

1 First of all we would like to thank both reviewers for their positive reviews of our man-
2 uscript. Both reviewers have raised mainly minor questions which we will answer point
3 by point below. Our answers are shown in italic and changes to manuscript are shown
4 in red.

5
6 **Reviewer #1: Darryn Waugh**

7
8 This manuscript presents measurements of stratospheric CO₂, CH₄, and CO together
9 with estimates of the mean age from balloon borne AirCore measurements. This new
10 low cost measurement technique offers the opportunity for more regular measure-
11 ments of stratospheric CO₂ and mean age, which are badly needed to answer ques-
12 tions regarding possible changes in stratospheric age.

13 It is shown that the mean age can be estimated from AirCore CO₂ measurements,
14 although there are some differences between the age profiles from the same flight.
15 These differences (uncertainties in mean age) mean that the measurements presented
16 don't really answer the question of whether the age is increasing or decreasing over
17 long time scales. However, it is very important to show that the age can be estimated
18 from AirCore measurements, and hopefully many more measurements can be made
19 over coming years that will help to resolve this issue.

20 The manuscript will be of interest to many ACP readers, is well written, and will be
21 suitable for publication after only a few minor revisions.

22
23 *We thank the reviewer for this general positive assessment. There are always uncer-*
24 *tainties associated with observations and this is of course true for AirCore observa-*
25 *tions. We also agree that the new observations do not answer the question of a long-*
26 *term increase. However, we believe that the uncertainties are sufficiently small that,*
27 *using a larger number of observations than possible so far, they will in the long term*
28 *be able to provide a realistic picture of changes in mean age of air.*

29
30 **SPECIFIC COMMENTS**

31
32 Pg 2, line 21-23: A strengthening of BDC is expected from model calculations with
33 increasing CO₂, and I think you need to include "increasing CO₂" in this sentence.

34
35 *We added "**with increasing greenhouse gas concentrations**" to the text, as it is not only*
36 *CO₂.*

37
38 Also, I am not sure why you say "should be reflected". The same model calculations
39 with increasing CO₂ show a decrease in age (if trend calculated over a long enough
40 time period).

41
42 This sentences actually mixed models and what would be expected from observations.
43 We have rephrased this to make it clearer that this is the model expectation. We have
44 also added some references to model studies which were missing at this point.

45
46 *An increase in the strength of the BDC is expected from model calculation with increas-*
47 *ing greenhouse gas concentrations (Austin and Li, 2006;Butchart et al., 2006;Butchart,*
48 *2014). This is reflected in overall shorter transit times, thus also lower mean age values*
49 *in the models.*

50
51 Pg 13, line 6: "Figures"

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

Changed

Pg 19, line 10: There is something missing here “that the For CH4”

“This indicates that the” has been deleted.

Pg 19, line 14: “performed first observation” I think “the” is needed before “first”. Also,should it be “observations”?

Changed to “the first observations”

Figure 12: Why does the y-axis go from 0 to 10, when data is within 2 and 7. I know the authors have published figures with the same scale previously, but I think it would be much better to have a reduced vertical axis, as well as smaller symbols. Then it will be easier to see the values for individual measurements.

The Figure was of course meant to be an update, therefore we kept the same format in the submitted manuscript. However, we have replotted the data with a more narrow range following the reviewer suggestions.

Reviewer #2: Eric Ray

This paper describes new measurements of CO2, CH4 and CO taken using the Air-Core technique from two midlatitude sites over several years. These measurements are also used to estimate the mean age of air in the stratosphere in order to extend the mean age time series in the northern midlatitudes. Precise, vertical profile measurements of these trace gases in the stratosphere are rare and valuable for diagnosing the stratospheric circulation. The AirCore technique is a cost-effective means of obtaining these measurements, yet there are many details to consider and this paper is very thorough in describing how the measurements were obtained.

The topic is appropriate for ACP and I would recommend publication with consideration of the minor comments listed below.

Thank you for this positive feedback.

Minor comments

We have followed all the minor suggestions concerning wording mentioned by the reviewer, unless indicated in the following. .

- Pg. 1, line 20: change “from” to “with”
- Pg. 2, line 6: change to “parcel”
- Pg. 2, line 8: change “to” to “with”
- Pg. 4, line 5: remove “and” before “an”
- Pg. 5, lines 14-15: Change sentence to something like “The tubes are joined by solder and light weight adaptors.”
- Pg. 5, line 17: “tube is open ended.”
- Pg. 6, line 13: change “stronger” to “more”

1
2 *Changed to "faster"*
3
4 Pg. 6, line 14: " is in the wider tube."
5 Pg. 7, lines 8-9: "for up to 6 hours, which also allowed the instrument to remain heated
6 . . .
7 "
8 Pg. 7, line 15-16: "allows two lines, which are needed to connect the AirCore for the
9 analysis, to be flushed with a standard
10 "
11 Pg. 9, line 7: change to "assumption"
12 Pg. 9, line 10: change to "descend"
13 Pg. 10, lines 17-18: "will also take into account"
14 Pg. 11, line 1: add "the" before "starting"
15 Pg. 11, lines 13-14: " air small, the FG had mixing ratios close to those expected
16 "
17 Pg. 11, line 15: add comma after "PG"
18 Pg. 11, line 20: change "where" to "were"
19
20 Figures 5-7 and 8-10: would be nice to have these figures side by side to easily com-
21 pare the features.
22
23 *Thank you for this suggestion. However, we think that the Figures might either become*
24 *too small or, when including everything in one plot too busy. We believe that including*
25 *the vertical line to indicate the altitude of the tropopause adds some guidance to the*
26 *plots, which will allow for better comparison.*
27
28 Pg. 14, line 11: "In particular, rather small
29 ...
30 "
31 Pg. 14, line 29: replace "has been" with "was"
32 Pg. 14, line 32: on May 25, which reached a higher
33 ...
34 Pg. 15, line 10: remove "measurement"
35 Pg. 15, line 11: add "in" after "Timmins"
36
37 Pg. 15, line 16: You mention the thermal tropopause here, it might be nice to show this
38 on either a separate plot or combined with one of Figure 8-10. Same with Figure 5-7.
39 And what temperature data did you use?
40
41 *The thermal tropopause has been calculated using the WMO definition. The data used*
42 *where from radiosondes flown on the same balloons. We have no included the tropo-*
43 *pause altitude as a dashed line in all plots mentioned. Especially in the case of CO*
44 *there is an excellent agreement between the tropopause altitude and the sharp de-*
45 *crease of CO mixing ratios. This is also mentioned in the text and the explanation to*
46 *the tropopause altitude is included in all Figure captions.*
47
48 *Added to Figure captions:*
49 *The dashed lines represents the thermal tropopause according to the WMO definition.*
50
51 *Changed in text:*

1 *For all species there is a distinct change at the tropopause, which was observed*
2 *around 10.4 km altitude on May 20 and 10.9 km on May 25. The decrease in tracer*
3 *mixing ratios, especially for CO, is observed at the same altitude as the thermal tropo-*
4 *pause, showing that the altitude attribution as explained in section 2 yields realistic*
5 *results.*

6
7
8 Pg. 16, line 5: should be consistent with the units here, either pressure altitude or
9 pressure

10
11 *Changed to pressures below 30 hPa (approximately altitudes above 24 km)*

12
13 Figures 5-11: what about error bars on the profiles? It might make it too hard to see
14 features on plots with many profiles but it would be nice to see how the uncertainty in
15 the measurement varies with altitude and from flight to flight. Uncertainty on the mean
16 age profiles would be nice to see as well.

17
18 *The uncertainty of the measurements does not change from campaign to campaign,*
19 *as long as the performance of the analyzer remains the same. We found standard*
20 *deviations when measuring our standard of 0.025 ppm for CO₂, 5 ppb for CO and*
21 *below 0.2 ppb for CH₄. As these pure analytical precisions are smaller than the thick-*
22 *ness of the line (with the exception of CO) it would not make sense to include them in*
23 *the plots. Instead we have chosen to extend the short description of the analytical pre-*
24 *cision in the text.*

25
26 *Added in section on overall concept on p.4*

27
28 *Typical reproducibilities observed during field operations showed in precisions of 0.025*
29 *ppm of CO₂ and 0.2 ppb of CH₄. For CO, which was mainly used to distinguish between*
30 *ambient air and PG, typical precision was 5 ppb.*

31
32 *The same argument applies to the mean age values. These are not determined by*
33 *analytical precision. We have also added a paragraph on this in the chapter on mean*
34 *age, at the end of section 4.1 on vertical profile observations.*

35
36 *Note that the accuracy of the mean age values determined here is not limited by the*
37 *analytical precision of the Picarro analyser, which is typically 0.025 ppm, which is less*
38 *than a week when translated into mean age.*

39
40
41 Pg. 17, line 16: change “decrease” to “increase”

42
43 *Thank you, of course this was a mistake.*

44
45 Pg. 18, line 32: the Ray et al. (2014) paper seems more relevant to cite here

46
47 *This was actually a mistake and has been changed. I wanted to refer to the 2014 paper.*

48
49 Pg. 19, line 6: change “using” to “use”

50 Pg. 19, line 10: “that for CH₄”

51 Pg. 19, line 14: “further performed the first observations from the”

1 Pg. 20, line 18: change “content” to “context”

2

3 Figure 3 caption: change to “flown”. Also, may want to put some indication in this
4 figure of which part of the time series is the lowest vs. highest altitude sample since
5 it’s not totally obvious from a quick glance. Maybe also label the white spaces as PG
6 to indicate the push gas measurement and if there is a region where some of the FG
7 is measured that would be interesting as well.

8

9 *Instead of indicating this in the Figure, we would prefer to explain this in the Figure*
10 *Caption. There is no region where the standard is measured in this plot. We prefer not*
11 *to add an additional plot for standard measurements, in order not to increase the num-*
12 *ber of plots further.*

13

14 *We have added the following to the Figure caption:*

15 **The grey shaded areas denote the measurements of air from the AirCore. The strato-**
16 **spheric part of the profiles is always measured first. Before the measurements of AC2,**
17 **between the measurements of the AirCores and after the measurement of AC3, PG is**
18 **measured by the Picarro analyzer.**

19

20

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

3 Andreas Engel¹, Harald Bönisch^{1,2}, Markus Ullrich¹, Robert Sitals¹, Olivier Membrive³, Fran-
4 cois Danis³ and Cyril Crevoisier³

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

7 ² now at Karlsruhe Institute of Technology, KIT, Karlsruhe, Germany.

8 ³ 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~~with a large stratospheric balloon and were analysed for CO₂, CH₄
21 and partly CO. We show that there is good agreement between the different AirCores (better
22 than 0.1%) especially when vertical gradients are small. The measurements from Lindenberg
23 were performed using small low-cost balloons and yielded very comparable results. We have
24 used the observations to extend our long term data set of mean age observations at Northern
25 Hemisphere mid latitudes. The time series now covers more than 40 years and shows a small,
26 statistically not significant positive trend of 0.15 ± 0.18 years/decade. This trend is slightly
27 smaller than the previous estimate of 0.24 ± 0.22 years/decade which was based on observations
28 up to the year 2006. These observations are still in contrast to strong negative trends of mean
29 age as derived from some model calculations.

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~~ with it. The distribution of the statistical probability associated ~~with~~ to the different transit
9 times is called the age spectrum and represents a probability density function (pdf) for individ-
10 ual transit times to this air parcel. The first moment of the age spectrum is called the mean age
11 of air. While the age spectrum cannot be measured, mean age can be derived from observations
12 of inert trace gases under certain conditions. In case of an inert tracer with a perfectly linear
13 trend in the atmosphere, the time lag between the occurrence of a given mixing ratio of a tracer
14 in the troposphere and the occurrence of the same mixing ratio at some place in the stratosphere
15 would be the mean age of air. The two tracers which have been used most widely for this pur-
16 pose are CO₂ and SF₆. Neither of these gases increases completely linearly with time, so the
17 shape of 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 with increasing greenhouse gas concentrations (Austin and
23 Li, 2006; Butchart et al., 2006; Butchart, 2014). ~~_, which This is should be~~ reflected in overall
24 shorter transit times, thus also lower mean age values in the models.

25 The experimental data base of mean age observations for the verification of such changes is
26 sparse. It relies mainly on very sporadic balloon borne observations of CO₂ and SF₆ dating back
27 to 1975 (Engel et al., 2009) and on satellite observations of SF₆ (Stiller et al., 2012; Haenel et
28 al., 2015). The balloon borne observations used in Engel et al. (2009) were taken in a region
29 between 24 and 35 km where the vertical gradient in mean age at Northern Hemisphere mid
30 latitudes was found to be very small, leading to little variability in this region. The balloon data
31 was limited to a total of 28 flights and showed a positive trend of 0.24 years per decade for this
32 region, which was however estimated to be non-significant. Satellite observations of SF₆ used

1 in Stiller et al. (2012) and Haenel et al. (2015) were limited to the lifetime of the Envisat satellite
2 of about 10 years. They show an uneven distribution of trends with positive trends in the middle
3 stratosphere of the northern Hemisphere but negative trends in the Southern Hemisphere. Mod-
4 elling work by Garny et al. (2014) showed that mixing has a strong influence on mean age and
5 that enhanced mixing leads to higher mean ages in large parts of the stratosphere (“aging by
6 mixing”). Ploeger et al. (2015) then showed that trends in mean age are to a large degree also
7 influenced by trends in mixing and not only in residual transport. Overall, it has become clear
8 that the interpretation of changes in mean age as changes in residual circulation is inadequate,
9 but rather that it represents a combination of changes in mixing and in residual transport.

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

31 A very light weight AirCore developed at University Frankfurt for deployment on small, cheap
32 and easy to launch balloons as used for launching of e.g. ozone sondes is presented in section
33 2 together with the analytical set-up for measurements of the AirCore and the data retrieval. In

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

8 **2 University Frankfurt AirCore**

9 The AirCore used by University of Frankfurt was developed under two main aspects. The first
10 aspect is that the instrument should be sufficiently light to allow for flights under simple bal-
11 loons at mid latitudes in Europe. The second aspect is that the AirCore should be optimised to
12 allow measurements at high altitudes with an optimal resolution. The AirCore is currently used
13 for measurements of CO₂, CH₄ and CO.

14 **2.1 Overall concept**

15 As explained above, the University Frankfurt AirCore is designed to provide optimum resolu-
16 tion in the stratosphere while keeping the weight sufficiently low for use under a small balloon.
17 The vertical resolution, which can be achieved by AirCore measurements, will generally de-
18 pend on the geometry of the AirCore itself, on the effective volume of the analyser deployed
19 and on the storage time between collection of the sample and the analysis. The target of our
20 AirCore is to derive mean age from CO₂. As the loss of CH₄ in the stratosphere results in the
21 production of CO₂, CH₄ needs to be measured simultaneously. We therefore decided to use a
22 Picarro G2401 analyser for this, which is able to measure CO₂, CH₄, CO and H₂O with a tem-
23 poral resolution of about 2-3 seconds and very high precision, which is better than 0.01% for
24 CO₂ and 0.05% for CH₄ over a 5 sec period under typical ambient conditions. Typical repro-
25 ducibilities observed during field operations showed in precisions of 0.025 ppm of CO₂ and 0.2
26 ppb of CH₄. For CO, which was mainly used to distinguish between ambient air and PG, typical
27 precision was 5 ppb.

