending part of the peak is  
31 taken as the start of the AirCore, i.e. ambient stratospheric air. We chose to use this second



1 point as starting point and associate it with the amount of remaining FG determined in section  
2 2.4.1. The determination of starting and ending point of the AirCore analysis in the Picarro time  
3 series is critical in the correct assignment of the measured mixing ratio to the sampling location  
4 and altitude. Especially the starting point of the AirCore is a critical parameter as an offset of 1  
5 hPa will result in a significant shift in altitude in the stratosphere. The fourth step is then to  
6 calculate the molar amount of air passing through the Picarro and linking this to the molar  
7 amount sampled with the AirCore. The link between the molar amount and the time of meas-  
8 urement is straight forward, as the flow through the Picarro is regulated to be constant (in our  
9 case 40 ml/min) and also temperature and pressure of the measurement cell of the Picarro ana-  
10 lyser are controlled

#### 11 **2.4.4 Correction of mixing ratios for mixing between AirCore and fill-** 12 **gas**

13 In order to keep the effect of mixing between FG and ambient stratospheric air small, we have  
14 made the FG in order to have values close to those expected in the middle stratosphere. The  
15 FG, which is also used as PG has a mixing ratio of about 407.75 ppm of CO<sub>2</sub> and 1228.6 ppb  
16 of CH<sub>4</sub>. On the other hand, the PG has much higher CO (about 1400 ppb) in order to allow a  
17 clear distinction from both tropospheric and stratospheric air. Especially stratospheric air has  
18 much lower CO mixing ratios, which are on the order of 20 ppb (Engel et al., 2006b; Toon et  
19 al., 1999). Our measurements showed a gradual decrease of CO values from the high FG values  
20 to the significantly lower stratospheric mixing ratios. Values as low as 20 ppb were only ob-  
21 served sporadically, with values around 100 hPa pressure altitude typically being in the 30 ppb  
22 range. This enhancement could either be caused by CO production from the reaction of ozone  
23 with the tubing or it could be a measurement artefact as the Picarro is not well suited for such  
24 low CO mixing ratios. This gradual decrease from the FG values to stratospheric values is due  
25 to a combination of mixing and diffusion. While mixing is similar for all species, molecular  
26 diffusion depends on the diffusion coefficient and is different for each gas. The upper part of  
27 the profile is stored in the 2 mm O.D. tube. In this tube molecular diffusion only leads to a very  
28 gradual mixing of the two gases (FG and ambient air). Most of the gradient is due to mixing  
29 during the analysis (the limiting part is the volume of the analyser cell). Therefore, this gradient  
30 can be treated as a gradient caused by mixing and not diffusion, and the mixing should be sim-  
31 ilar for all species. We will thus use the large difference in CO to characterise the fraction of  
32 FG in the analysis and correct the observed mixing ratios of CH<sub>4</sub> and CO<sub>2</sub> for the remaining  
33 impact of FG. In order to determine the fraction of remaining FG an assumption on the expected



1 stratospheric mixing ratio of CO must be made. As we expect that the correction should ap-  
2 proach zero once the cell has been flushed a few times, we have chosen to use the average CO  
3 value observed between 80 and 100 hPa as the expected value. Using this target value the frac-  
4 tion of FG is calculated from the difference between the measured and the expected CO mixing  
5 ratios and the observed mixing ratio from the Picarro measurements is corrected accordingly.

### 6 **3 Atmospheric observations**

7 The AirCore developed at University Frankfurt is sufficiently light to be flown with a small  
8 balloon. However, we performed our first test flights using large stratospheric balloons  
9 launched by CNES from Timmins in Ontario. Two such test flights were performed in order to  
10 compare our results with those of other groups. The first test flights were performed in 2014.  
11 The results from the first flight in 2014 is reported by Membrive et al. (2016). Due to a balloon  
12 trajectory which was not adapted to AirCore measurements (long ceiling and long float of the  
13 balloon around 20 km altitude) the profiles obtained for CO<sub>2</sub> from AirCore could not be used  
14 to derive mean age, as the AirCore showed unrealistically low values of CO<sub>2</sub> around the float  
15 altitude, possibly due to an interference with the sample dryer (Membrive et al., 2016). These  
16 data are therefore not discussed in this paper. During a second flight of the same payload as  
17 reported in Membrive et al. (2016), the vertical velocities were much better adapted and we  
18 could derive profiles of CO<sub>2</sub>, CO and CH<sub>4</sub>. These are presented in section 3.1. In section 3.2.  
19 we present the first results from our AirCore measurements at mid latitudes using a small and  
20 easy to launch rubber balloon of similar type as used for ozone soundings.

#### 21 **3.1 Timmins 2015**

22 The payload launched from Timmins in the year 2015 was very similar to the one described in  
23 Membrive et al. (2016). It consisted of a combination of two AirCores by University Frankfurt,  
24 one high-resolution AirCore (Membrive et al., 2016) and two light weight AirCores by the  
25 Laboratoire de Meteorologie Dynamique (LMD). In contrast to the Picarro G2401 used by  
26 University Frankfurt, the LMD team used a G2301 analyser, which lacks the capacity to meas-  
27 ure CO. The payload also included two pico-SDLA spectrometers (Ghysels et al., 2014; Durry  
28 and Hauchecorne, 2005) for measurements of CO<sub>2</sub> and CH<sub>4</sub>, which are based on in-situ infrared  
29 absorption measurements. Results from these latter measurements were perturbed due to ther-  
30 mal drifts in laser emission wavelength and are not available at the time of writing. The balloon  
31 was launched from Timmins, Ontario, on August 22, 2015 and reached a minimum pressure of



1 about 11 hPa. In order to reach a zone where a safe landing was possible, the balloon was left  
2 to drift westwards and a slow descent of the balloon was started in the early morning of August  
3 23 (8:30 U.T.). The payload was separated from the balloon just below 100 hPa pressure and  
4 the payload landed at about 10:40 U.T. The recovery team was able to recover the payload such  
5 that the analysis could be started about 4 hours after landing.

6 Figure 5-7 show the vertical profiles of CO, CH<sub>4</sub> and CO<sub>2</sub> as measured with the Picarro analyser  
7 for both AirCores by GUF and in comparison to the LMD AirCores (only for CH<sub>4</sub> and CO<sub>2</sub>).  
8 The altitude attribution is based on the CO peak as described in section 2.4. One of the AirCores  
9 (AC-2) was operated with the automatic closure valve and thus did not lose any air while warm-  
10 ing up on the ground after landing. The profile from this AirCore extends to the ground, while  
11 other profile (AC-3) ends higher up due to the loss of air. First of all, two peaks in CO are  
12 observed in the troposphere, which are found at the same altitude for both AirCores. These  
13 could have been caused by biomass burning from wildfires occurring over western Canada dur-  
14 ing the period of observations. Lowest values of CO in the stratosphere are on the order of 10-  
15 20 ppb, in agreement with expected steady state values (Toon et al., 1999;Engel et al., 2006b).  
16 AC-3, which was measured after AC- 2 shows an increase in CO mixing ratios above 20 km,  
17 which is most probably due to the longer storage time, resulting in more diffusive mixing with  
18 remaining Fill Gas.

19 Figure 6 shows the vertical profiles of CH<sub>4</sub> derived from the 5 independent AirCores all  
20 mounted on the same gondola. A remarkably good agreement is observed, as already shown for  
21 observations in 2014 (Membrive et al., 2016). As also discussed in (Membrive et al., 2016) it  
22 is obvious that the AirCore-HR is able to capture fine scale vertical structures which are not  
23 present in the profiles derived from the light weight AirCore of University Frankfurt nor from  
24 the light weight AirCore of LMD, which have a similar vertical resolution in the troposphere  
25 but less vertical resolution in the stratosphere. The vertical profile of the light weight LMD  
26 AirCore is only derived up to about 23 km altitude. Above 19 km altitude the light weight LMD  
27 AirCore shows some deviations from the High Resolution AirCore and the University Frankfurt  
28 AirCores. The University Frankfurt AirCore on the other hand is capable of capturing some  
29 local structure around 21-22 km altitude, although the two local minima from the High Reso-  
30 lution AirCore are smeared out to one broader minimum. Above 23 km altitude there seems to  
31 be a small altitude mismatch between the University Frankfurt and the High Resolution Air-  
32 Core, which is however less than 1 km. This altitude discrepancy is explained by the uncertainty  
33 in matching the Picarro measurements to the AirCore sampling, which is also treated slightly



1 differently in the LMD and the University Frankfurt retrieval. In order to compare the values  
2 of the different AirCores, we binned the data into 1 km intervals and then calculated averages  
3 for each AirCore in these bins. In the troposphere (values between 3 and 13 km altitude) the  
4 standard deviation between these 1 km bins is 1.4 ppb, or 0.08%. In the stratosphere the devia-  
5 tions are higher due to the large vertical gradient. Absolute deviations are on average (between  
6 15 and 24 km altitude) 11 ppb or 0.75%. The agreement of the two University Frankfurt Air-  
7 Cores is much better (0.17 ppb or 0.001% in the troposphere and 3.8 ppb or 0.25% in the strat-  
8 osphere), as is that of the two light weight LMD AirCores (0.28 ppb or 0.0015% in the tropo-  
9 sphere and 1.6 ppb or 0.1% in the stratosphere).