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

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

1
2 The same amount of air stored in a short tube with large inner diameter will be stretched out
3 over a much shorter distance than in a narrow and longer tube. The diffusive flux is thus lower
4 when using a longer and thinner tube. As the amount of sample collected by AirCore is propor-
5 tional to the ambient pressure, very little air is collected at high altitudes. In order to minimize
6 loss of vertical resolution with altitude, it is thus desirable to have thin and long tubes for the
7 storage of stratospheric air. On the other hand, the absolute amount of air collected by the Air-
8 Core is limited by the total volume of the tube, which is low for tubing with small inner diam-
9 eter. We have therefore decided to construct an AirCore from different diameter tubes in such
10 a way that the high altitude air is stored in the thin diameter tubing part of the AirCore while
11 the overall volume is provided by wider diameter tubing in which the lower altitude air will
12 eventually be stored. The AirCore operated at University Frankfurt is thus composed of 20 m
13 of 8mm O.D. tubing, and 40 m each of 4 and 2 mm outer diameter tubing. The thinnest walled
14 tubing we could identify were 0.2 mm wall thickness for 8 mm and 4 mm outer diameter tube.
15 A 2 mm outer diameter tube with an 0.12 mm wall thickness is available. The volume per
16 weight is highest for the large outer diameter tubing. All tubings were custom produced for the
17 production of our AirCores. The tubes are joined by solder and light weight adaptors ~~allowing~~
18 ~~to solder the tubes together~~. As suggested in Karion et al. (2010), all tubes were silanized prior
19 to soldering them together. The AirCore is closed during flight on the 2 mm side, while the 8
20 mm O.D. tube is the open ended ~~side of AirCore~~. The calculated weight of the AirCore based
21 on the specifications of the tubes is 1.4 kg for the 100 m long tube. The final weight of the tube
22 was, however, slightly higher due to the wall thickness being on the high side of the specified
23 tolerance. An automated closure valve (Chen et al., 2017) is added on the closed side and a
24 sample 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.
25 tube of 50 mm length containing a total of 4cm^3 of $\text{Mg}(\text{ClO}_4)_2$. The AirCore is mounted in a
26 Styrofoam box for thermal insulation and mechanical protection. As the temperature of the
27 AirCore during the collection determines the amount of air, which can be sampled, we monitor
28 this temperature with a minimum of three temperature sensors. The automatic closure valve
29 (Chen et al., 2017) closes the AirCore after landing. This valve is controlled by a light weight
30 electronics package which also includes the data logger for the temperature sensors and was
31 developed at University Groningen (Chen et al., 2017). The overall weight of the AirCore in
32 flight mode and using the University Groningen electronics package and closure valve is about
33 2.5 kg including a protective housing.

1 **2.2 Estimated vertical resolution**

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

27 **2.3 Operation and analytical setup**

28 Before the flight the AirCore is checked for leak tightness and cleanliness. As a first test, a gas
29 of known concentration is measured either directly or by passing it through the AirCore and the
30 measurements are compared. As a further test, the AirCore is filled with a gas of known con-
31 centration and analysed again after a storage time of 24 hours. Only if the CO₂ and CH₄ readings
32 from both values agree within the uncertainties, the AirCore is considered as clean and leak

1 tight. It is then filled with a fill gas (FG) of known CO₂, CH₄ and CO concentration no longer
2 than 24 hours before flight. Before flight the automatic valve mounted on the inlet side of the
3 AirCore is opened.

4 The AirCore should be analysed as quickly after the flight as possible as molecular diffusion
5 decreases the achievable vertical resolution. During the flight in Timmins, Ontario, this oc-
6 curred about 4 hours after the ~300 km flight, while the analysis started within an hour after
7 landing during the flights launched from Lindenberg. In order to achieve this fast analysis, the
8 analytical setup consisting of a Picarro analyser and a gas control system must be deployed in
9 the field. For this purpose, we mounted the analytical system in a car when operating from
10 Timmins and inside our laboratory bus during flights from Lindenberg. The setup also included
11 a battery-operated inverter allowing to run the Picarro for up to 6 hours, ~~thus which~~ also ~~allow-~~
12 ~~ing-allowed to keep~~ the instrument to remain heated and under constant flow while driving to
13 the predicted landing area. We use the same gas as Fill Gas (FG) and Push Gas (PG). This gas-
14 mixture contains typical atmospheric CO₂ values, typical CH₄ values expected around 30 km
15 altitude and significantly higher CO values than observed either in the troposphere or in the
16 stratosphere. Based on the CO values, it is thus possible to distinguish between the sampled
17 atmospheric air, the PG and the FG, which is left in the tube.

18 The gas flow system used for the analysis of AirCore is shown in Figure 2. This system allows
19 the two lines, which are needed to connect the AirCore for the analysis, to be flushed ~~the two~~
20 ~~lines which are needed to connect the AirCore for the analysis~~ with a standard gas (Cal Gas) or
21 the push gas used for the analysis (connection and flushing, upper panel in Figure 2). During
22 the connection all dead volumes of the connectors can be flushed, minimizing the contamina-
23 tion from ambient air. During the connection the Picarro is flushed with push gas. The pressure
24 of the PG is regulated to slightly above ambient pressure (typically 1030 hPa) and the flow
25 through the Picarro is regulated to 40 ml/min. Once all lines are flushed and connected and the
26 Picarro gives a stable reading of the expected value for the PG, the two-position position valve
27 can be switched. PG regulated at 1030 hPa is then flushed through the AirCore with a flow of
28 40 ml/min. The stratospheric (upper altitude) air is flushed out first. Before stratospheric air
29 arrives at the Picarro analyser, the standard gas that was used for flushing the connection lines
30 will arrive first, followed by the remaining FG from the AirCore. The amount of FG left will
31 depend on the lowest pressure reached during flight and on the temperature of the AirCore
32 during that phase (see section data retrieval). A typical example of the raw analytical results
33 from the measurements of two AirCores embarked simultaneously on board the flight from

1 Timmins in 2015 (see section 3.1) is shown in Figure 3. Figure 4 shows a zoom on the CO
2 measurements shortly after switching the rotary valve. The PG with its high CO values close to
3 1.4 ppm is measured. Then the CO values drop due to the lower values of the calibration gas
4 with which the connection line was flushed. This is then followed by the FG remaining in the
5 tube. Note that during this flight the amount of FG left was not sufficient for the Picarro to
6 arrive at its expected value of close to 1.4 ppm. After the passing of the peak with high CO
7 from the FG, the values drop sharply showing much lower CO values. These lower CO values
8 are expected in the middle stratosphere (Toon et al., 1999;Engel et al., 2006b) due to the pho-
9 tochemical balance between production of CO from oxidation of CH₄ and the breakdown of
10 CO due to oxidation with the OH radical. The transition from high CO (remaining FG) to low
11 CO thus marks the beginning of the sampled air at the upper part of the profile. In a similar
12 way, the transition from rather low tropospheric CO to high CO marks the time when all the
13 sampled air has been pushed out of the AirCore and the PG used to push the air out of the
14 AirCore is seen by the analyser.

15 **2.4 Data retrieval**

16 The Picarro analyser will deliver a time series of mixing ratios as a function of measurement
17 time. The absolute values of the Picarro analyser are transferred to the WMO scale (X2007
18 scale for CO₂ and X 2004a scale for CH₄) based on a calibration function derived from absolute
19 values of 4 gas bottles with a range of CO₂ values between 390 and 416 ppm of CO₂ and 1.07
20 to 1.91 ppm of CH₄ (only 3 gas bottles). The mixing ratios determined by the Picarro analyser
21 have to be matched to the altitude at which the air was sampled by the AirCore during the flight.
22 The basis of this altitude attribution is the ideal gas law and the molar amount sampled at each
23 altitude during the flight. This matching is achieved in a 4 stage process. First (i) the amount of
24 remaining Fill Gas is determined, then (ii) the sampling of air based on the ideal gas law is
25 calculated. In the third step (iii) the start and end times of AirCore in the analyser time series
26 are determined and finally (iv) the sampling and the analysis can be matched based on the molar
27 amount.

2.4.1 Determination of remaining Fill Gas

In the case of slow vertical displacement of the balloon, pressure equilibrium between the AirCore and the surrounding air can be assumed. Under this assumption of an instantaneous pressure equilibrium, the molar amount n of an ideal gas stored in volume V at pressure p and temperature T is according to the ideal gas law:

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

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

As noted above, the assumptions about pressure equilibrium between air inside the AirCore and outside air needs to be made in this calculation. While this is certainly a valid assumption for a slow descent of the balloon, it will be less valid the faster the descent of the balloon. In the case of a rubber balloon which will burst while still ascending and then immediately start to descent the situation is even more difficult, as the pressure inside the AirCore will actually be higher than the outside pressure during the beginning of the descent, because a non-equilibrium will exist both for the emptying of the tube during ascent and the re-filling of the tube during the descent. The size of this non-equilibrium effect will depend on the geometry of the AirCore but also on the filling of the sample dryer. In particular, this latter may provide a significant flow restriction if the $\text{Mg}(\text{ClO}_4)_2$ is packed very densely. The amount of FG left in the AirCore is thus expected to differ significantly from the equilibrium amount calculated before based on the minimum in $\frac{p}{T}$. We have taken particular care to have a short and loosely packed dryer providing minimal flow restriction. As the FG used in our case differs significantly in CO values from ambient air and from the calibration gas used, it is possible to determine the amount of remaining FG by integrating the CO peak observed during the measurement of the AirCore (Chen et al., 2017) as illustrated in Figure 4. When switching from the bypass to the measurements mode, the gas inside the Picarro measurement cell is first replaced by the calibration gas, which was used to flush the transfer line to the AirCore during the connection. The calibration gas (Cal Gas) is then replaced by the FG which remained in the AirCore and then by ambient stratospheric air. All of these gases are partially mixed and all of them contain some CO. In

1 order to separate the amount of CO due to PG and Cal Gas from the signal due to remaining
2 FG, we performed a measurement in a similar set-up but with our AirCore filled with pure
3 nitrogen, which contained no detectable amounts of CO. The CO in this set-up is thus not due
4 to remaining FG and can be used to correct the offset due to PG and Cal Gas when integrating
5 the CO peak from the remaining FG. Using the known mixing ratio of CO in the FG, the molar
6 amount of remaining FG can be determined. In the case of the two fast descent profiles from
7 Lindenberg (see section 3), the pressure of remaining FG was determined to be 17.2 hPa and
8 7.3 hPa, respectively, while the corresponding pressures derived from the minimum in $\frac{p}{T}$ was
9 slightly lower at 15.2 hPa and 7 hPa, respectively. The differences are rather small, correspond-
10 ing to altitude differences of a km or less, as the flow restriction of our AirCore is low due to
11 the large inner diameter of the 8 mm tube (which carries the largest part of the volume) and the
12 carefully packed sample dryer. In the following we have therefore only corrected this effect by
13 adopting the upper sampling pressure during the Lindenberg flights to the value calculated from
14 the integration of the CO peak of the remaining FG.

15 **2.4.2 Sampling of ambient air with AirCore**

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

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

2.4.3 Matching AirCore and Picarro data

In the third step we determine the starting and ending point in the measurements of the air mass sampled and stored in the AirCore with the Picarro (see Figure 2). This is achieved by fitting a Gaussian curve to the CO peak from the remaining FG (see Figure 4). In case that there is so much FG left that the CO peak reaches a plateau the left and right side of the remaining CO from FG are fitted separately using only one side of the Gaussian for fitting. The time when the peak reaches half its height is chosen as the start time. The time derived for the rising CO peak is then taken as the start time of the FG, the time derived for the descending part of the peak is taken as the start of the AirCore, i.e. ambient stratospheric air. We chose to use this second point as the starting point and associate it with the amount of remaining FG determined in section 2.4.1. The determination of starting and ending point of the AirCore analysis in the Picarro time series is critical in the correct assignment of the measured mixing ratio to the sampling location and altitude. Especially the starting point of the AirCore is a critical parameter as an offset of 1 hPa will result in a significant shift in altitude in the stratosphere. The fourth step is then to calculate the molar amount of air passing through the Picarro and linking this to the molar amount sampled with the AirCore. The link between the molar amount and the time of measurement is straight forward, as the flow through the Picarro is regulated to be constant (in our case 40 ml/min) and also temperature and pressure of the measurement cell of the Picarro analyser are controlled

2.4.4 Correction of mixing ratios for mixing between AirCore and fill-gas

In order to keep the effect of mixing between FG and ambient stratospheric air small, ~~we have made the FG in order to have had mixing ratios values~~ close to those expected in the middle stratosphere. The FG, which is also used as PG₂ has a mixing ratio of about 407.75 ppm of CO₂ and 1228.6 ppb of CH₄. On the other hand, the PG has much higher CO (about 1400 ppb) in order to allow a clear distinction from both tropospheric and stratospheric air. Especially stratospheric air has much lower CO mixing ratios, which are on the order of 20 ppb (Engel et al., 2006b; Toon et al., 1999). Our measurements showed a gradual decrease of CO values from the high FG values to the significantly lower stratospheric mixing ratios. Values as low as 20 ppb ~~w~~here only observed sporadically, with values around 100 hPa pressure altitude typically being in the 30 ppb range. This enhancement could either be caused by CO production from the reaction of ozone with the tubing or it could be a measurement artefact as the Picarro is not well

1 suited for such low CO mixing ratios. This gradual decrease from the FG values to stratospheric
2 values is due to a combination of mixing and diffusion. While mixing is similar for all species,
3 molecular diffusion depends on the diffusion coefficient and is different for each gas. The upper
4 part of the profile is stored in the 2 mm O.D. tube. In this tube molecular diffusion only leads
5 to a very gradual mixing of the two gases (FG and ambient air). Most of the gradient is due to
6 mixing during the analysis (the limiting part is the volume of the analyser cell). Therefore, this
7 gradient can be treated as a gradient caused by mixing and not diffusion, and the mixing should
8 be similar for all species. We will thus use the large difference in CO to characterise the fraction
9 of FG in the analysis and correct the observed mixing ratios of CH₄ and CO₂ for the remaining
10 impact of FG. In order to determine the fraction of remaining FG an assumption on the expected
11 stratospheric mixing ratio of CO must be made. As we expect that the correction should ap-
12 proach zero once the cell has been flushed a few times, we have chosen to use the average CO
13 value observed between 80 and 100 hPa as the expected value. Using this target value the frac-
14 tion of FG is calculated from the difference between the measured and the expected CO mixing
15 ratios and the observed mixing ratio from the Picarro measurements is corrected accordingly.

16 **3 Atmospheric observations**

17 The AirCore developed at University Frankfurt is sufficiently light to be flown with a small
18 balloon. However, we performed our first test flights using large stratospheric balloons
19 launched by CNES from Timmins in Ontario. Two such test flights were performed in order to
20 compare our results with those of other groups. The first test flights were performed in 2014.
21 The results from the first flight in 2014 is reported by Membrive et al. (2016). Due to a balloon
22 trajectory which was not adapted to AirCore measurements (long ceiling and long float of the
23 balloon around 20 km altitude) the profiles obtained for CO₂ from AirCore could not be used
24 to derive mean age, as the AirCore showed unrealistically low values of CO₂ around the float
25 altitude, possibly due to an interference with the sample dryer (Membrive et al., 2016). These
26 data are therefore not discussed in this paper. During a second flight of the same payload as
27 reported in Membrive et al. (2016), the vertical velocities were much better adapted and we
28 could derive profiles of CO₂, CO and CH₄. These are presented in section 3.1. In section 3.2.
29 we present the first results from our AirCore measurements at mid latitudes using a small and
30 easy to launch rubber balloon of similar type as used for ozone soundings.

1 **3.1 Timmins 2015**

2 The payload launched from Timmins in the year 2015 was very similar to the one described in
3 Membrive et al. (2016). It consisted of a combination of two AirCores by University Frankfurt,
4 one high-resolution AirCore (Membrive et al., 2016) and two light weight AirCores by the
5 Laboratoire de Meteorologie Dynamique (LMD). In contrast to the Picarro G2401 used by
6 University Frankfurt, the LMD team used a G2301 analyser, which lacks the capacity to meas-
7 ure CO. The payload also included two pico-SDLA spectrometers (Ghysels et al., 2014;Durry
8 and Hauchecorne, 2005) for measurements of CO₂ and CH₄, which are based on in-situ infrared
9 absorption measurements. Results from these latter measurements were perturbed due to ther-
10 mal drifts in laser emission wavelength and are not available at the time of writing. The balloon
11 was launched from Timmins, Ontario, on August 22, 2015 and reached a minimum pressure of
12 about 11 hPa. In order to reach a zone where a safe landing was possible, the balloon was left
13 to drift westwards and a slow descent of the balloon was started in the early morning of August
14 23 (8:30 U.T.). The payload was separated from the balloon just below 100 hPa pressure and
15 the payload landed at about 10:40 U.T. The recovery team was able to recover the payload such
16 that the analysis could be started about 4 hours after landing.

17 Figures 5-7 show the vertical profiles of CO, CH₄ and CO₂ as measured with the Picarro ana-
18 lyser for both AirCores by GUF and in comparison to the LMD AirCores (only for CH₄ and
19 CO₂). The altitude attribution is based on the CO peak as described in section 2.4. One of the
20 AirCores (AC-2) was operated with the automatic closure valve and thus did not lose any air
21 while warming up on the ground after landing. The profile from this AirCore extends to the
22 ground, while other profile (AC-3) ends higher up due to the loss of air. First of all, two peaks
23 in CO are observed in the troposphere, which are found at the same altitude for both AirCores.
24 These could have been caused by biomass burning from wildfires occurring over western Can-
25 ada during the period of observations. Lowest values of CO in the stratosphere are on the order
26 of 10-20 ppb, in agreement with expected steady state values (Toon et al., 1999;Engel et al.,
27 2006b). AC-3, which was measured after AC- 2 shows an increase in CO mixing ratios above
28 20 km, which is most probably due to the longer storage time, resulting in more diffusive mixing
29 with remaining Fill Gas.

30 Figure 6 shows the vertical profiles of CH₄ derived from the 5 independent AirCores all
31 mounted on the same gondola. A remarkably good agreement is observed, as already shown for
32 observations in 2014 (Membrive et al., 2016). As also discussed in (Membrive et al., 2016) it
33 is obvious that the AirCore-HR is able to capture fine scale vertical structures which are not

1 present in the profiles derived from the light weight AirCore of University Frankfurt nor from
2 the light weight AirCore of LMD, which have a similar vertical resolution in the troposphere
3 but less vertical resolution in the stratosphere. The vertical profile of the light weight LMD
4 AirCore is only derived up to about 23 km altitude. Above 19 km altitude the light weight LMD
5 AirCore shows some deviations from the High Resolution AirCore and the University Frankfurt
6 AirCores. The University Frankfurt AirCore on the other hand is capable of capturing some
7 local structure around 21-22 km altitude, although the two local minima from the High Reso-
8 lution AirCore are smeared out to one broader minimum. Above 23 km altitude there seems to
9 be a small altitude mismatch between the University Frankfurt and the High Resolution Air-
10 Core, which is however less than 1 km. This altitude discrepancy is explained by the uncertainty
11 in matching the Picarro measurements to the AirCore sampling, which is also treated slightly
12 differently in the LMD and the University Frankfurt retrieval. In order to compare the values
13 of the different AirCores, we binned the data into 1 km intervals and then calculated averages
14 for each AirCore in these bins. In the troposphere (values between 3 and 13 km altitude) the
15 standard deviation between these 1 km bins is 1.4 ppb, or 0.08%. In the stratosphere the devia-
16 tions are higher due to the large vertical gradient. Absolute deviations are on average (between
17 15 and 24 km altitude) 11 ppb or 0.75%. The agreement of the two University Frankfurt Air-
18 Cores is much better (0.17 ppb or 0.001% in the troposphere and 3.8 ppb or 0.25% in the strat-
19 osphere), as is that of the two light weight LMD AirCores (0.28 ppb or 0.0015% in the tropo-
20 sphere and 1.6 ppb or 0.1% in the stratosphere).

21 The CO₂ measurements from the five AirCore are compared in Figure 7. The overall shapes of
22 the profiles from the different AirCores show good agreement. In particular, also rather small
23 scale phenomena are resolved and observed in all AirCores. For instance the small scale struc-
24 ture at around 13 km is observed in all AirCores, again showing that the sampling and the
25 altitude attribution gives consistent results. As already discussed by Membrive et al. (2016),
26 CO₂ measurements seem to show more deviations. However, it should be noticed that the range
27 shown for CO₂ is much smaller than for CH₄. In contrast to CH₄ the deviations in the tropo-
28 sphere and the stratosphere are very similar, as the vertical gradient is similar. In absolute terms,
29 the deviations are typically 0.35 ppm or about 0.09%. This deviation is thus on a very similar
30 level as observed for CH₄ in the troposphere. Overall, this agreement is very good, taking into
31 account that the different AirCores partly use different data retrieval algorithms and have dif-
32 ferent geometries and thus also different vertical resolutions. As in the case of CH₄, we note
33 that the agreement between the two University Frankfurt AirCores is much better (0.04 ppm or

1 0.01% in the troposphere and 0.17 ppm or 0.04% in the stratosphere), as is the agreement be-
2 tween the two light weight LMD AirCores (0.05 ppm or 0.015% in the troposphere and 0.07
3 ppm or 0.02% in the stratosphere). This shows that the differences are systematic and must be
4 related to the geometries of the different AirCores and the related uncertainties in the altitude
5 attributions.

6 **3.2 Lindenberg 2016**

7 A first test campaign to study the use of our AirCore using small balloons ~~has been~~was con-
8 ducted from the Lindenberg Meteorological Observatory, Germany. AirCores were launched
9 on May 20, 2016 and May 25, 2016. The balloon used for the first flight was a TA 1500 balloon.
10 A larger balloon (TA 3000) was used for the flight on May 25, ~~thus allowing to reach~~which
11 ~~reached~~ a higher ceiling altitude. Ceiling pressures were 15.2 and 7 hPa, respectively. Large
12 parachutes were used in order to slow down the descent speed and minimize the effects due to
13 non-equilibrium of pressure inside of the AirCore and outside pressure. For both measurement
14 flights we were able to recover the AirCore very fast and start the analysis within an hour after
15 landing. The retrieval procedure was similar to the one for the flight from Timmins in 2015
16 with the exception that we derived the pressure at which sampling began not from the measure-
17 ments of ambient pressure but from the integration of the CO peak as described in section 2.4.1.
18 (diploma thesis Markus Ullrich, University Frankfurt, Dec. 2016).

19 Figures 8 to 10 show the vertical profiles of CO, CH₄ and CO₂ from the two flights conducted
20 in May 2016. For CO the general agreement between both ~~measurement~~flights is very good,
21 even though they are five days apart. CO values are higher than observed in Timmins in 2015.
22 This could either be due to the use of a different Picarro analyser (note that these values are
23 close to the detection limits of CO) or to enhanced CO in early spring e.g. due to descending
24 mesospheric air during the polar winter. For all species there is a distinct change at the tropo-
25 pause, ~~which is observed~~ around 10.4 km altitude on May 20 and 10.9 km on May 25. ~~11 km~~
26 ~~altitude with a sharp drop in mixing ratios~~. The decrease in tracer mixing ratios, especially for
27 CO, is observed at the same altitude as the thermal tropopause, ~~i.e. at 11 km altitude~~, showing
28 that the altitude attribution as explained in section 2 yields realistic results.

29 For CH₄ and CO this is due to the chemical loss in the stratosphere, whereas CO₂ is very long
30 lived in the stratosphere. The decrease in CO₂ values above the tropopause is mainly caused by
31 the high values of CO₂ in the northern hemisphere troposphere during spring, while the air

1 above the tropopause partly entered through the tropical tropopause and partly during late sum-
2 mer of the preceding year when tropospheric CO₂ values were lower due to the seasonal cycle
3 (Boenisch et al., 2009). Both CH₄ and CO₂ show some fine structures in the stratosphere during
4 both flights. There is a local maximum in CO₂ and CH₄ at around 21 km altitude on May 20
5 and a similar local maximum is observed on May 25 at about 20.5 km altitude. The maxima
6 and minima in CO₂ and CH₄ are collocated at the same altitude. Therefore, this is clearly a
7 dynamical feature where CO₂ rich (younger) air (see section 4) is advected which at the same
8 time has higher CH₄ mixing ratios. Such air masses would be expected to occur in the tropics
9 or subtropics. As the dynamical interpretation of the profiles is not the focus of this paper, this
10 is not investigated further e.g. by using meteorological data.

11 **4 Age of air from AirCore**

12 The main aim of our AirCore activities is to determine mean age of air and use this to extend
13 our long time series of mean age from balloon observations (Engel et al., 2009). The two tracers
14 most commonly used to derive mean age are CO₂ and SF₆. As shown in Engel et al. (2009), the
15 vertical gradient of mean age becomes rather small at pressures ~~altitudes above~~below 30 hPa
16 (approximately altitudes above 24 km). The mean value of mean age above this altitude has
17 been used to investigate long term changes in mean age and in the stratospheric circulation
18 (Engel et al., 2009). An ideal tracer for the derivations of mean age should have neither sinks
19 nor sources in the middle atmosphere and show a monotonous, linear trend in the lower atmos-
20 phere (Hall and Plumb, 1994; Waugh and Hall, 2002). Neither CO₂ nor SF₆ completely fulfil
21 these requirements (Engel et al., 2009) leading to uncertainties in the mean age values derived
22 from observations. In the case of CO₂ there are three specific issues which need to be consid-
23 ered: (i) the source of CO₂ in the middle atmosphere due to the oxidation of CH₄, (ii) the sea-
24 sonal cycle of CO₂ and (iii) the deviation of the deseasonalized long term trend of CO₂ in the
25 troposphere from linearity. The procedure to calculate mean age and how to take these issues
26 into account is the same as in Engel et al. (2009) and only briefly summarized here. As CH₄ is
27 oxidised in the stratosphere and thus provides a source for CO₂ in the stratosphere, the amount
28 of CO₂ produced from the oxidation has to be subtracted from the observed CO₂ mixing ratio.
29 The CO₂ produced in the stratosphere is derived from the observed CH₄ by taking the difference
30 to the deseasonalized tropospheric CH₄ at the time of measurements. In this procedure the fact
31 that CH₄ has a tropospheric trend and takes some time to propagate to the stratosphere is ig-
32 nored. The error in mean age due to this simplification is less than half a month. CO₂ has a

1 seasonal cycle in the troposphere which can propagate into the lower stratosphere (Andrews et
2 al., 2001a; Andrews et al., 2001b; Hints et al., 1998; Boenisch et al., 2009; Engel et al., 2006a).
3 Rosenlof et al. (1997) found that the seasonal cycle in water vapour is observable up to potential
4 temperatures of about 450 K and termed this region the tropically controlled transition layer. In
5 the stratospheric overworld (above 450 K potential temperature) short term influences e.g. due
6 to seasonal cycles in the troposphere or tropopause region are much smaller. CO₂ can thus only
7 be used as an age tracer for air at potential temperatures above 450 K where the mixing ratios
8 are not influenced by seasonality in the troposphere anymore. Our analysis of mean age is thus
9 restricted to potential temperatures above 450 K. Thirdly, the deseasonalized tropospheric trend
10 of CO₂ in the troposphere deviates from a perfect linear increase. The mean age derived from
11 CO₂ observations will thus depend on the shape of the age spectrum. To compensate for the
12 effects of this deviation on the mean age values derived, we again followed the same approach
13 as in Engel et al. (2009). We use a parameterization of the width of the age spectrum Δ as
14 function of mean age Γ as suggested by Hall and Plumb (1994), i.e. $\frac{\Delta^2}{\Gamma} = 0.7 \text{ years}$ with the
15 general shape of the age spectrum being an inverse Gaussian function. We have further adapted
16 the fitting period for the tropospheric trend so as to represent 98% of the air input for each
17 individual data point (i.e. shorter time periods for the fit are applied for younger air), in order
18 to find the best possible description of the tropospheric input time series.

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

21

22 **4.1 Vertical profile observations**

23 Figure 11 shows the mean age profiles for the two flights from Lindenberg in May 2016 and
24 the two AirCores flown simultaneously in August 2015 from Timmins. The data have been
25 filtered to exclude air masses with potential temperature below 450 K where the CO₂ seasonal
26 cycle is still expected to have a significant impact. As for many other profile observations of
27 mean age (Andrews et al., 2001a; Engel et al., 2009; Schmidt and Khedim, 1991) an increase
28 ~~decrease~~ of mean age with altitude is observed up to about 23-24 km altitude, above which the
29 vertical gradient becomes very small. Mean age values above this layer are on the order of 5
30 years, in very good agreement with other long term data sets. The observations from Timmins
31 in August 2015 show slightly higher mean age values than the observations in May 2016 from

1 LindenberG in Germany. This could be explained by the seasonal cycle in mean age derived
2 from MIPAS Envisat observations of SF₆, showing youngest air in the northern hemisphere
3 mid latitudes above 25 km during winter and oldest air during summer (Stiller et al., 2012). The
4 younger spring measurements from LindenberG could thus still be influenced from the lower
5 mean age values during winter, while the older observations from Timmins in August 2015
6 should be during the maximum of the seasonal cycle. Note that the accuracy of the mean age
7 values determined here is not limited by the analytical precision of the Picarro analyser, which
8 is typically 0.025 ppm, which is less than a week when translated into mean age.