10 The CO<sub>2</sub> measurements from the five AirCore are compared in Figure 7. The overall shapes of  
11 the profiles from the different AirCores show good agreement. In particular also rather small  
12 scale phenomena are resolved and observed in all AirCores. For instance the small scale struc-  
13 ture at around 13 km is observed in all AirCores, again showing that the sampling and the  
14 altitude attribution gives consistent results. As already discussed by Membrive et al. (2016),  
15 CO<sub>2</sub> measurements seem to show more deviations. However, it should be noticed that the range  
16 shown for CO<sub>2</sub> is much smaller than for CH<sub>4</sub>. In contrast to CH<sub>4</sub> the deviations in the tropo-  
17 sphere and the stratosphere are very similar, as the vertical gradient is similar. In absolute terms,  
18 the deviations are typically 0.35 ppm or about 0.09%. This deviation is thus on a very similar  
19 level as observed for CH<sub>4</sub> in the troposphere. Overall, this agreement is very good, taking into  
20 account that the different AirCores partly use different data retrieval algorithms and have dif-  
21 ferent geometries and thus also different vertical resolutions. As in the case of CH<sub>4</sub>, we note  
22 that the agreement between the two University Frankfurt AirCores is much better (0.04 ppm or  
23 0.01% in the troposphere and 0.17 ppm or 0.04% in the stratosphere), as is the agreement be-  
24 tween the two light weight LMD AirCores (0.05 ppm or 0.015% in the troposphere and 0.07  
25 ppm or 0.02% in the stratosphere). This shows that the differences are systematic and must be  
26 related to the geometries of the different AirCores and the related uncertainties in the altitude  
27 attributions.

## 28 **3.2 Lindenberg 2016**

29 A first test campaign to study the use of our AirCore using small balloons has been conducted  
30 from the Lindenberg Meteorological Observatory, Germany. AirCores were launched on May  
31 20, 2016 and May 25, 2016. The balloon used for the first flight was a TA 1500 balloon. A  
32 larger balloon (TA 3000) was used for the flight on May 25, thus allowing to reach a higher



1 ceiling altitude. Ceiling pressures were 15.2 and 7 hPa, respectively. Large parachutes were  
2 used in order to slow down the descent speed and minimize the effects due to non-equilibrium  
3 of pressure inside of the AirCore and outside pressure. For both measurement flights we were  
4 able to recover the AirCore very fast and start the analysis within an hour after landing. The  
5 retrieval procedure was similar to the one for the flight from Timmins in 2015 with the excep-  
6 tion that we derived the pressure at which sampling began not from the measurements of am-  
7 bient pressure but from the integration of the CO peak as described in section 2.4.1. (diploma  
8 thesis Markus Ullrich, University Frankfurt, Dec. 2016).

9 Figures 8 to 10 show the vertical profiles of CO, CH<sub>4</sub> and CO<sub>2</sub> from the two flights conducted  
10 in May 2016. For CO the general agreement between both measurement flights is very good,  
11 even though they are five days apart. CO values are higher than observed in Timmins 2015.  
12 This could either be due to the use of a different Picarro analyser (note that these values are  
13 close to the detection limits of CO) or to enhanced CO in early spring e.g. due to descending  
14 mesospheric air during the polar winter. For all species there is a distinct change at the tropo-  
15 pause around 11 km altitude with a sharp drop in mixing ratios. The decrease in tracer mixing  
16 ratios is observed at the same altitude as the thermal tropopause, i.e. at 11 km altitude, showing  
17 that the altitude attribution as explained in section 2 yields realistic results.

18 For CH<sub>4</sub> and CO this is due to the chemical loss in the stratosphere, whereas CO<sub>2</sub> is very long  
19 lived in the stratosphere. The decrease in CO<sub>2</sub> values above the tropopause is mainly caused by  
20 the high values of CO<sub>2</sub> in the northern hemisphere troposphere during spring, while the air  
21 above the tropopause partly entered through the tropical tropopause and partly during late sum-  
22 mer of the preceding year when tropospheric CO<sub>2</sub> values were lower due to the seasonal cycle  
23 (Boenisch et al., 2009). Both CH<sub>4</sub> and CO<sub>2</sub> show some fine structures in the stratosphere during  
24 both flights. There is a local maximum in CO<sub>2</sub> and CH<sub>4</sub> at around 21 km altitude on May 20  
25 and a similar local maximum is observed on May 25 at about 20.5 km altitude. The maxima  
26 and minima in CO<sub>2</sub> and CH<sub>4</sub> are collocated at the same altitude. Therefore, this is clearly a  
27 dynamical feature where CO<sub>2</sub> rich (younger) air (see section 4) is advected which at the same  
28 time has higher CH<sub>4</sub> mixing ratios. Such air masses would be expected to occur in the tropics  
29 or subtropics. As the dynamical interpretation of the profiles is not the focus of this paper, this  
30 is not investigated further e.g. by using meteorological data.





## 1 **4 Age of air from AirCore**

2 The main aim of our AirCore activities is to determine mean age of air and use this to extend  
3 our long time series of mean age from balloon observations (Engel et al., 2009). The two tracers  
4 most commonly used to derive mean age are CO<sub>2</sub> and SF<sub>6</sub>. As shown in Engel et al. (2009), the  
5 vertical gradient of mean age becomes rather small at pressure altitudes above 30 hPa. The  
6 mean value of mean age above this altitude has been used to investigate long term changes in  
7 mean age and in the stratospheric circulation (Engel et al., 2009). An ideal tracer for the deri-  
8 vations of mean age should have neither sinks nor sources in the middle atmosphere and show  
9 a monotonous, linear trend in the lower atmosphere (Hall and Plumb, 1994; Waugh and Hall,  
10 2002). Neither CO<sub>2</sub> nor SF<sub>6</sub> completely fulfil these requirements (Engel et al., 2009) leading to  
11 uncertainties in the mean age values derived from observations. In the case of CO<sub>2</sub> there are  
12 three specific issues which need to be considered: (i) the source of CO<sub>2</sub> in the middle atmos-  
13 phere due to the oxidation of CH<sub>4</sub>, (ii) the seasonal cycle of CO<sub>2</sub> and (iii) the deviation of the  
14 deseasonalized long term trend of CO<sub>2</sub> in the troposphere from linearity. The procedure to cal-  
15 culate mean age and how to take these issues into account is the same as in Engel et al. (2009)  
16 and only briefly summarized here. As CH<sub>4</sub> is oxidised in the stratosphere and thus provides a  
17 source for CO<sub>2</sub> in the stratosphere, the amount of CO<sub>2</sub> produced from the oxidation has to be  
18 subtracted from the observed CO<sub>2</sub> mixing ratio. The CO<sub>2</sub> produced in the stratosphere is derived  
19 from the observed CH<sub>4</sub> by taking the difference to the deseasonalized tropospheric CH<sub>4</sub> at the  
20 time of measurements. In this procedure the fact that CH<sub>4</sub> has a tropospheric trend and takes  
21 some time to propagate to the stratosphere is ignored. The error in mean age due to this simpli-  
22 fication is less than half a month. CO<sub>2</sub> has a seasonal cycle in the troposphere which can prop-  
23 agate into the lower stratosphere (Andrews et al., 2001a; Andrews et al., 2001b; Hintsä et al.,  
24 1998; Boenisch et al., 2009; Engel et al., 2006a). Rosenlof et al. (1997) found that the seasonal  
25 cycle in water vapour is observable up to potential temperatures of about 450 K and termed this  
26 region the tropically controlled transition layer. In the stratospheric overworld (above 450 K  
27 potential temperature) short term influences e.g. due to seasonal cycles in the troposphere or  
28 tropopause region are much smaller. CO<sub>2</sub> can thus only be used as an age tracer for air at po-  
29 tential temperatures above 450 K where the mixing ratios are not influenced by seasonality in  
30 the troposphere anymore. Our analysis of mean age is thus restricted to potential temperatures  
31 above 450 K. Thirdly, the deseasonalized tropospheric trend of CO<sub>2</sub> in the troposphere deviates  
32 from a perfect linear increase. The mean age derived from CO<sub>2</sub> observations will thus depend  
33 on the shape of the age spectrum. To compensate for the effects of this deviation on the mean





1 age values derived, we again followed the same approach as in Engel et al. (2009). We use a  
2 parameterization of the width of the age spectrum  $\Delta$  as function of mean age  $\Gamma$  as suggested by  
3 Hall and Plumb (1994), i.e.  $\frac{\Delta^2}{\Gamma} = 0.7 \text{ years}$  with the general shape of the age spectrum being  
4 an inverse Gaussian function. We have further adapted the fitting period for the tropospheric  
5 trend so as to represent 98% of the air input for each individual data point (i.e. shorter time  
6 periods for the fit are applied for younger air), in order to find the best possible description of  
7 the tropospheric input time series.

8 The influence on all three effects on the mean age values has been included in the error analysis,  
9 again following Engel et al. (2009).

10

#### 11 **4.1 Vertical profile observations**

12 Figure 11 shows the mean age profiles for the two flights from Lindenberg in May 2016 and  
13 the two AirCores flown simultaneously in August 2015 from Timmins. The data have been  
14 filtered to exclude air masses with potential temperature below 450 K where the CO<sub>2</sub> seasonal  
15 cycle is still expected to have a significant impact. As for many other profile observations of  
16 mean age (Andrews et al., 2001a; Engel et al., 2009; Schmidt and Khedim, 1991) a decrease of  
17 mean age with altitude is observed up to about 23-24 km altitude, above which the vertical  
18 gradient becomes very small. Mean age values above this layer are on the order of 5 years, in  
19 very good agreement with other long term data sets. The observations from Timmins in August  
20 2015 show slightly higher mean age values than the observations in May 2016 from Lindenberg  
21 in Germany. This could be explained by the seasonal cycle in mean age derived from MIPAS  
22 Envisat observations of SF<sub>6</sub>, showing youngest air in the northern hemisphere mid latitudes  
23 above 25 km during winter and oldest air during summer (Stiller et al., 2012). The younger  
24 spring measurements from Lindenberg could thus still be influenced from the lower mean age  
25 values during winter, while the older observations from Timmins in August 2015 should be  
26 during the maximum of the seasonal cycle.

#### 27 **4.2 Extension of long term time series**

28 As explained above, we want to use AirCore observation to extend our long time series of  
29 stratospheric mean age observations (Engel et al., 2009). The calculation of a temporal trend in  
30 mean age is complicated by the sparsity of the data set in combination with a vertical gradient



1 in mean age. As the AirCore observations, in agreement with other balloon data, only show a  
2 very small vertical gradient above an altitude of 23-24 km, corresponding to about 30 hPa, we  
3 have adopted the same procedure as used in Engel et al. (2009), i.e. we average all data between  
4 30 hPa and 5 hPa and calculate an average value of mean age for this region of the strato-  
5 sphere.

6 The last data point in Engel et al. (2009) was from the year 2005. There is thus a gap of 10 years  
7 between these last measurements and the new AirCore data. Overall the mean values derived  
8 from the AirCore data are in very good agreement with the values published in Engel et al.  
9 (2009). The mean values for mean age above 30 hPa from the Timmins flights are  $4.9\pm 1$  and  
10  $5.3\pm 1$  years, while the Lindenberg flights yield slightly lower mean age values at  $4.7\pm 1$  and  
11  $4.8\pm 1$  years. Note that the uncertainty ranges include uncertainties in the estimated representa-  
12 tiveness, the derivation of mean age and the observations themselves, based on the error assess-  
13 ment given in Engel et al. (2009). Using all the data available, we derive a new estimate of the  
14 long term trend in mean age for the mid latitude stratosphere of the Northern Hemisphere be-  
15 tween 30 and 5 hPa. The time period covered is now more than 40 years (1975-2016), albeit  
16 with a very restricted number of profile observations. The updated trend is now calculated to  
17 be  $0.15\pm 0.18$  years/decade. This trend is smaller than the previous estimate ( $0.24\pm 0.22$   
18 years/decade), but agrees within the uncertainty range. The positive trend is not significant  
19 within the one sigma uncertainty range. Due to the reduced uncertainty of the new estimate, the  
20 largest negative trend which would be compatible with our data within the two sigma uncer-  
21 tainty range remains nearly unchanged ( $-0.21$  years/decade instead of  $-0.2$  years /decade).

## 22 **5 Summary and conclusion**

23 Observations of stratospheric trace gases are well suited to investigate chemical and physical  
24 processes in the stratosphere. They are also well suited to investigate long term changes in the  
25 stratosphere. In particular, for the investigation of long term changes, high precision and accu-  
26 racy are needed in combination with rather low costs (Müller et al., 2016; Moore et al., 2014).  
27 Most in-situ measurements in the stratosphere require the use of large and expensive balloons  
28 to carry instruments above altitudes of 20 km. The new technique of AirCore (Karion et al.,  
29 2010; Membrive et al., 2016) is ideally suited to provide such low cost long term observations.  
30 We have thus investigated the usefulness of AirCore for investigations of long term evolution  
31 of mean age in order to extend the existing balloon data set used in Engel et al. (2009) and Ray  
32 et al. (2010). University Frankfurt has developed an AirCore system from three different inner



1 diameter tubes, targeted at an optimal vertical resolution in the stratosphere, while still being  
2 sufficiently light weight to be deployed on a small balloon. During an intercomparison cam-  
3 paign in Timmins, Ontario in August 2015 we compared 5 different AirCores. We have shown  
4 that the AirCore technique can be used to derive high precision vertical profiles of CO<sub>2</sub> and  
5 CH<sub>4</sub>. Both LMD and University Frankfurt measurements are referenced to the same scales, but  
6 using independent calibrations. This shows that the results are also of high accuracy. For both  
7 trace gases the comparison between the different independent AirCores was better than 0.1%  
8 when vertical gradients are small, as is the case for CO<sub>2</sub> in the mid latitude stratosphere above  
9 a pressure altitude of 30 hPa (about 24 km altitude) and for tropospheric CH<sub>4</sub>. This indicates  
10 that the For CH<sub>4</sub> in the stratosphere, where there is a large vertical gradient the typical agree-  
11 ment was still better than 1%. The agreement between two similar AirCores, which sampled in  
12 parallel was always better than the agreement between different AirCores when sampling in  
13 parallel. This shows that the geometry, the analysis system and the data retrieval of the AirCore  
14 has a significant impact. We have further performed first observation from the mid latitude site  
15 of Lindenberg in Germany using small rubber balloons. Due to careful planning, it was possible  
16 to analyse the AirCores within one hour after landing. We showed that the CO peak from the  
17 remaining Fill Gas in the AirCore can be used to derive the maximum sampling altitude. In the  
18 case of the observations from Lindenberg the maximum sampling altitudes were only slightly  
19 lower than the maximum pressure altitude of the balloon. This is a good indication that the flow  
20 restriction was rather small and that the pressure equilibrium between the tube and outside air  
21 is rather fast. This was achieved in particular due to the use of a large inner diameter tube for  
22 the main volume of the AirCore and by using a sample dryer which was optimised for minimum  
23 flow restriction. Nevertheless, the altitude attribution of the sampled air remains a difficult is-  
24 sue, in particular when descent rates are high. The use of balloon techniques allowing for rather  
25 slow descents should thus be considered when setting up AirCore measurements sites.