9 **4.2 Extension of long term time series**

10 As explained above, we want to use AirCore observation to extend our long time series of
11 stratospheric mean age observations (Engel et al., 2009). The calculation of a temporal trend in
12 mean age is complicated by the sparsity of the data set in combination with a vertical gradient
13 in mean age. As the AirCore observations, in agreement with other balloon data, only show a
14 very small vertical gradient above an altitude of 23-24 km, corresponding to about 30 hPa, we
15 have adopted the same procedure as used in Engel et al. (2009), i.e. we average all data between
16 30 hPa and 5 hPa and calculate an average value of mean age for this region of the strato-
17 sphere.

18 The last data point in Engel et al. (2009) was from the year 2005. There is thus a gap of 10 years
19 between these last measurements and the new AirCore data. Overall the mean values derived
20 from the AirCore data are in very good agreement with the values published in Engel et al.
21 (2009). The mean values for mean age above 30 hPa from the Timmins flights are 4.9 ± 1 and
22 5.3 ± 1 years, while the LindenberG flights yield slightly lower mean age values at 4.7 ± 1 and
23 4.8 ± 1 years. Note that the uncertainty ranges include uncertainties in the estimated representa-
24 tiveness, the derivation of mean age and the observations themselves, based on the error assess-
25 ment given in Engel et al. (2009). Using all the data available, we derive a new estimate of the
26 long term trend in mean age for the mid latitude stratosphere of the Northern Hemisphere be-
27 tween 30 and 5 hPa. The time period covered is now more than 40 years (1975-2016), albeit
28 with a very restricted number of profile observations. The updated trend is now calculated to
29 be 0.15 ± 0.18 years/decade. This trend is smaller than the previous estimate (0.24 ± 0.22
30 years/decade), but agrees within the uncertainty range. The positive trend is not significant
31 within the one sigma uncertainty range. Due to the reduced uncertainty of the new estimate, the

1 largest negative trend which would be compatible with our data within the two sigma uncer-
2 tainty range remains nearly unchanged (-0.21 years/decade instead of -0.2 years /decade).

3 **5 Summary and conclusion**

4 Observations of stratospheric trace gases are well suited to investigate chemical and physical
5 processes in the stratosphere. They are also well suited to investigate long term changes in the
6 stratosphere. In particular, for the investigation of long term changes, high precision and accu-
7 racy are needed in combination with rather low costs (Müller et al., 2016; Moore et al., 2014).
8 Most in-situ measurements in the stratosphere require the use of large and expensive balloons
9 to carry instruments above altitudes of 20 km. The new technique of AirCore (Karion et al.,
10 2010; Membrive et al., 2016) is ideally suited to provide such low cost long term observations.
11 We have thus investigated the usefulness of AirCore for investigations of long term evolution
12 of mean age in order to extend the existing balloon data set used in Engel et al. (2009) and (Ray
13 et al., 2014). University Frankfurt has developed an AirCore system from three different inner
14 diameter tubes, targeted at an optimal vertical resolution in the stratosphere, while still being
15 sufficiently light weight to be deployed on a small balloon. During an intercomparison cam-
16 paign in Timmins, Ontario in August 2015 we compared 5 different AirCores. We have shown
17 that the AirCore technique can be used to derive high precision vertical profiles of CO₂ and
18 CH₄. Both LMD and University Frankfurt measurements are referenced to the same scales, but
19 ~~using~~ independent calibrations. This shows that the results are also of high accuracy. For both
20 trace gases the comparison between the different independent AirCores was better than 0.1%
21 when vertical gradients are small, as is the case for CO₂ in the mid latitude stratosphere above
22 a pressure altitude of 30 hPa (about 24 km altitude) and for tropospheric CH₄. ~~This indicates~~
23 ~~that the~~ For CH₄ in the stratosphere, where there is a large vertical gradient the typical agree-
24 ment was still better than 1%. The agreement between two similar AirCores, which sampled in
25 parallel was always better than the agreement between different AirCores when sampling in
26 parallel. This shows that the geometry, the analysis system and the data retrieval of the AirCore
27 has a significant impact. We have further performed the first observations from the mid latitude
28 site of Lindenberg in Germany using small rubber balloons. Due to careful planning, it was
29 possible to analyse the AirCores within one hour after landing. We showed that the CO peak
30 from the remaining Fill Gas in the AirCore can be used to derive the maximum sampling alti-
31 tude. In the case of the observations from Lindenberg the maximum sampling altitudes were
32 only slightly lower than the maximum pressure altitude of the balloon. This is a good indication

1 that the flow restriction was rather small and that the pressure equilibrium between the tube and
2 outside air is rather fast. This was achieved in particular due to the use of a large inner diameter
3 tube for the main volume of the AirCore and by using a sample dryer which was optimised for
4 minimum flow restriction. Nevertheless, the altitude attribution of the sampled air remains a
5 difficult issue, in particular when descent rates are high. The use of balloon techniques allowing
6 for rather slow descents should thus be considered when setting up AirCore measurements sites.

7 We have used the new observations to calculate mean age of stratospheric air. The results from
8 our AirCore observations are in very good agreement with previous observations using whole
9 air sampling techniques (Engel et al., 2009) with values ranging from 4.7 to 5.3 years of mean
10 age above a pressure altitude of 30 hPa. We have used these data to extend our long term time
11 series of balloon borne mean age observations. This time series now dates from 1975 to 2016,
12 thus spanning a total of more than 40 years. The long term trend of mean age in the northern
13 hemisphere mid latitude stratosphere deduced from this data set is 0.15 ± 0.18 years/decade. This
14 trend is smaller than the previous estimate (0.24 ± 0.22) years/decade but remains well within
15 the uncertainty limit. Based on this analysis, we thus sustain our result that no significant change
16 in mean age of air for the mid latitude stratosphere of the Northern Hemisphere can be derived
17 from our data set. Despite the smaller positive trend derived from this extended data set, large
18 negative changes in mean age in this region can still be excluded, as the uncertainty on the
19 derived trend has been reduced. A negative trend in mean age of more than -0.2 years/decade
20 for the middle stratosphere of the Northern Hemisphere mid latitudes can still be excluded with
21 95% confidence.

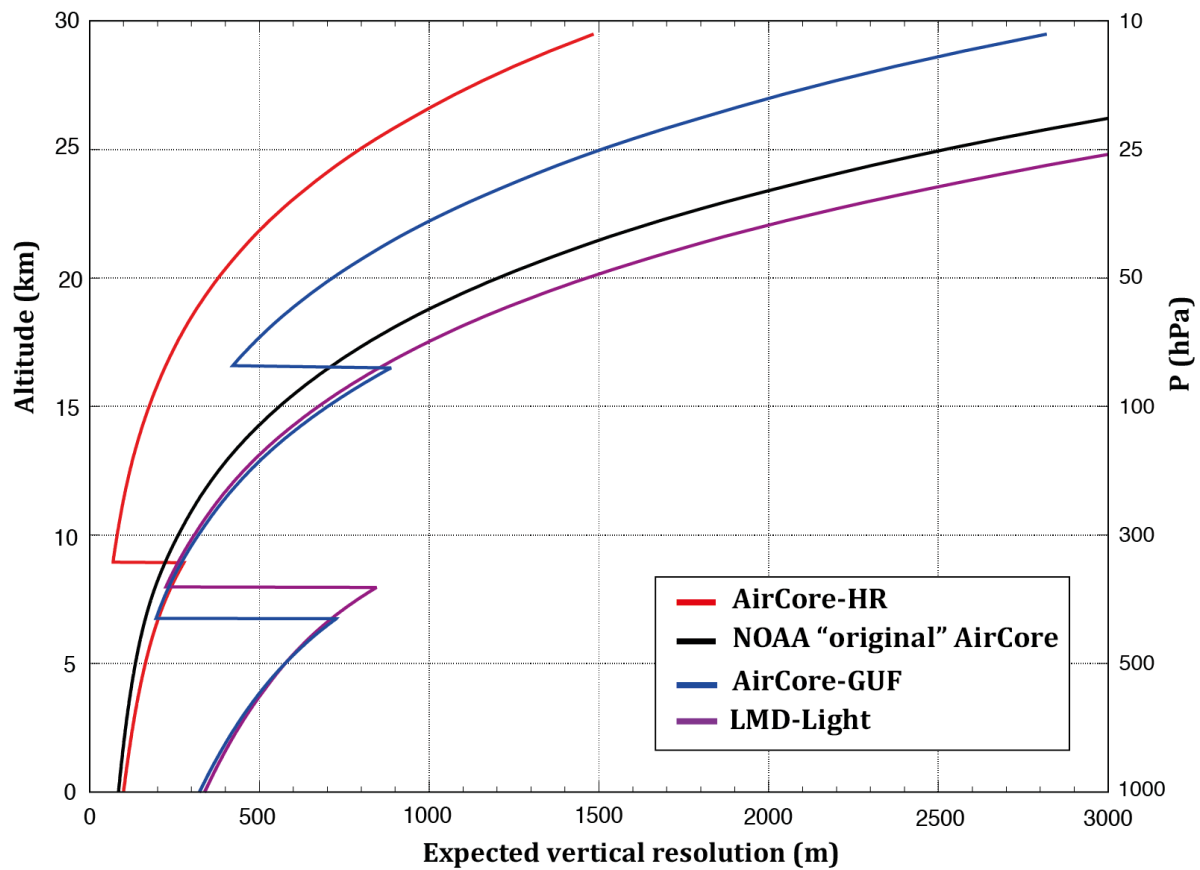
22 We conclude that we have shown that AirCore measurements even when using small balloons
23 can be used to derive vertical profiles of CO_2 and CH_4 . These observations are of sufficient
24 quality to derive mean age of air and use this to extend the currently available data set of strat-
25 ospheric mean age observations. We suggest that long term observations using AirCore from a
26 few selected stations covering different latitude bands may provide a useful tool to investigate
27 long term changes in mean age. An extension of the AirCore technique to other tracers gases
28 as suggested by (Moore et al., 2014) may provide a valuable addition as these gases can also be
29 used to study long term changes in the stratosphere. Müller et al. (2016) suggested that a long
30 term network for water vapour measurements in the stratosphere should be set up to monitor
31 this radiatively important trace gas. We suggest that such a network could be complemented by
32 AirCore observations. Such additional AirCore observations would put the observations of

1 changing water vapour into the general context of a changing stratospheric circulation. In ad-
2 dition, if both measurements are performed simultaneously, the observations of Methane from
3 the AirCore instruments and H₂O from the water vapour network could be used to derive the
4 sum of 2*CH₄ + H₂O, which has been identified to show much less variability in the strato-
5 sphere than H₂O.

6 **Acknowledgements**

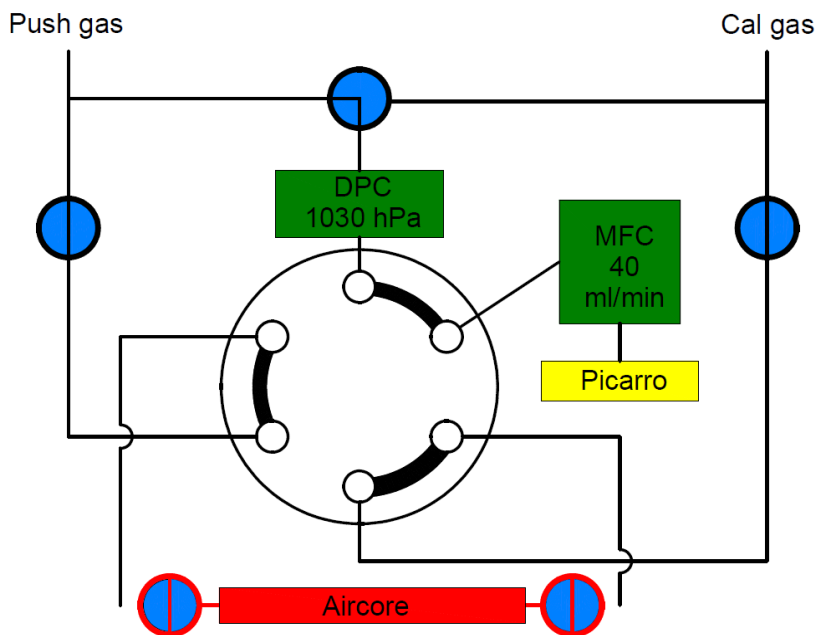
7 The work of University Frankfurt on AirCore has been funded through the ROMIC programme
8 of the German Ministry of Science and Education (Grant Nr. 01LG1221) and the EU Infra-
9 structure Project RINGO (Grant agreement. 730944). We would like to thank the French Space
10 Agency CNES for balloon operations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

16

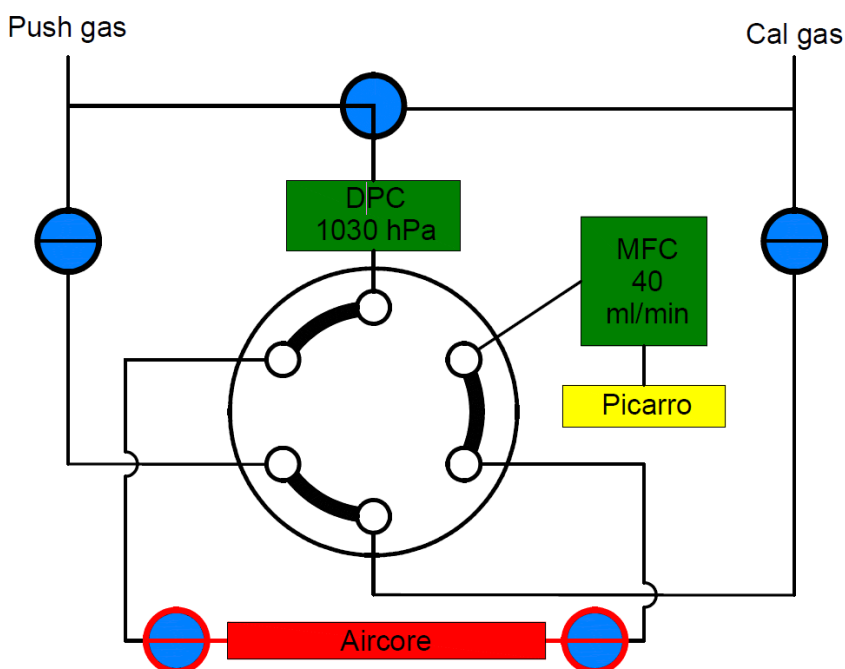


1
 2 Figure 1: Calculated vertical resolution for CO₂ with the Goethe University Frankfurt (GUF)
 3 AirCore (AirCore-GUF) in comparison to other AirCores (see text for description), assuming
 4 a delay of 3 hours between collection and sampling, a measurements flow of 40 ml/min and an
 5 effective cell 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