26 We have used the new observations to calculate mean age of stratospheric air. The results from  
27 our AirCore observations are in very good agreement with previous observations using whole  
28 air sampling techniques (Engel et al., 2009) with values ranging from 4.7 to 5.3 years of mean  
29 age above a pressure altitude of 30 hPa. We have used these data to extend our long term time  
30 series of balloon borne mean age observations. This time series now dates from 1975 to 2016,  
31 thus spanning a total of more than 40 years. The long term trend of mean age in the northern  
32 hemisphere mid latitude stratosphere deduced from this data set is  $0.15 \pm 0.18$  years/decade. This  
33 trend is smaller than the previous estimate ( $0.24 \pm 0.22$ ) years/decade but remains well within  
34 the uncertainty limit. Based on this analysis, we thus sustain our result that no significant change

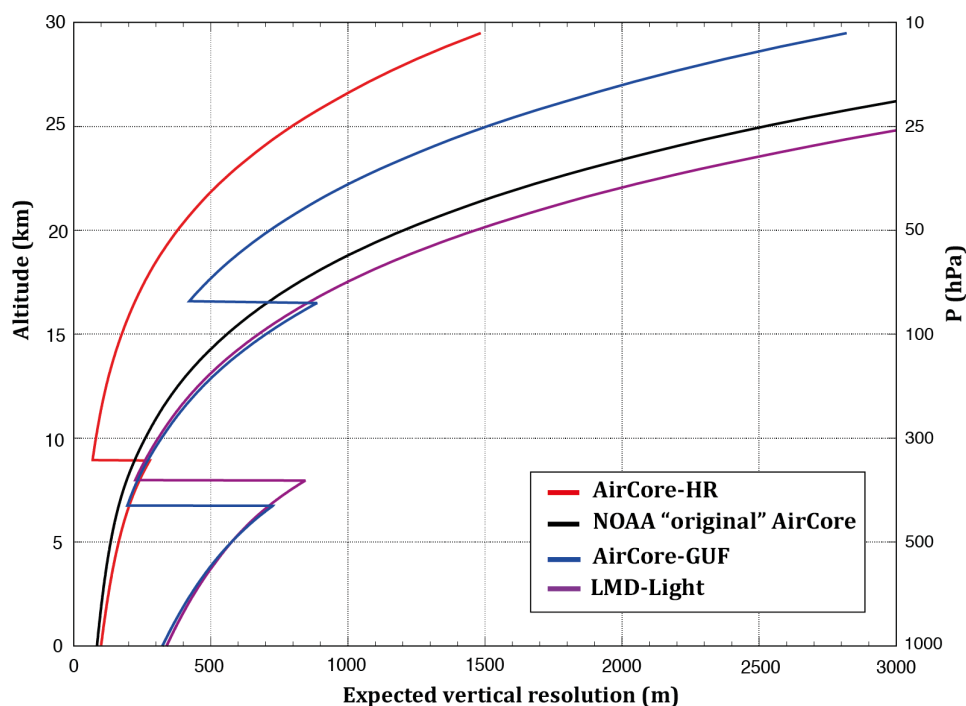


1 in mean age of air for the mid latitude stratosphere of the Northern Hemisphere can be derived  
2 from our data set. Despite the smaller positive trend derived from this extended data set, large  
3 negative changes in mean age in this region can still be excluded, as the uncertainty on the  
4 derived trend has been reduced. A negative trend in mean age of more than -0.2 years/decade  
5 for the middle stratosphere of the Northern Hemisphere mid latitudes can still be excluded with  
6 95% confidence.

7 We conclude that we have shown that AirCore measurements even when using small balloons  
8 can be used to derive vertical profiles of CO<sub>2</sub> and CH<sub>4</sub>. These observations are of sufficient  
9 quality to derive mean age of air and use this to extend the currently available data set of strat-  
10 ospheric mean age observations. We suggest that long term observations using AirCore from a  
11 few selected stations covering different latitude bands may provide a useful tool to investigate  
12 long term changes in mean age. An extension of the AirCore technique to other tracers gases  
13 as suggested by (Moore et al., 2014) may provide a valuable addition as these gases can also be  
14 used to study long term changes in the stratosphere. Müller et al. (2016) suggested that a long  
15 term network for water vapour measurements in the stratosphere should be set up to monitor  
16 this radiatively important trace gas. We suggest that such a network could be complemented by  
17 AirCore observations. Such additional AirCore observations would put the observations of  
18 changing water vapour into the general content of a changing stratospheric circulation. In addi-  
19 tion, if both measurements are performed simultaneously, the observations of Methane from  
20 the AirCore instruments and H<sub>2</sub>O from the water vapour network could be used to derive the  
21 sum of 2\*CH<sub>4</sub> + H<sub>2</sub>O, which has been identified to show much less variability in the strato-  
22 sphere than H<sub>2</sub>O.

## 23 **Acknowledgements**

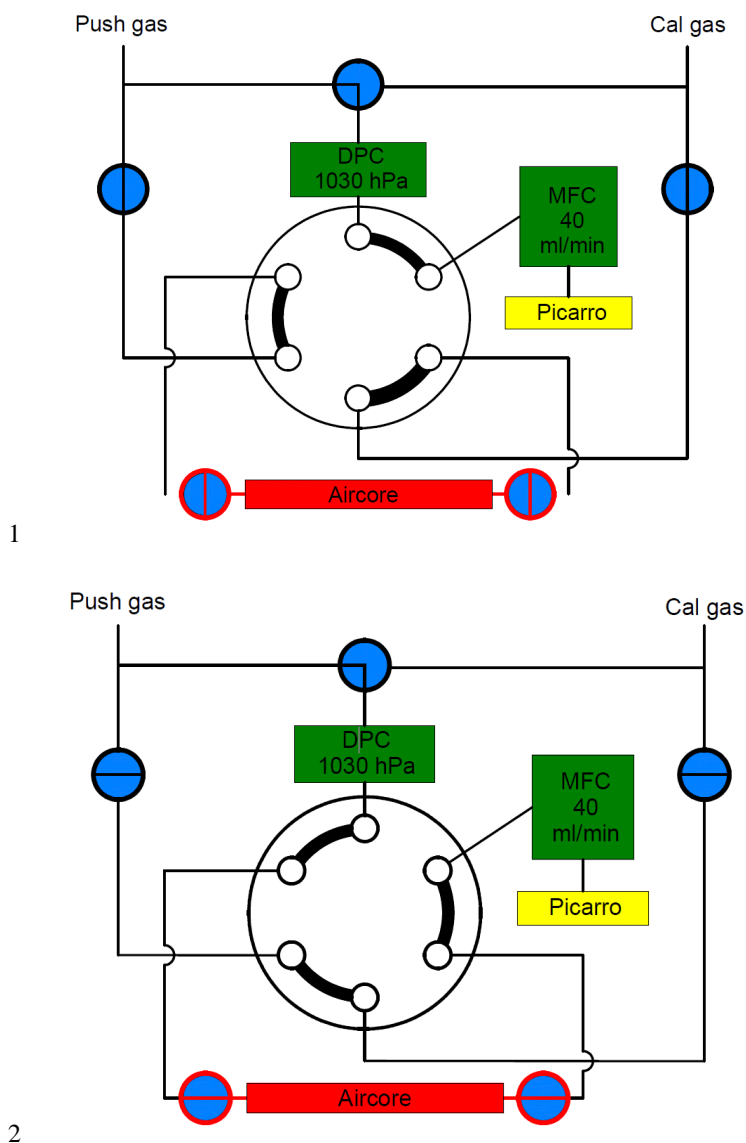
24 The work of University Frankfurt on AirCore has been funded through the ROMIC programme  
25 of the German Ministry of Science and Education (Grant Nr. 01LG1221) and the EU Infra-  
26 structure Project RINGO (Grant agreement. 730944). We would like to thank the French Space  
27 Agency CNES for balloon operations in Timmins and the team of Ruud Dirksen from the Ger-  
28 man Weather Service (DWD) in Lindenberg. The support of the workshops and technicians at  
29 University Frankfurt is gratefully acknowledged. Special Thanks go to Huilin Chen from Uni-  
30 versity of Groningen in the Netherlands for many valuable discussions on AirCore techniques  
31 and an introduction to AirCore measurements during measurements from Sodankylä. Olivier  
32 Membrive was funded by EIT/Climate-KIC, a body of the European Union.