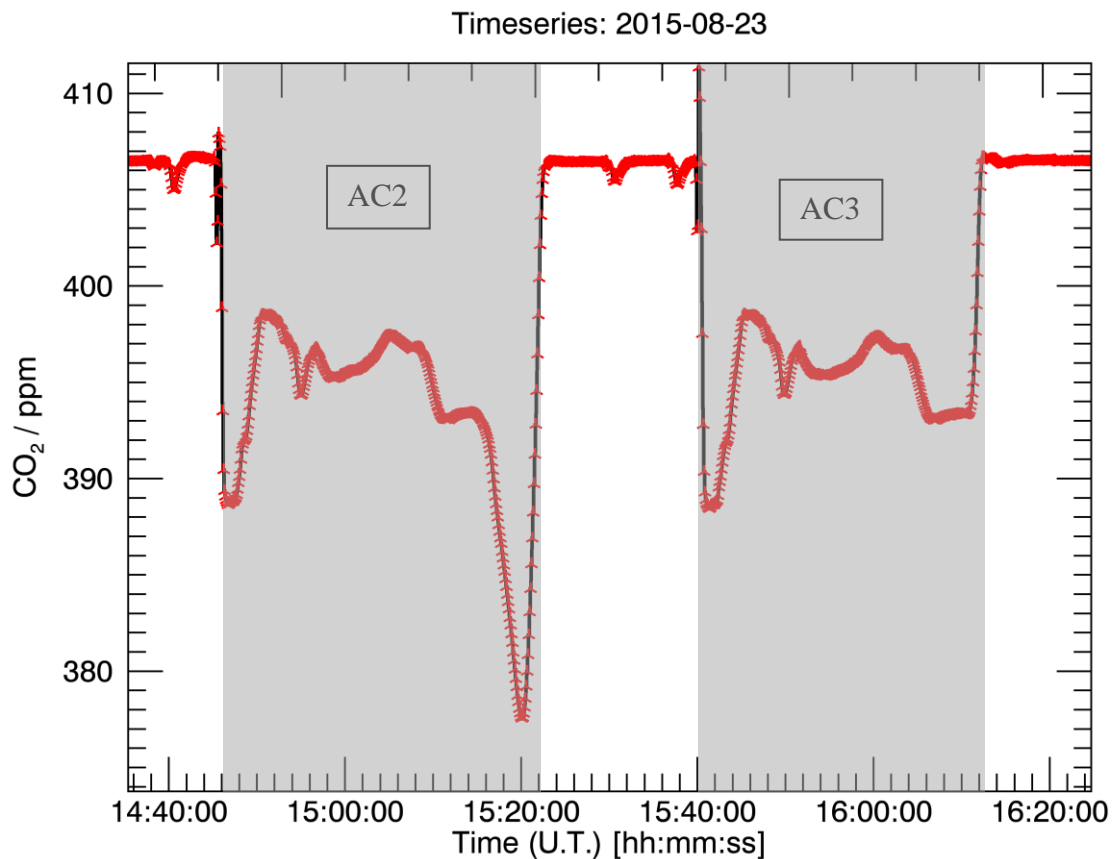


1



2

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

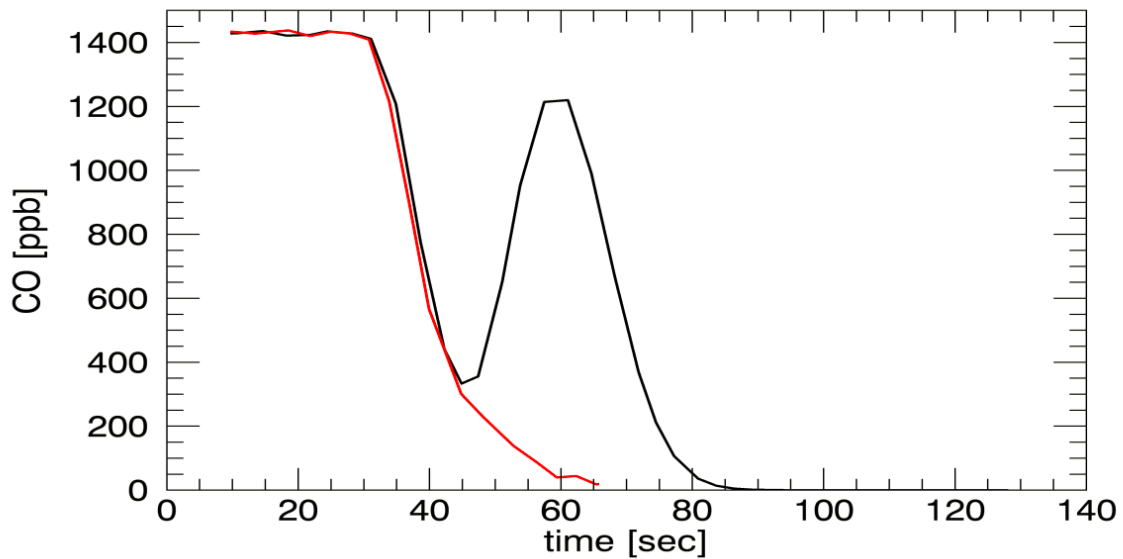
2 Figure 3: raw analytical results for CO₂ from the measurements of the two AirCores flow_n from
 3 Timmins in 2015. Note that AC 2, which was measured first, contained a closure valve, while
 4 AC 3 was left open until the recovery team was able to reach the instrument. The lowest part
 5 of the AC 3 profile was therefore lost due to the warming of the AirCore on ground. The grey
 6 shaded areas denote the measurements of air from the AirCore. The stratospheric part of the
 7 profiles is always measured first. Before the measurements of AC2, between the measurements
 8 of the AirCores and after the measurement of AC3, PG is measured by the Picarro analyzer.

9

10

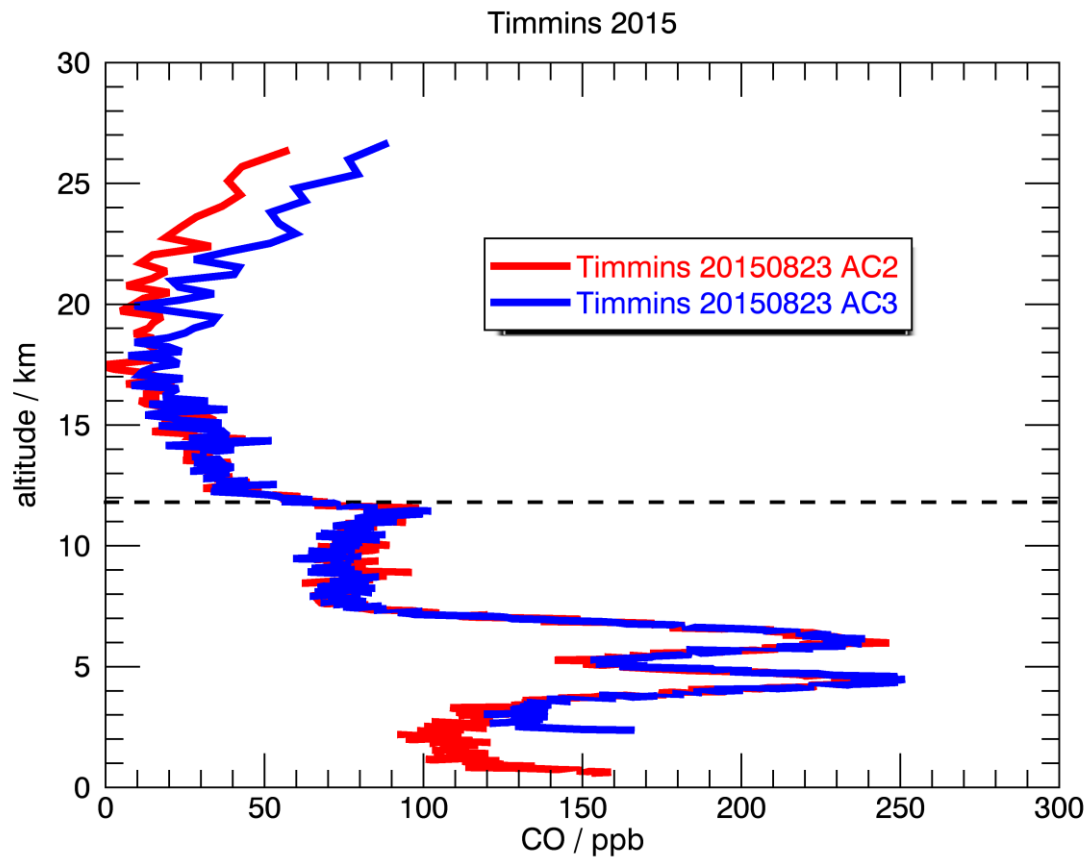
11

1

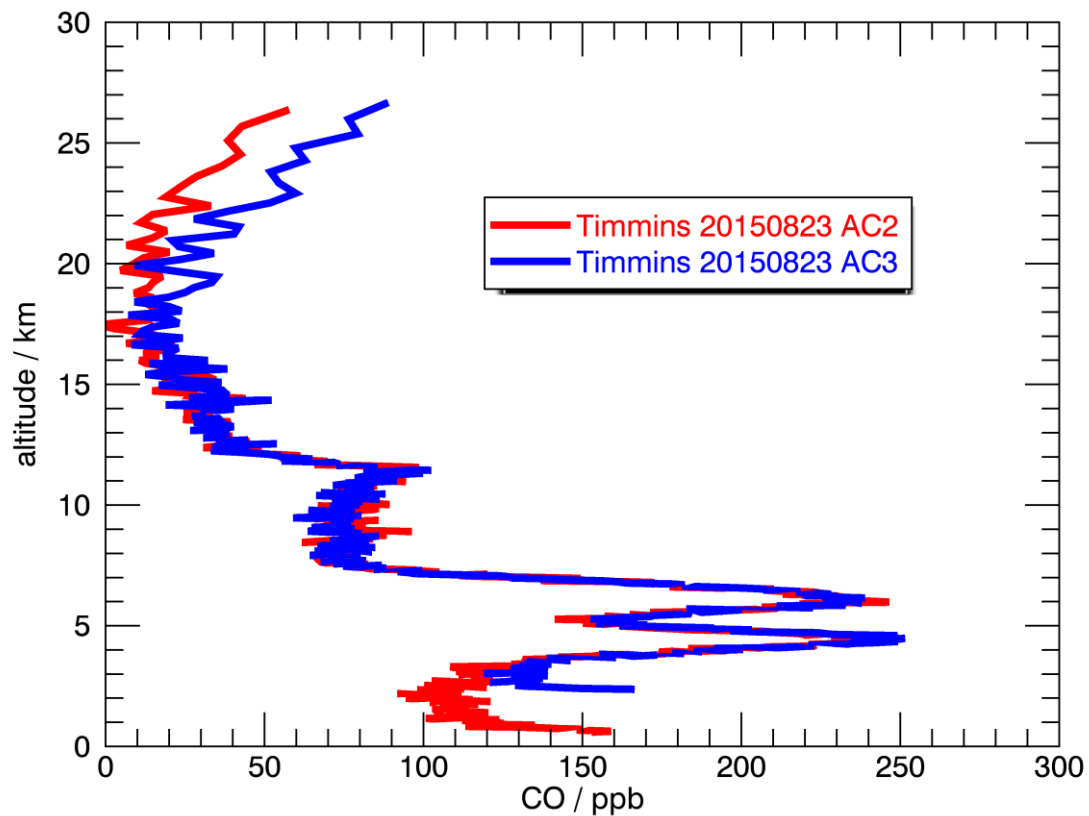


2

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.