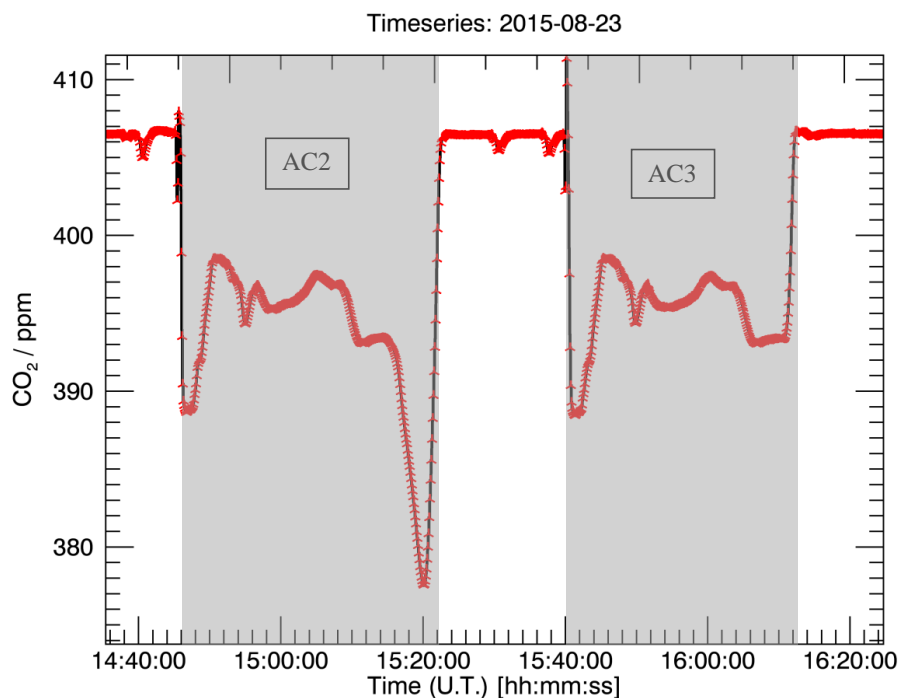
1

2 Figure 1: Calculated vertical resolution for CO<sub>2</sub> with the Goethe University Frankfurt (GUF)  
3 AirCore (AirCore-GUF) in comparison to other AirCores (see text for description), assuming  
4 a delay of 3 hours between collection and sampling, a measurements flow of 40 ml/min and an  
5 effective cell volume of 6 ml. The AirCore-HR and LMD-Light Aircores are operated by LMD,  
6 while the Noaa "original" AirCore refers to the AirCore described by Karion et al. (2010).

7



3 Figure 2: Analytical Setup for the measurement of AirCore. The AirCore including the valves  
4 which are flown is shown in red. In the Bypass/Flushing position (upper panel) the Push Gas  
5 (PG) is measured bypassing the AirCore. The transfer lines to the AirCore can be flushed with  
6 PG or with a calibration standard (Cal Gas), allowing to connect the AirCore to the analytical  
7 system without contamination. For the analysis the transfer lines to the AirCore are closed, the  
8 AirCore valves are opened and the two position valve is switched to the Measurements mode  
9 (lower panel). The PG is passed through the AirCore and pushes the air to the Picarro. Pressure  
10 and flow are controlled allowing for a very constant air flow.



1  
2 Figure 3: raw analytical results for CO<sub>2</sub> from the measurements of the two AirCores flow from  
3 Timmins in 2015. Note that AC 2, which was measured first, contained a closure valve, while  
4 AC 3 was left open until the recovery team was able to reach the instrument. The lowest part  
5 of the AC 3 profile was therefore lost due to the warming of the AirCore on ground.

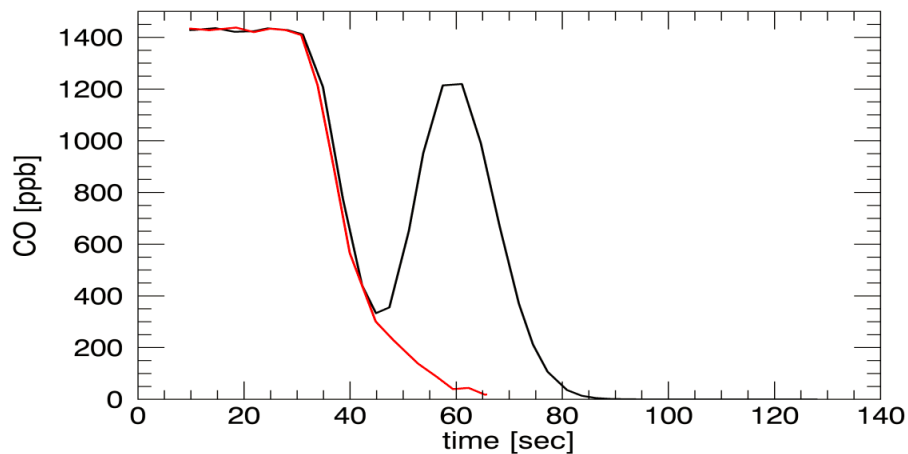
6

7

8



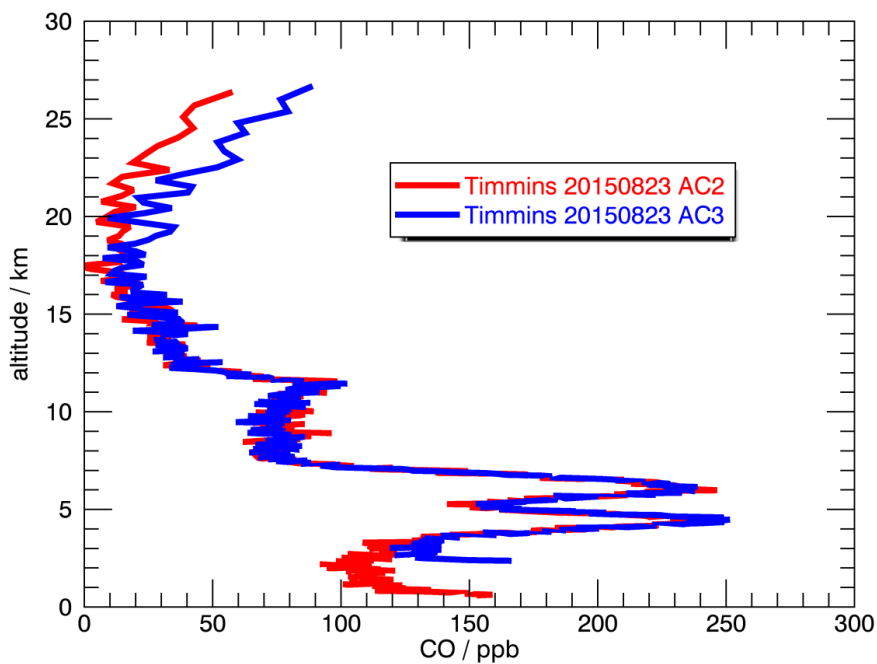
1



2

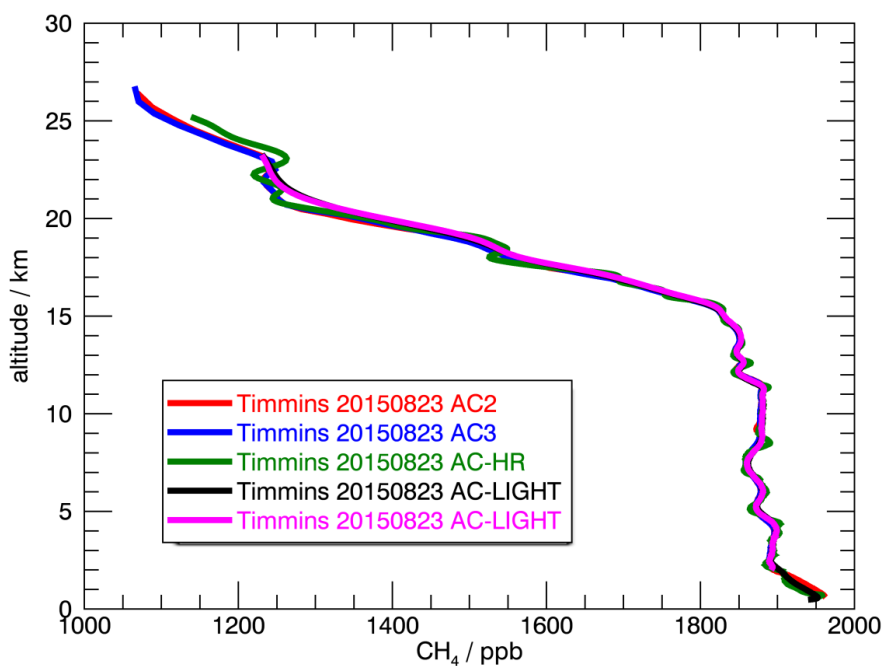
3 Figure 4: zoom on CO measurements from the flight on May 25, 2016. After switching the two  
4 position valves to measurement mode. Before switching, the analyser measures the high CO  
5 mixing ratios of the PG, then a decrease in CO is observed, representing the low CO values of  
6 the Cal gas used for flushing the transfer lines, and finally the CO peak from the remaining FG  
7 (note that PG and FG are taken from the same gas cylinder and thus have identical mixing  
8 ratios) is measured. After the remaining PG has passed the analyser, the CO values drop to the  
9 expected low stratospheric CO values. The red line shows the CO values measured using the  
10 same setup but analyzing an AirCore filled with CO-free nitrogen. The area between the black  
11 CO peak and the red baseline represents the amount of FG left in the AirCore.