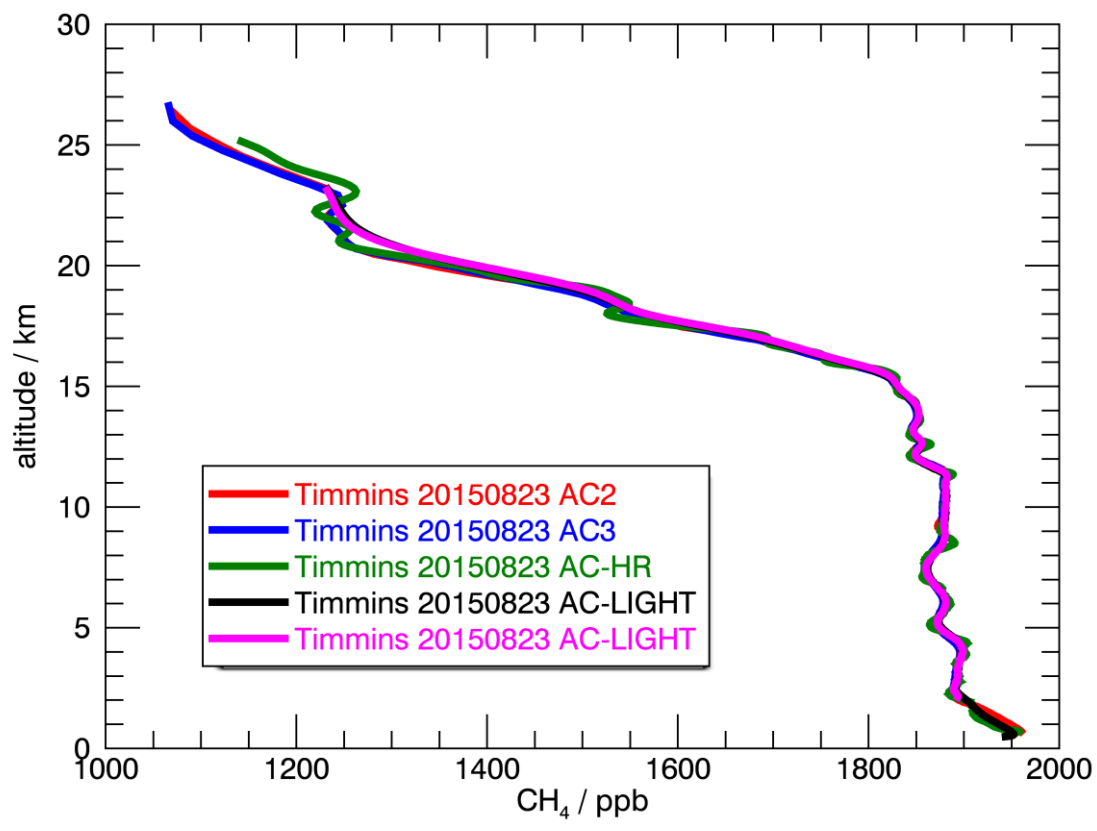


1

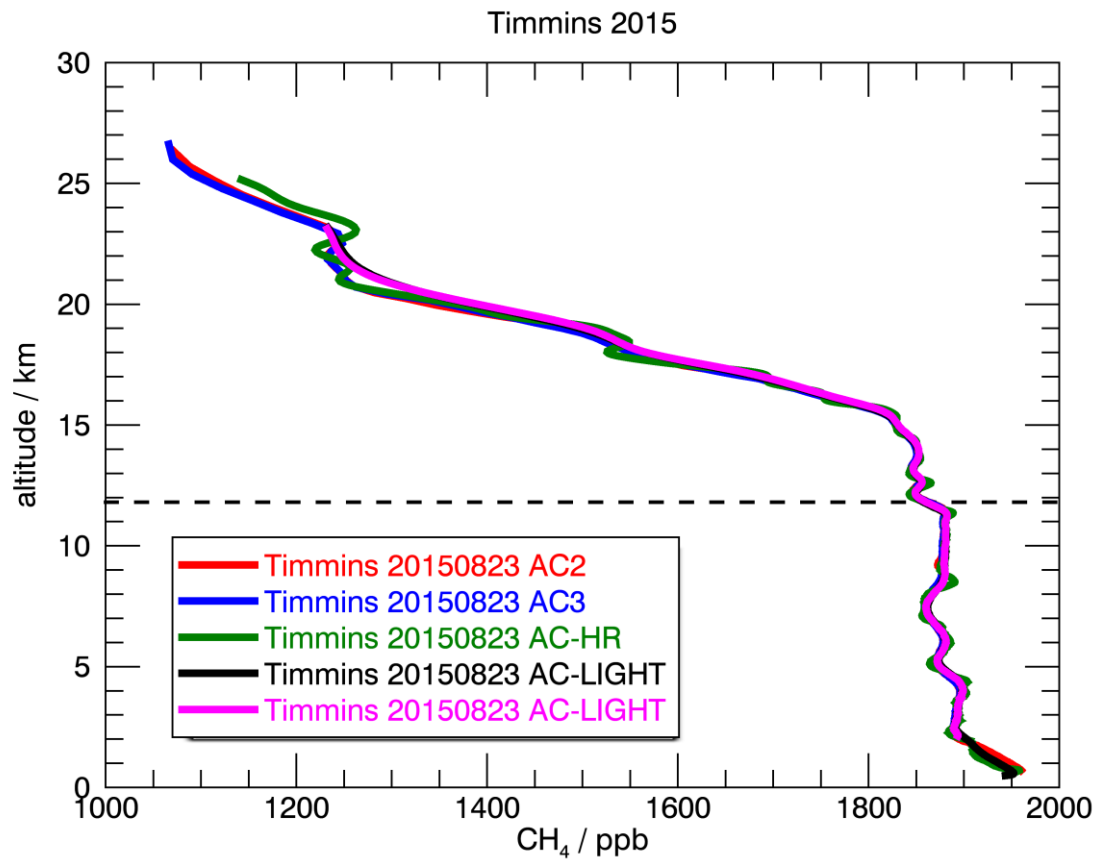


1

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.
 6 The dashed lines represents the thermal tropopause according to the WMO definition.

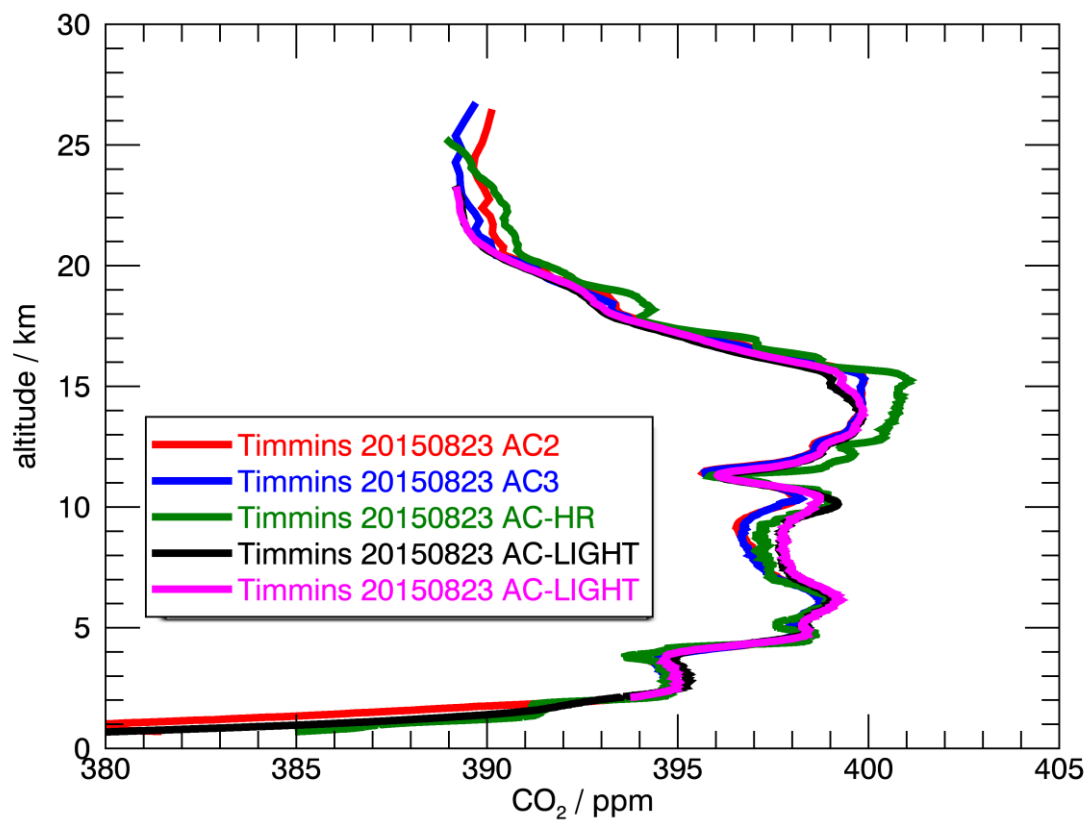


1

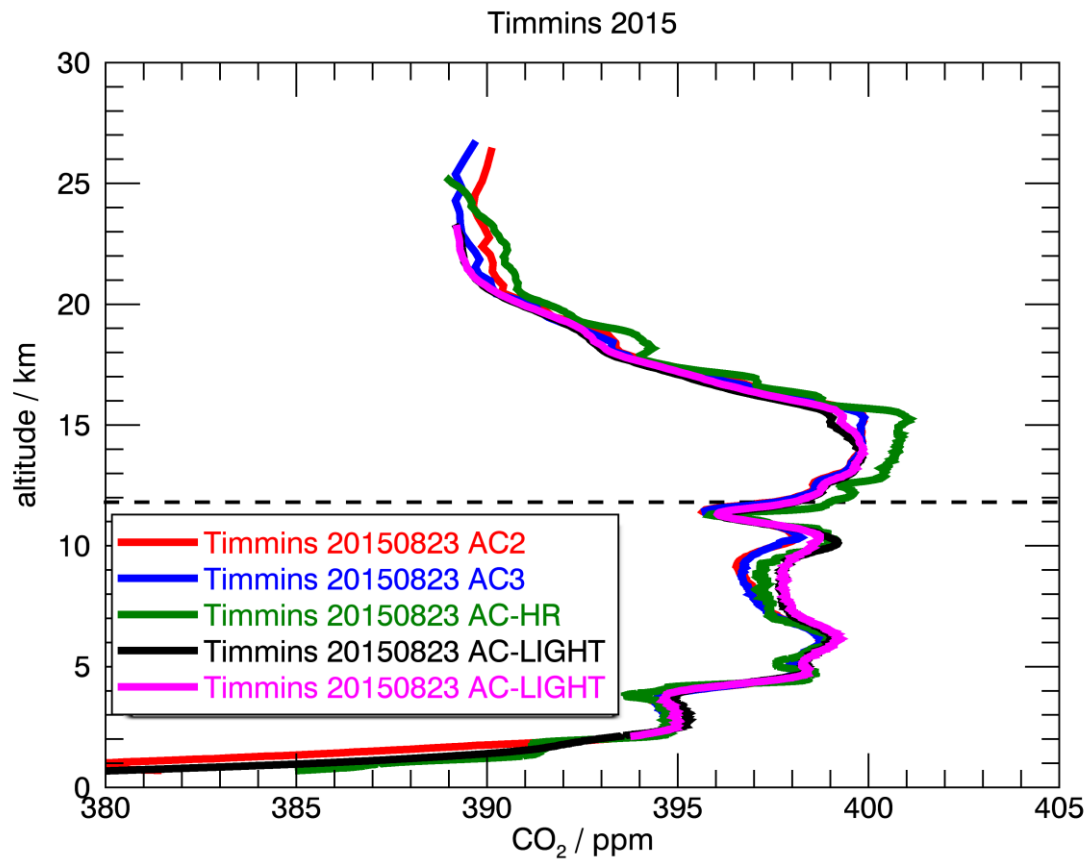


1

2 Figure 6: Vertical profiles of CH₄ 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. The dashed lines represents the thermal tropopause according to the WMO
 8 definition.



1

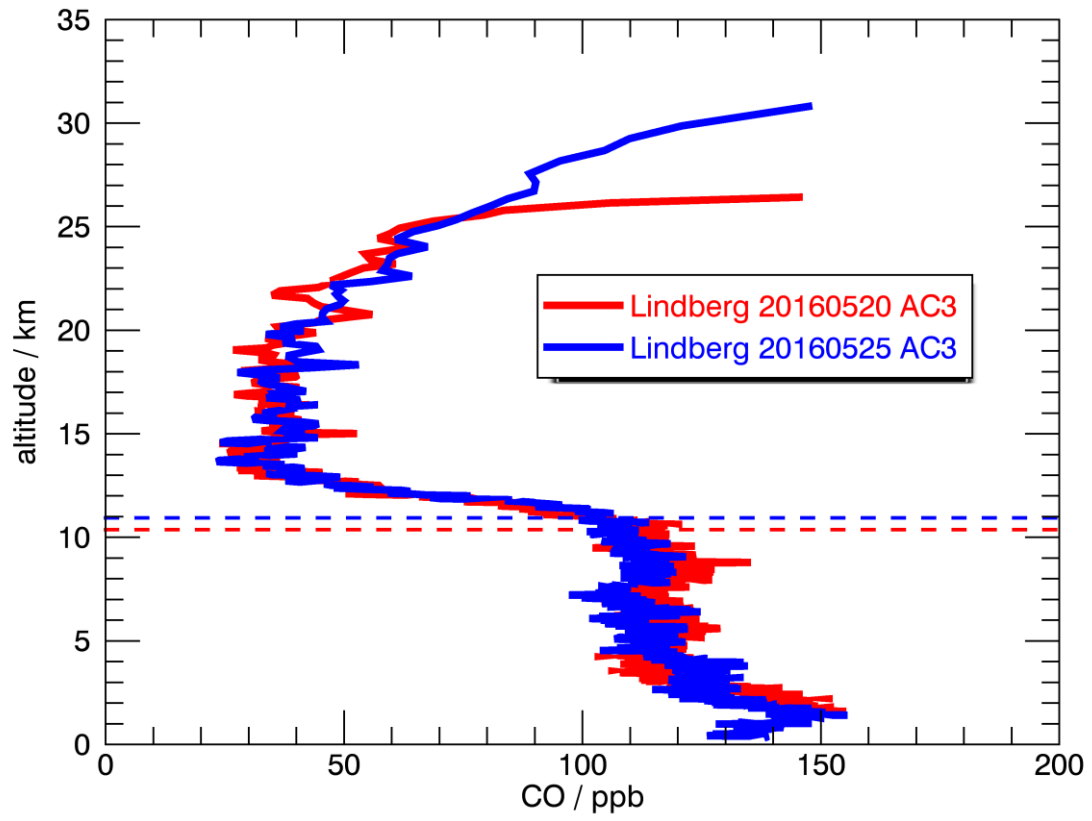


1

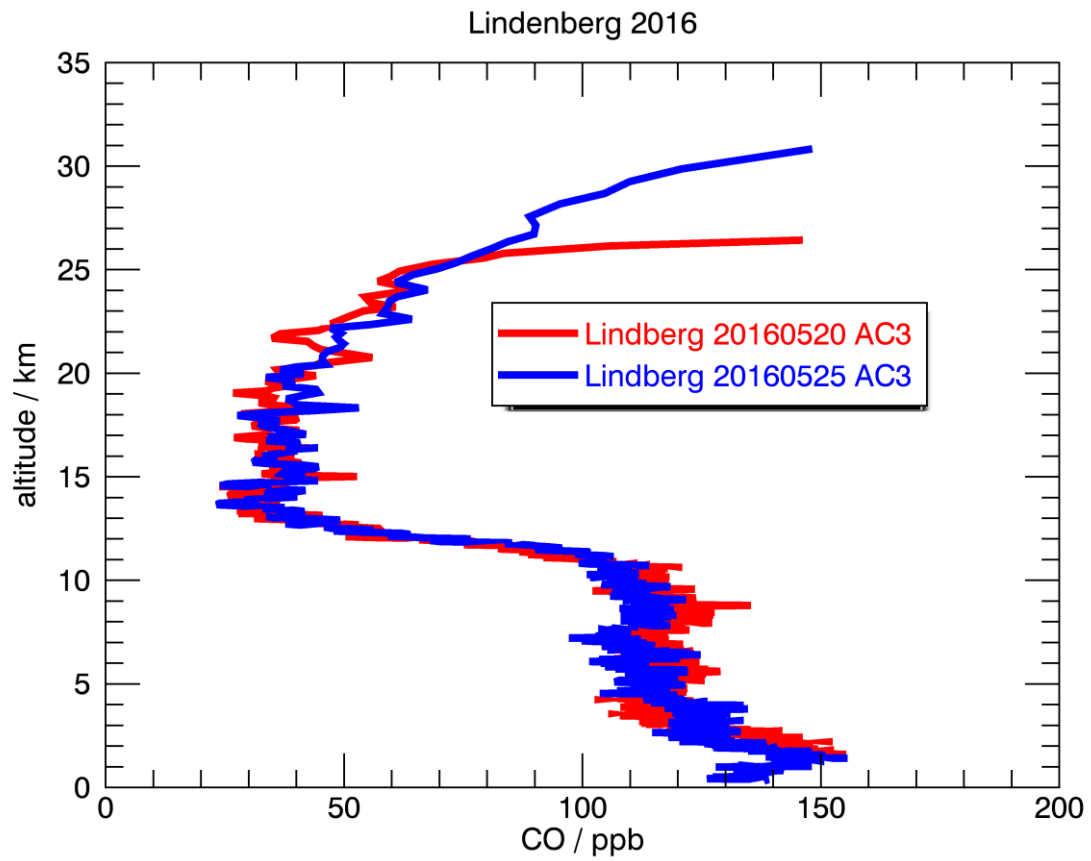
2 Figure 7: Vertical profiles of CO₂ derived for the flight on August 23 2015 from Timmins,
 3 Ontario, Canada. The overall structure are captured very well by all AirCores. Again, more fine
 4 structure is obvious in high resolution AirCore. See text for discussion of the differences be-
 5 tween the different AirCores. The dashed lines represents the thermal tropopause according to
 6 the WMO definition.

7

Lindenberg 2016

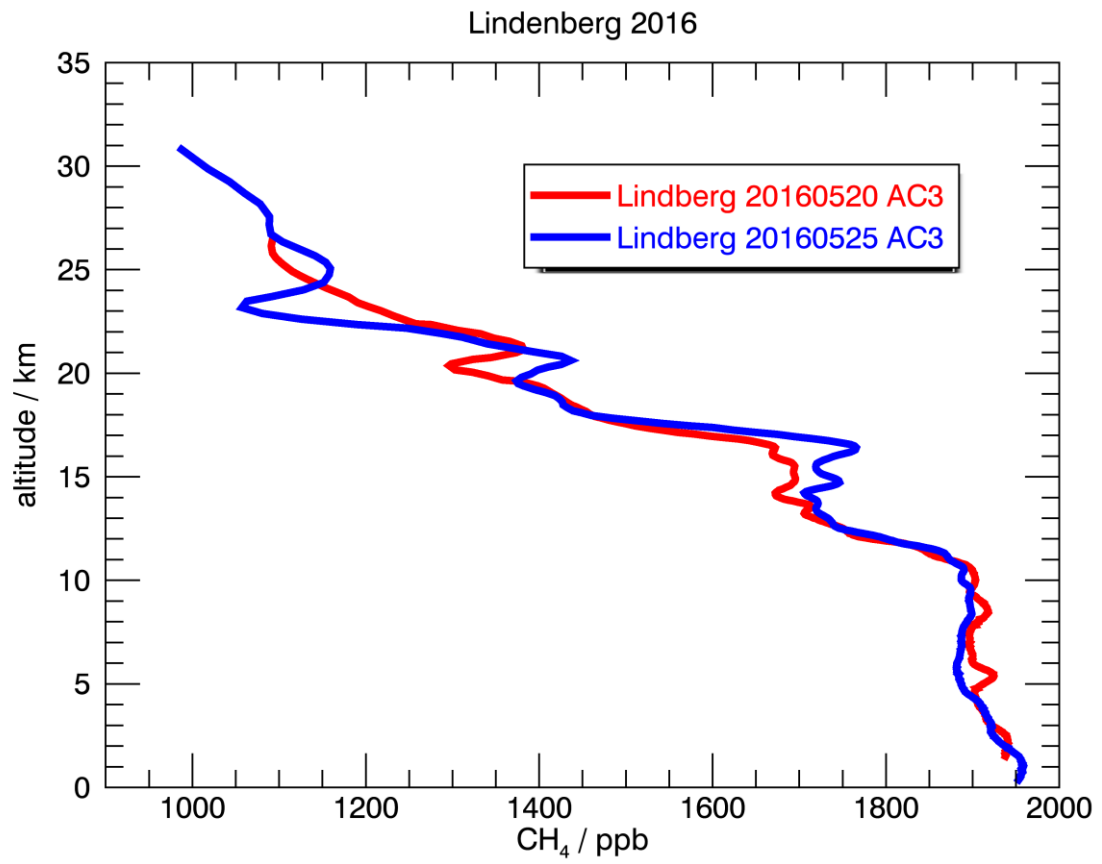


1

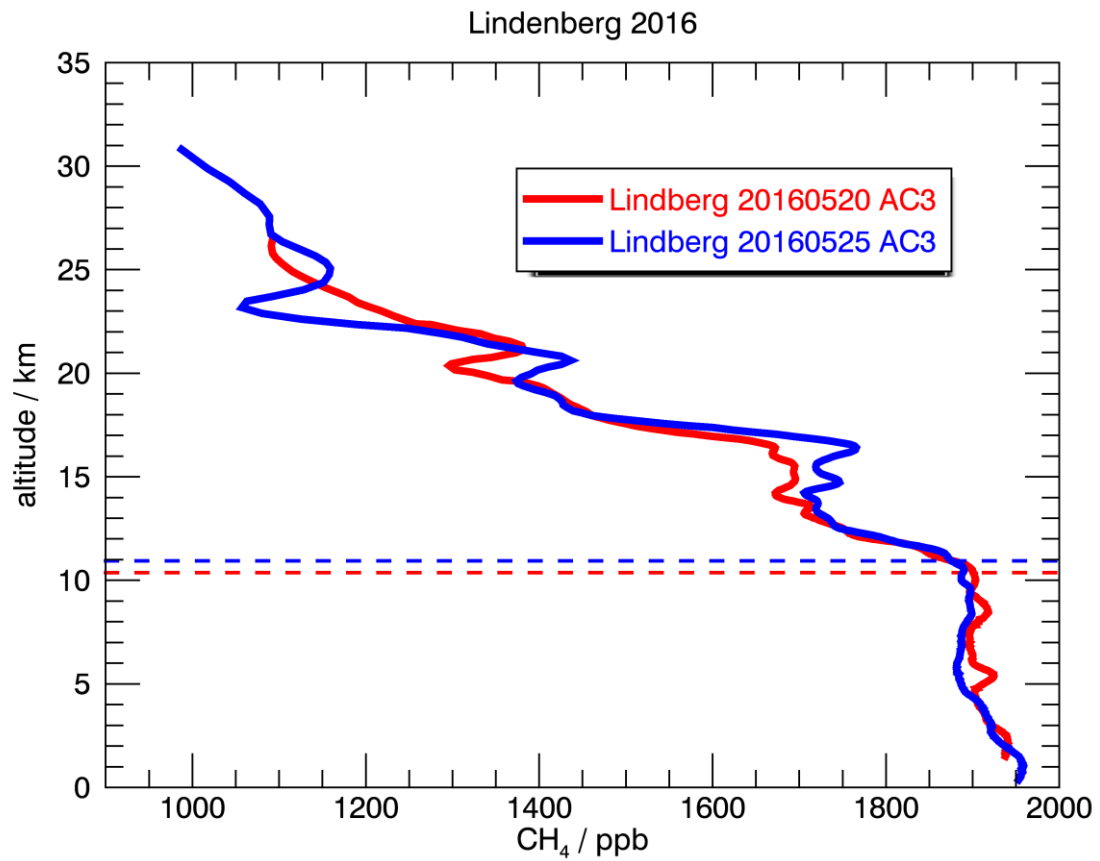


1
 2 Figure 8: Vertical profiles of CO derived for the flights on May 20 and may 25 2016 from
 3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.
 4 The dashed lines represents the thermal tropopause according to the WMO definition.

5

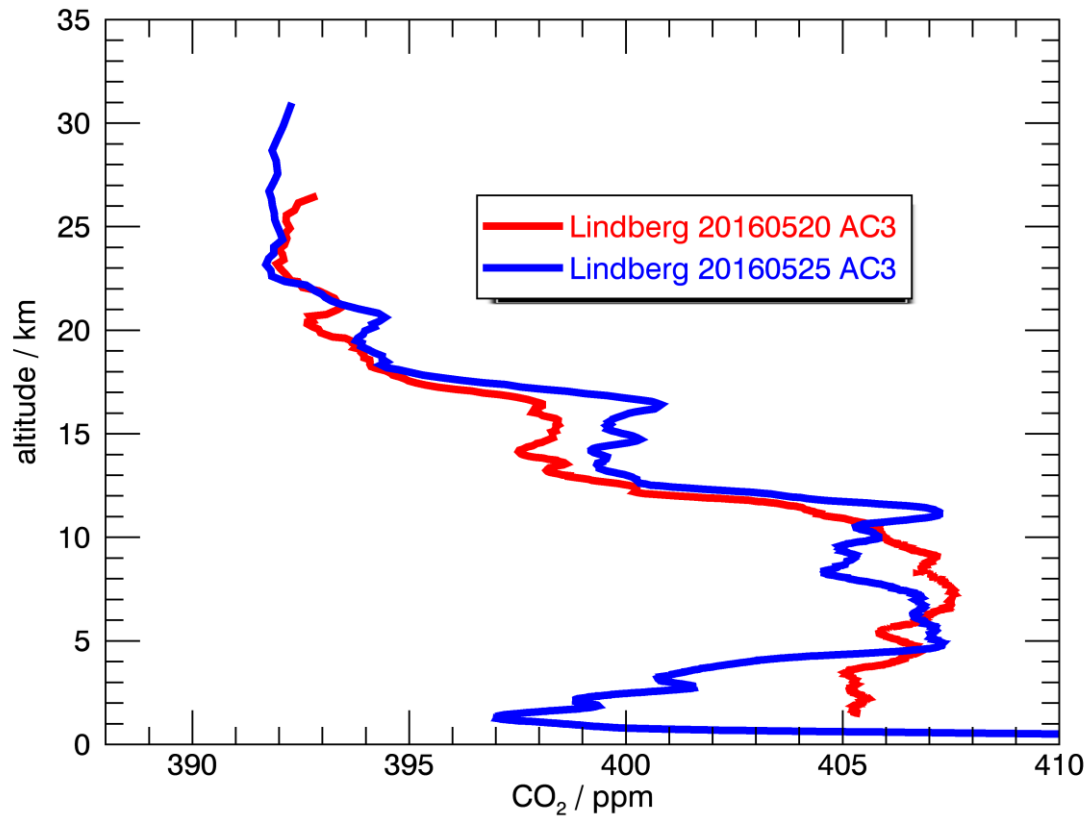


1

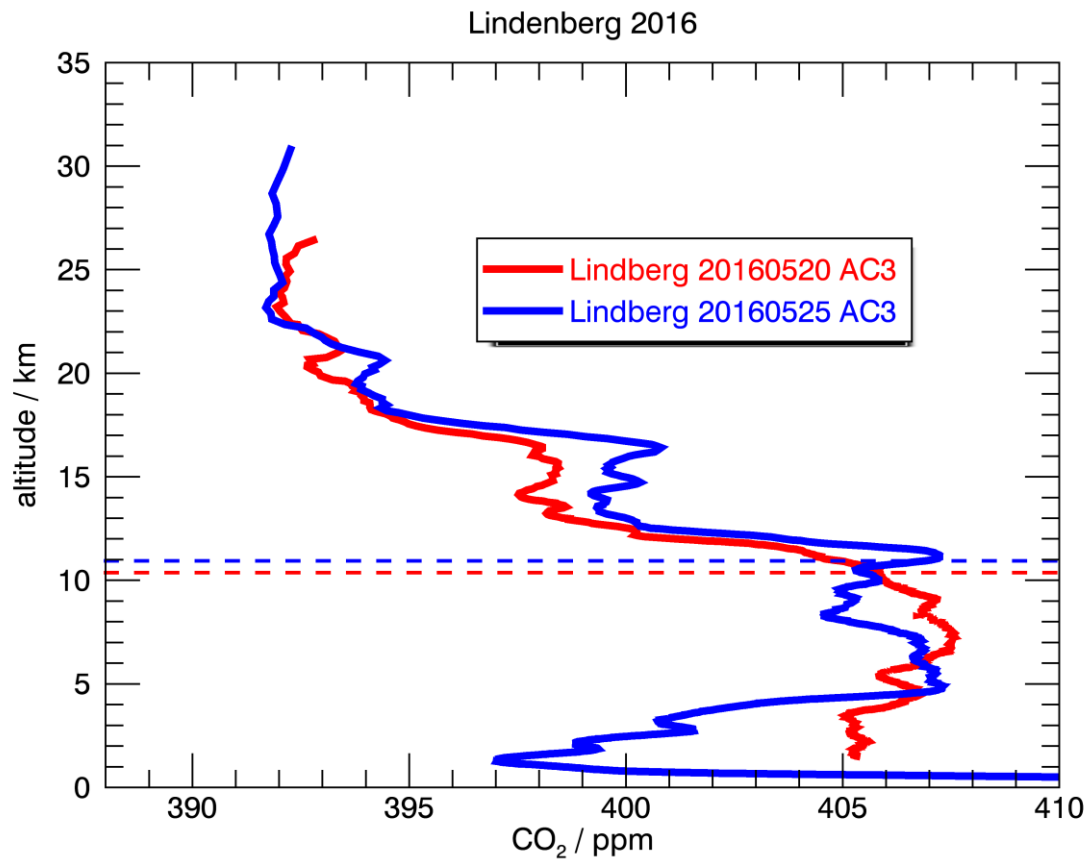


- 1
- 2 Figure 9: Vertical profiles of CH₄ derived for the flights on May 20 and May 25 2016 from
- 3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.
- 4 The dashed lines represents the thermal tropopause according to the WMO definition.