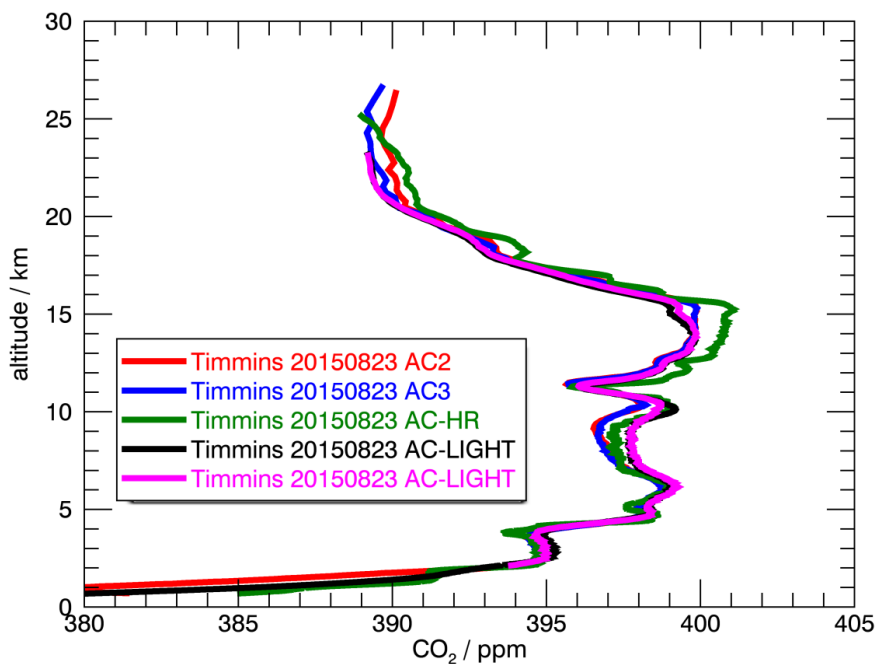
1

2 Figure 5: Vertical profiles of CO derived for the flight on August 23 2015 from Timmins, On-  
3 tario, Canada. The two peaks with enhanced CO around 5 km altitude are observed in both  
4 AirCores and are probably caused by wild fires occurring in Canada during August 2015. There  
5 are no CO measurements from the LMD AirCores due to the Picarro analyzer used by LMD.



1

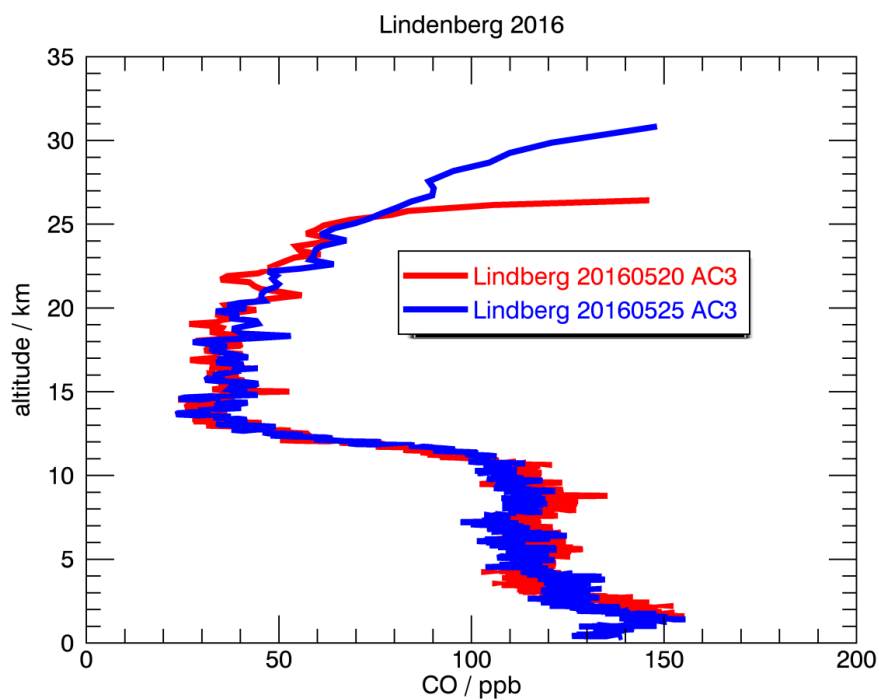
2 Figure 6: Vertical profiles of CH<sub>4</sub> derived for the flight on August 23 2015 from Timmins,  
3 Ontario, Canada. Excellent agreement is observed between all AirCores. There is a slight high  
4 bias of the light LMD AirCores above 20 km with respect to both the University Frankfurt Air-  
5 Cores (red and blue trace) and the high resolution (HR) AirCore (green trace). The fine struc-  
6 tures observed by the HR AirCore are smeared out in the light weight AirCores by University  
7 Frankfurt and LMD



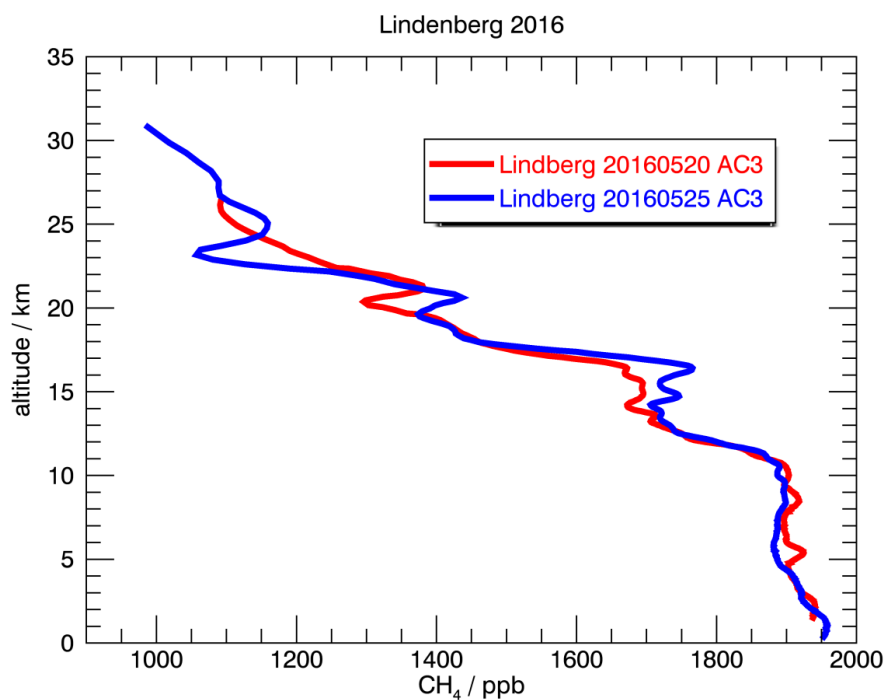
1

2 Figure 7: Vertical profiles of CO<sub>2</sub> derived for the flight on August 23 2015 from Timmins,  
3 Ontario, Canada. The overall structure are captured very well by all AirCores. Again, more fine  
4 structure is obvious in high resolution AirCore. See text for discussion of the differences be-  
5 tween the different AirCores.

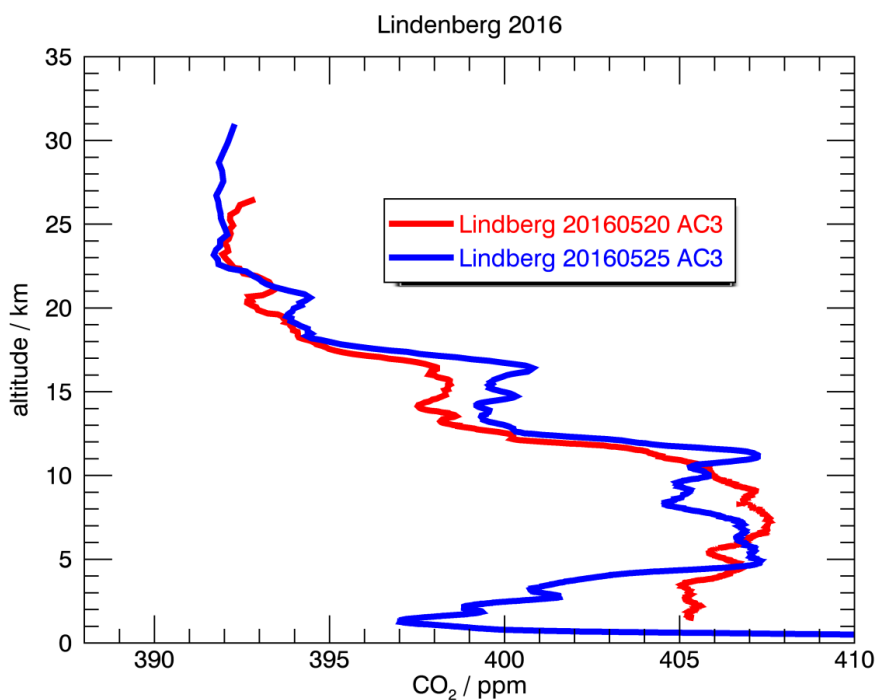
6



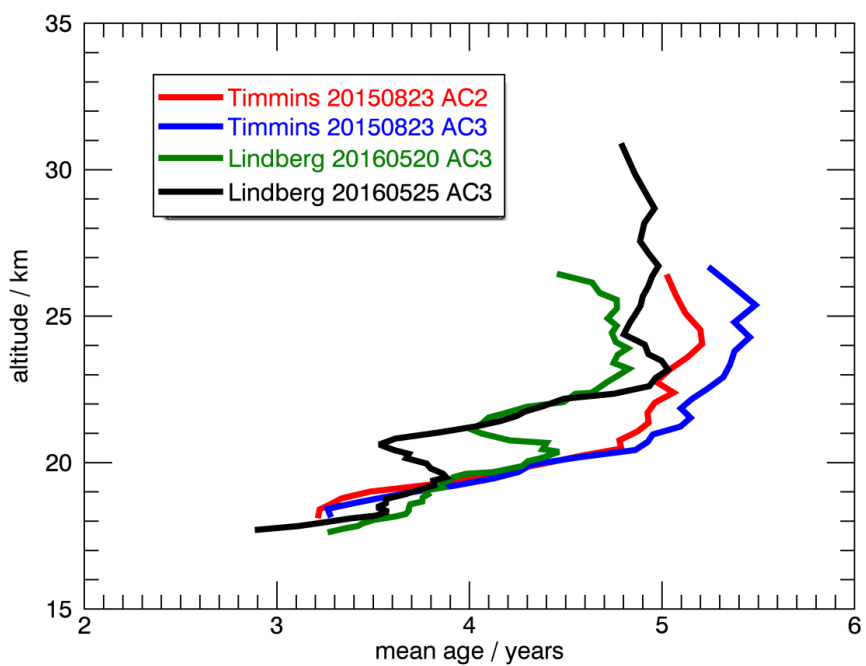
1  
2 Figure 8: Vertical profiles of CO derived for the flights on May 20 and May 25 2016 from  
3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.  
4



- 1
- 2 Figure 9: Vertical profiles of CH<sub>4</sub> derived for the flights on May 20 and May 25 2016 from
- 3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.

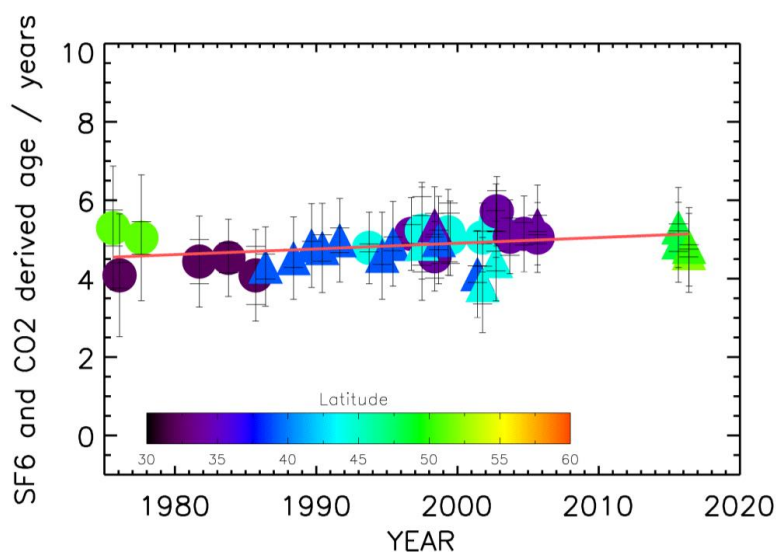


- 1
- 2 Figure 10: Vertical profiles of CO<sub>2</sub> derived for the flights on May 20 and May 25 2016 from
- 3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.



1

2 Figure 11: Vertical profiles of CO<sub>2</sub> derived mean age for the AirCore observations by Univer-  
3 sity Frankfurt in 2015 in Timmins, Canada and 2016 in Lindenberg, Germany.



1

2 Figure 12: Time series of mean age derived from balloon observations. The data prior to 2010  
3 are those presented in Engel et al. (2009). The data from 2015 and 2016 are derived from the  
4 AirCore measurements presented here. Each data point represents the average value of mean  
5 age derived above 30 hPa and up to 5 hPa. The inner error bars represent the variability (error  
6 of the mean), the larger outer error bars include the uncertainty as discussed in Engel et al.  
7 (2009). A non significant trend of  $0.15 (\pm 0.18)$  years per decade is derived from these observa-  
8 tions.

9





## 1 References

- 2 Andrews, A. E., Boering, K. A., Daube, B. C., Wofsy, S. C., Loewenstein, M., Jost, H.,  
3 Podolske, J. R., Webster, C. R., Herman, R. L., Scott, D. C., Flesch, G. J., Moyer, E. J.,  
4 Elkins, J. W., Dutton, G. S., Hurst, D. F., Moore, F. L., Ray, E. A., Romashkin, P. A., and  
5 Strahan, S. E.: Mean ages of stratospheric air derived from in situ observations of CO<sub>2</sub>, CH<sub>4</sub>,  
6 and N<sub>2</sub>O, *J. Geophys. Res.*, *106*, 32295-32314, 10.1029/2001jd000465, 2001a.
- 7 Andrews, A. E., Boering, K. A., Wofsy, S. C., Daube, B. C., Jones, D. B., Alex, S.,  
8 Loewenstein, M., Podolske, J. R., and Strahan, S. E.: Empirical age spectra for the midlatitude  
9 lower stratosphere from in situ observations of CO<sub>2</sub>: Quantitative evidence for a subtropical  
10 "barrier" to horizontal transport, *J. Geophys. Res.*, *106*, 10257-10274, 2001b.
- 11 Boenisch, H., Engel, A., Curtius, J., Birner, T., and Hoor, P.: Quantifying transport into the  
12 lowermost stratosphere using simultaneous in-situ measurements of SF<sub>6</sub> and CO<sub>2</sub>, *Atm. Chem.*  
13 *Phys.*, *9*, 5905-5919, 2009.
- 14 Chen, H., R. Kivi, Heikkinen, P., Kers, B., Vries, M. d., Hatakka, J., Laurila, T., Sweeney, C.,  
15 and Tans, P.: High-latitude balloon observations of CO<sub>2</sub>/CH<sub>4</sub>/CO using AirCore: evaluation  
16 of Sodankylä TCCON retrievals, *Atmos. Meas. Tech.*, *in preparation*, 2017.
- 17 Durry, G., and Hauchecorne, A.: Evidence for long-lived polar vortex air in the mid-latitude  
18 summer stratosphere from in situ laser diode CH<sub>4</sub> and H<sub>2</sub>O measurements, *Atmos. Chem.*  
19 *Phys.*, *5*, 1467-1472, 10.5194/acp-5-1467-2005, 2005.
- 20 Engel, A., Bonisch, H., Brunner, D., Fischer, H., Franke, H., Gunther, G., Gurk, C., Hegglin,  
21 M., Hoor, P., Konigstedt, R., Krebsbach, M., Maser, R., Parchatka, U., Peter, T., Schell, D.,  
22 Schiller, C., Schmidt, U., Spelten, N., Szabo, T., Weers, U., Wernli, H., Wetter, T., and Wirth,  
23 V.: Highly resolved observations of trace gases in the lowermost stratosphere and upper  
24 troposphere from the Spurt project: an overview, *Atm. Chem. Phys.*, *6*, 283-301, 2006a.
- 25 Engel, A., Mobius, T., Haase, H. P., Bonisch, H., Wetter, T., Schmidt, U., Levin, I.,  
26 Reddmann, T., Oelhaf, H., Wetzell, G., Grunow, K., Huret, N., and Pirre, M.: Observation of  
27 mesospheric air inside the arctic stratospheric polar vortex in early 2003, *Atm. Chem. Phys.*, *6*,  
28 267-282, 2006b.