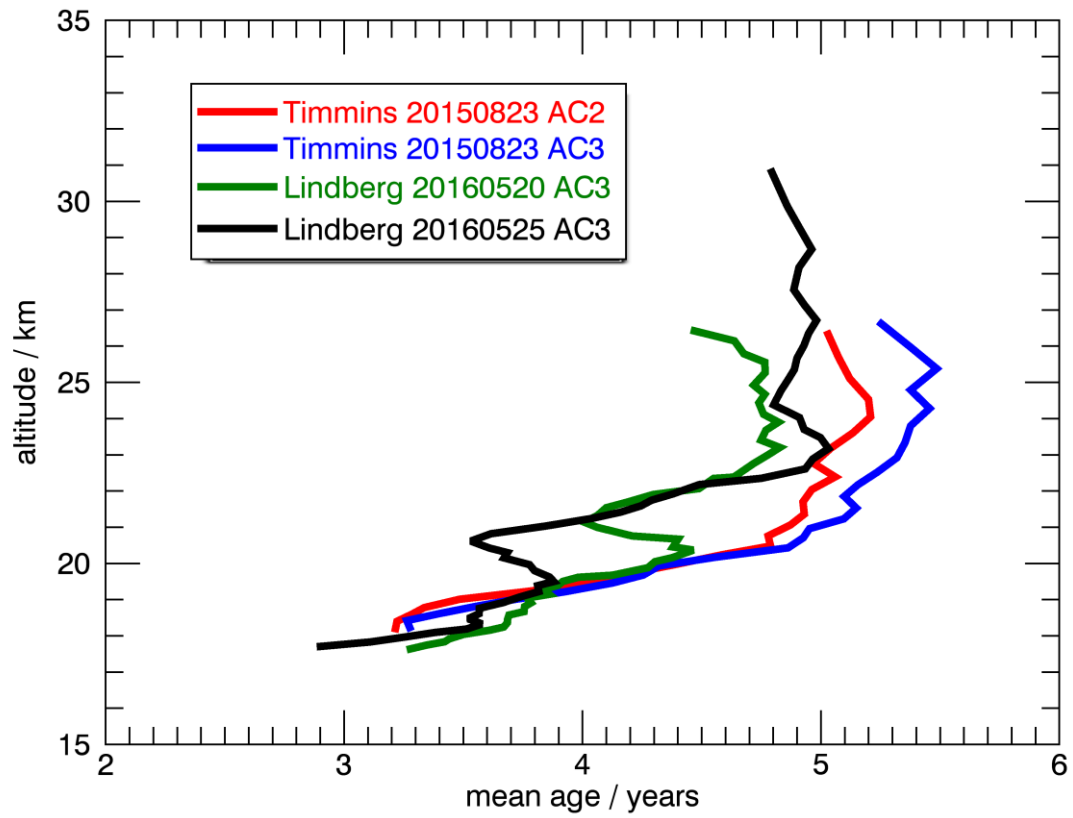
Lindenberg 2016



1

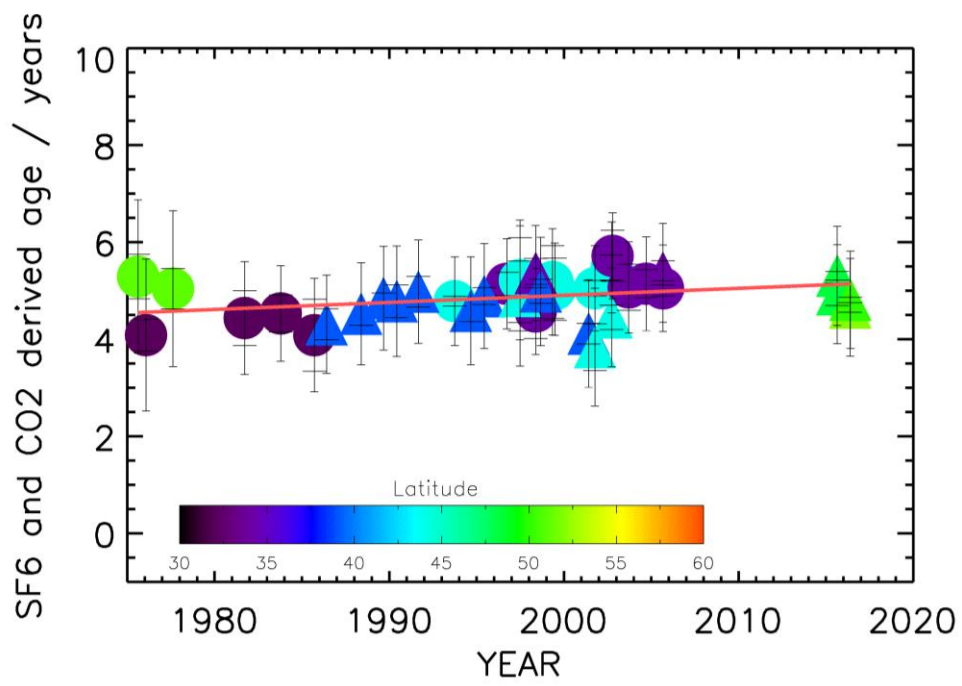


- 1
- 2 Figure 10: Vertical profiles of CO₂ derived for the flights on May 20 and may 25 2016 from
- 3 Lindenberg in Germany. The flight on May 25 reached higher altitudes due to a larger balloon.
- 4 The dashed lines represents the thermal tropopause according to the WMO definition.

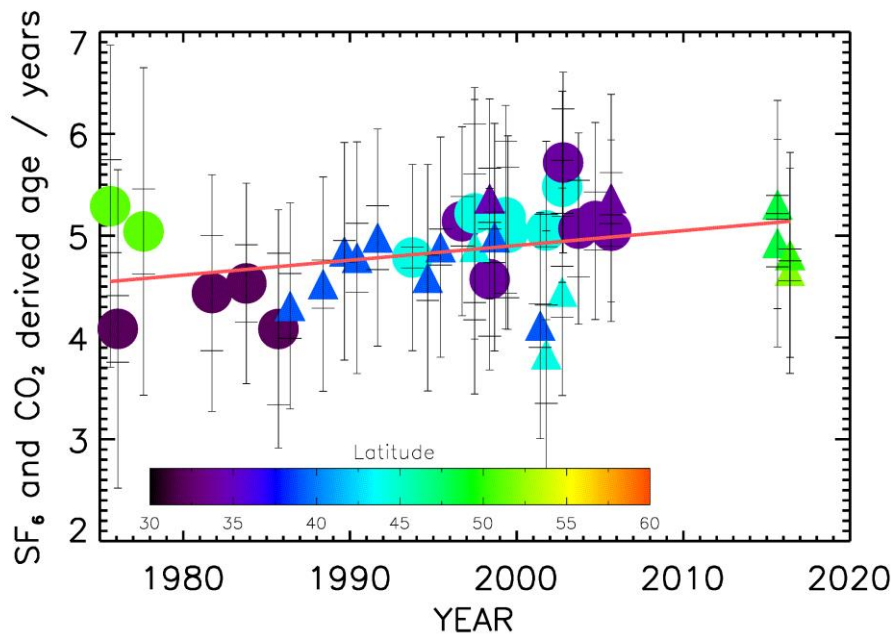


1

2 Figure 11: Vertical profiles of CO₂ derived mean age for the AirCore observations by Univer-
 3 sity Frankfurt in 2015 in Timmins, Canada and 2016 in Lindenberg, Germany.



1



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 CO₂, CH₄,
6 and N₂O, *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 CO₂: Quantitative evidence for a subtropical
10 "barrier" to horizontal transport, *J. Geophys. Res.*, *106*, 10257-10274, 2001b.
- 11 Austin, J., and Li, F.: On the relationship between the strength of the Brewer-Dobson
12 circulation and the age of stratospheric air, *Geophys. Res. Lett.*, *33*, -, Artn L17807
13 Doi 10.1029/2006gl026867, 2006.
- 14 Boenisch, H., Engel, A., Curtius, J., Birner, T., and Hoor, P.: Quantifying transport into the
15 lowermost stratosphere using simultaneous in-situ measurements of SF₆ and CO₂, *Atm. Chem.*
16 *Phys.*, *9*, 5905-5919, 2009.
- 17 Butchart, N., Scaife, A. A., Bourqui, M., de Grandpre, J., Hare, S. H. E., Kettleborough, J.,
18 Langematz, U., Manzini, E., Sassi, F., Shibata, K., Shindell, D., and Sigmond, M.:
19 Simulations of anthropogenic change in the strength of the Brewer-Dobson circulation,
20 *Climate Dynamics*, *27*, 727-741, 10.1007/s00382-006-0162-4, 2006.
- 21 Butchart, N.: The Brewer-Dobson circulation, *Reviews of Geophysics*, *52*, 157-184,
22 10.1002/2013RG000448, 2014.
- 23 Chen, H., R. Kivi, Heikkinen, P., Kers, B., Vries, M. d., Hatakka, J., Laurila, T., Sweeney, C.,
24 and Tans, P.: High-latitude balloon observations of CO₂/CH₄/CO using AirCore: evaluation
25 of Sodankylä TCCON retrievals, *Atmos. Meas. Tech.*, in preperation, 2017.

- 1 Durry, G., and Hauchecorne, A.: Evidence for long-lived polar vortex air in the mid-latitude
2 summer stratosphere from in situ laser diode CH₄ and H₂O measurements, *Atmos. Chem.*
3 *Phys.*, 5, 1467-1472, 10.5194/acp-5-1467-2005, 2005.
- 4 Engel, A., Bonisch, H., Brunner, D., Fischer, H., Franke, H., Gunther, G., Gurk, C., Hegglin,
5 M., Hoor, P., Konigstedt, R., Krebsbach, M., Maser, R., Parchatka, U., Peter, T., Schell, D.,
6 Schiller, C., Schmidt, U., Spelten, N., Szabo, T., Weers, U., Wernli, H., Wetter, T., and Wirth,
7 V.: Highly resolved observations of trace gases in the lowermost stratosphere and upper
8 troposphere from the Spurt project: an overview, *Atm. Chem. Phys.*, 6, 283-301, 2006a.
- 9 Engel, A., Mobius, T., Haase, H. P., Bonisch, H., Wetter, T., Schmidt, U., Levin, I.,
10 Reddmann, T., Oelhaf, H., Wetzel, G., Grunow, K., Huret, N., and Pirre, M.: Observation of
11 mesospheric air inside the arctic stratospheric polar vortex in early 2003, *Atm. Chem. Phys.*, 6,
12 267-282, 2006b.
- 13 Engel, A., Mobius, T., Bonisch, H., Schmidt, U., Heinz, R., Levin, I., Atlas, E., Aoki, S.,
14 Nakazawa, T., Sugawara, S., Moore, F., Hurst, D., Elkins, J., Schauffler, S., Andrews, A., and
15 Boering, K.: Age of stratospheric air unchanged within uncertainties over the past 30 years,
16 *Nature Geosci.*, 2, 28-31, 10.1038/NGEO388, 2009.
- 17 Garny, H., Birner, T., Bönisch, H., and Bunzel, F.: The effects of mixing on age of air,
18 *Journal of Geophysical Research: Atmospheres*, 119, 7015-7034, 10.1002/2013JD021417,
19 2014.
- 20 Ghysels, M., Gomez, L., Cousin, J., Tran, H., Amarouche, N., Engel, A., Levin, I., and Durry,
21 G.: Temperature dependences of air-broadening, air-narrowing and line-mixing coefficients of
22 the methane nu(3) R(6) manifold lines-Application to in-situ measurements of atmospheric
23 methane, *Journal of Quantitative Spectroscopy & Radiative Transfer*, 133, 206-216,
24 10.1016/j.jqsrt.2013.08.003, 2014.
- 25 Haenel, F. J., Stiller, G. P., von Clarmann, T., Funke, B., Eckert, E., Glatthor, N., Grabowski,
26 U., Kellmann, S., Kiefer, M., Linden, A., and Reddmann, T.: Reassessment of MIPAS age of
27 air trends and variability, *Atmos. Chem. Phys. Discuss.*, 15, 14685-14732, 10.5194/acpd-15-
28 14685-2015, 2015.

1 Hall, T. M., and Plumb, R. A.: Age as a diagnostic of stratospheric transport, *J. Geophys.*
2 *Res.*, *99*, 1059-1070, 10.1029/93jd03192, 1994.

3 Hintsa, E. J., Boering, K. A., Weinstock, E. M., Anderson, J. G., Gary, B. L., Pfister, L.,
4 Daube, B. C., Wofsy, S. C., Loewenstein, M., Podolske, J. R., Margitan, J. J., and Bui, T. P.:
5 Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of
6 H₂O, CO₂, N₂O and O₃, *Geophys. Res. Lett.*, *25*, 2655-2658, 1998.

7 Karion, A., Sweeney, C., Tans, P., and Newberger, T.: AirCore: An Innovative Atmospheric
8 Sampling System, *Journal of Atmospheric and Oceanic Technology*, *27*, 1839-1853,
9 doi:10.1175/2010JTECHA1448.1, 2010.

10 Kida, H.: General-Circulation of Air Parcels and Transport Characteristics Derived from a
11 Hemispheric Gcm .2. Very Long-Term Motions of Air Parcels in the Troposphere and
12 Stratosphere, *Journal of the Meteorological Society of Japan*, *61*, 510-523, 1983.

13 Membrive, O., Crevoisier, C., Sweeney, C., Danis, F., Hertzog, A., Engel, A., Bönisch, H.,
14 and Picon, L.: AirCore-HR: A high resolution column sampling to enhance the vertical
15 description of CH₄ and CO₂, *Atmos. Meas. Tech. Discuss.*, *2016*, 1-31, 10.5194/amt-2016-
16 236, 2016.

17 Moore, F. L., Ray, E. A., Rosenlof, K. H., Elkins, J. W., Tans, P., Karion, A., and Sweeney,
18 C.: A Cost-Effective Trace Gas Measurement Program for Long-Term Monitoring of the
19 Stratospheric Circulation, *Bulletin of the American Meteorological Society*, *95*, 147-155,
20 10.1175/bams-d-12-00153.1, 2014.

21 Müller, R., Kunz, A., Hurst, D. F., Rolf, C., Krämer, M., and Riese, M.: The need for accurate
22 long-term measurements of water vapor in the upper troposphere and lower stratosphere with
23 global coverage, *Earth's Future*, *4*, 25-32, 10.1002/2015EF000321, 2016.

24 Ploeger, F., Abalos, M., Birner, T., Konopka, P., Legras, B., Müller, R., and Riese, M.:
25 Quantifying the effects of mixing and residual circulation on trends of stratospheric mean age
26 of air, *Geophys. Res. Lett.*, *42*, 2047-2054, 10.1002/2014GL062927, 2015.

- 1 Ray, E. A., Moore, F. L., Rosenlof, K. H., Davis, S. M., Sweeney, C., Tans, P., Wang, T.,
2 Elkins, J. W., Bönisch, H., Engel, A., Sugawara, S., Nakazawa, T., and Aoki, S.: Improving
3 stratospheric transport trend analysis based on SF6 and CO2 measurements, *Journal of*
4 *Geophysical Research: Atmospheres*, *119*, 14,110-114,128, 10.1002/2014JD021802, 2014.
- 5 Rosenlof, K. H., Tuck, A. F., Kelly, K. K., Russell, J. M., and McCormick, M. P.:
6 Hemispheric asymmetries in water vapor and inferences about transport in the lower
7 stratosphere, *J. Geophys. Res.*, *102*, 13213-13234, 10.1029/97jd00873, 1997.
- 8 Schmidt, U., and Khedim, A.: Insitu measurements of carbon-dioxide in the winter arctic
9 vortex and at midlatitudes - an indicator of the age of stratospheric air, *Geophys. Res. Lett.*, *18*,
10 763-766, 10.1029/91gl00022, 1991.
- 11 Stiller, G. P., von Clarmann, T., Haenel, F., Funke, B., Glatthor, N., Grabowski, U.,
12 Kellmann, S., Kiefer, M., Linden, A., Lossow, S., and Lopez-Puertas, M.: Observed temporal
13 evolution of global mean age of stratospheric air for the 2002 to 2010 period, *Atm. Chem.*
14 *Phys.*, *12*, 3311-3331, DOI 10.5194/acp-12-3311-2012, 2012.
- 15 Toon, G. C., Blavier, J. F., Sen, B., Margitan, J. J., Webster, C. R., May, R. D., Fahey, D.,
16 Gao, R., Del Negro, L., Proffitt, M., Elkins, J., Romashkin, P. A., Hurst, D. F., Oltmans, S.,
17 Atlas, E., Schauffler, S., Flocke, F., Bui, T. P., Stimpfle, R. M., Bonne, G. P., Voss, P. B., and
18 Cohen, R. C.: Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric
19 trace gases, *Journal of Geophysical Research: Atmospheres*, *104*, 26779-26790,
20 10.1029/1999JD900379, 1999.
- 21 Waugh, D. W., and Hall, T. M.: Age of stratospheric air: Theory, observations, and models,
22 *Reviews of Geophysics*, *40*, 10.1029/2000rg000101, 2002.

23