- 1 Engel, A., Mobius, T., Bonisch, H., Schmidt, U., Heinz, R., Levin, I., Atlas, E., Aoki, S.,  
2 Nakazawa, T., Sugawara, S., Moore, F., Hurst, D., Elkins, J., Schauffler, S., Andrews, A., and  
3 Boering, K.: Age of stratospheric air unchanged within uncertainties over the past 30 years,  
4 *Nature Geosci.*, 2, 28-31, 10.1038/NGEO388, 2009.
- 5 Garny, H., Birner, T., Bönisch, H., and Bunzel, F.: The effects of mixing on age of air,  
6 *Journal of Geophysical Research: Atmospheres*, 119, 7015-7034, 10.1002/2013JD021417,  
7 2014.
- 8 Ghysels, M., Gomez, L., Cousin, J., Tran, H., Amarouche, N., Engel, A., Levin, I., and Durrý,  
9 G.: Temperature dependences of air-broadening, air-narrowing and line-mixing coefficients of  
10 the methane nu(3) R(6) manifold lines-Application to in-situ measurements of atmospheric  
11 methane, *Journal of Quantitative Spectroscopy & Radiative Transfer*, 133, 206-216,  
12 10.1016/j.jqsrt.2013.08.003, 2014.
- 13 Haedel, F. J., Stiller, G. P., von Clarmann, T., Funke, B., Eckert, E., Glatthor, N., Grabowski,  
14 U., Kellmann, S., Kiefer, M., Linden, A., and Reddmann, T.: Reassessment of MIPAS age of  
15 air trends and variability, *Atmos. Chem. Phys. Discuss.*, 15, 14685-14732, 10.5194/acpd-15-  
16 14685-2015, 2015.
- 17 Hall, T. M., and Plumb, R. A.: Age as a diagnostic of stratospheric transport, *J. Geophys.*  
18 *Res.*, 99, 1059-1070, 10.1029/93jd03192, 1994.
- 19 Hintsä, E. J., Boering, K. A., Weinstock, E. M., Anderson, J. G., Gary, B. L., Pfister, L.,  
20 Daube, B. C., Wofsy, S. C., Loewenstein, M., Podolske, J. R., Margitan, J. J., and Bui, T. P.:  
21 Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of  
22 H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O and O<sub>3</sub>, *Geophys. Res. Lett.*, 25, 2655-2658, 1998.
- 23 Karion, A., Sweeney, C., Tans, P., and Newberger, T.: AirCore: An Innovative Atmospheric  
24 Sampling System, *Journal of Atmospheric and Oceanic Technology*, 27, 1839-1853,  
25 doi:10.1175/2010JTECHA1448.1, 2010.
- 26 Kida, H.: General-Circulation of Air Parcels and Transport Characteristics Derived from a  
27 Hemispheric Gcm .2. Very Long-Term Motions of Air Parcels in the Troposphere and  
28 Stratosphere, *Journal of the Meteorological Society of Japan*, 61, 510-523, 1983.



- 1 Membrive, O., Crevoisier, C., Sweeney, C., Danis, F., Hertzog, A., Engel, A., Bönisch, H.,  
2 and Picon, L.: AirCore-HR: A high resolution column sampling to enhance the vertical  
3 description of CH<sub>4</sub> and CO<sub>2</sub>, *Atmos. Meas. Tech. Discuss.*, 2016, 1-31, 10.5194/amt-2016-  
4 236, 2016.
- 5 Moore, F. L., Ray, E. A., Rosenlof, K. H., Elkins, J. W., Tans, P., Karion, A., and Sweeney,  
6 C.: A Cost-Effective Trace Gas Measurement Program for Long-Term Monitoring of the  
7 Stratospheric Circulation, *Bulletin of the American Meteorological Society*, 95, 147-155,  
8 10.1175/bams-d-12-00153.1, 2014.
- 9 Müller, R., Kunz, A., Hurst, D. F., Rolf, C., Krämer, M., and Riese, M.: The need for accurate  
10 long-term measurements of water vapor in the upper troposphere and lower stratosphere with  
11 global coverage, *Earth's Future*, 4, 25-32, 10.1002/2015EF000321, 2016.
- 12 Ploeger, F., Abalos, M., Birner, T., Konopka, P., Legras, B., Müller, R., and Riese, M.:  
13 Quantifying the effects of mixing and residual circulation on trends of stratospheric mean age  
14 of air, *Geophys. Res. Lett.*, 42, 2047-2054, 10.1002/2014GL062927, 2015.
- 15 Ray, E. A., Moore, F. L., Rosenlof, K. H., Davis, S. M., Boenisch, H., Morgenstern, O.,  
16 Smale, D., Rozanov, E., Hegglin, M., Pitari, G., Mancini, E., Braesicke, P., Butchart, N.,  
17 Hardiman, S., Li, F., Shibata, K., and Plummer, D. A.: Evidence for changes in stratospheric  
18 transport and mixing over the past three decades based on multiple data sets and tropical leaky  
19 pipe analysis, *J. Geophys. Res.*, 115, Doi 10.1029/2010jd014206, 2010.
- 20 Rosenlof, K. H., Tuck, A. F., Kelly, K. K., Russell, J. M., and McCormick, M. P.:  
21 Hemispheric asymmetries in water vapor and inferences about transport in the lower  
22 stratosphere, *J. Geophys. Res.*, 102, 13213-13234, 10.1029/97jd00873, 1997.
- 23 Schmidt, U., and Khedim, A.: In situ measurements of carbon-dioxide in the winter arctic  
24 vortex and at midlatitudes - an indicator of the age of stratospheric air, *Geophys. Res. Lett.*, 18,  
25 763-766, 10.1029/91gl00022, 1991.
- 26 Stiller, G. P., von Clarmann, T., Haenel, F., Funke, B., Glatthor, N., Grabowski, U.,  
27 Kellmann, S., Kiefer, M., Linden, A., Lossow, S., and Lopez-Puertas, M.: Observed temporal



- 1 evolution of global mean age of stratospheric air for the 2002 to 2010 period, *Atm. Chem.*
- 2 *Phys.*, *12*, 3311-3331, DOI 10.5194/acp-12-3311-2012, 2012.
  
- 3 Toon, G. C., Blavier, J. F., Sen, B., Margitan, J. J., Webster, C. R., May, R. D., Fahey, D.,
- 4 Gao, R., Del Negro, L., Proffitt, M., Elkins, J., Romashkin, P. A., Hurst, D. F., Oltmans, S.,
- 5 Atlas, E., Schauffler, S., Flocke, F., Bui, T. P., Stimpfle, R. M., Bonne, G. P., Voss, P. B., and
- 6 Cohen, R. C.: Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric
- 7 trace gases, *Journal of Geophysical Research: Atmospheres*, *104*, 26779-26790,
- 8 10.1029/1999JD900379, 1999.
  
- 9 Waugh, D. W., and Hall, T. M.: Age of stratospheric air: Theory, observations, and models,
- 10 *Reviews of Geophysics*, *40*, 10.1029/2000rg000101, 2002.
  
- 11