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LISA: a lightweight stratospheric air sampler

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Abstract. We developed a new LIghtweight Stratospheric Air sampler (LISA). The LISA sampler is designed to collect four bag samples in the stratosphere during a balloon flight for CO_2, CH_4 and CO mole fraction measurements. It consists of 4 Multi-Layer Foil (MLF) sampling bags, a custom-made manifold, and a diaphragm pump, with a total weight of ~2.5 kg. A series of laboratory storage tests were performed to assess the stability of CO_2, CH_4, CO and H_2O mole fractions in both MLF and Tedlar bags. The MLF bag was chosen due to its better overall performance than the Tedlar bag for the four species CO_2, CH_4, CO and H_2O. Furthermore, we evaluated the performance of the pump under low-pressure conditions to optimise a trade-off between the vertical resolution and the sample size.

The LISA sampler was flown on the same balloon flight with an AirCore in Sodankylä, Finland (67.368°N, 26.633°E, 179 m.a.s.l.) on 26 April and 4-7 September, 2017. A total of 15 stratospheric air samples were obtained during the ascent of four flights. The sample size ranges between 800 to 180 mL for the altitude between 12 and 25 km, with the corresponding vertical resolution ranging from 0.5 to 1.5 km. The collected air samples were analysed for CO_2, CH_4 and CO mole fractions, and evaluated against AirCore retrieved profiles, showing mean differences of 0.84 ppm for CO_2, 1.8 ppb for CH_4 and 6.3 ppb for CO, respectively.

High-accuracy stratospheric measurements of greenhouse gas mole fractions are useful to validate remote sensing measurements from ground and from space, which has been primarily performed by comparison with collocated aircraft measurements (0.15 – 13 km), and more recently with AirCore observations (0 – 30 km). While AirCore is capable of achieving high-accuracy greenhouse gas mole fraction measurements, it is challenging to obtain accurate altitude registration for AirCore measurements. The LISA sampler provides a viable low-cost tool for retrieving stratospheric air samples for greenhouse gas measurements that is complementary to AirCore. Furthermore, The LISA sampler is advantageous in both the vertical resolution and the sample size to perform routine stratospheric measurements of isotopic compositions of trace gases.

Introduction

The stratosphere plays an important role in the climate of the earth, and is affected by ongoing climate change. Stratospheric changes in ozone and water vapour levels in turn affect climate and climate variability (Baldwin et al., 2007). Sampling

stratospheric air up to 35 km can currently only be achieved on balloon-borne platforms. The cryogenic sampling method (Lueb et al., 1975) is the most employed technique. As outlined in Fabian, 1981, cryogenic sampling overcomes the problem of small samples that are obtained from the grab sampling technique. Typically, cryogenic samplers retrieve ~15 samples of 10 to 20 litre at STP (Standard Temperature and Pressure) (Fabian, 1981; Honda, 2004; Lueb et al., 1975) with a sufficiently good vertical resolution of ~1 km (Schmidt et al., 1987). The downside of these samplers is their heavy weight (100-250 kg), which requires sophisticated planning and significant resources for a single launch. As a result of the intensive operation, stratospheric observations have been sparsely made both in time and space. Existing sampling is mainly restricted to the Northern Hemisphere mid-latitudes and polar regions, with the tropics under-sampled. Recently, a simplified cryogenic sampler capable of retrieving one sample per flight (22 kg) using liquid neon (Morimoto et al., 2009) was developed, and was launched from a research vessel to retrieve stratospheric air samples in the tropics (Fuke et al., 2014).

Nevertheless, a significant number of stratospheric air samples have been collected with remarkable scientific efforts. Several campaigns have been performed and corresponding results have been used in many studies of the stratospheric chemistry and physics. Laube et al., 2010, presented several profiles of halocarbons, relevant to stratospheric ozone depletion and the mean age of air. The mean age of air, a good tracer for atmospheric transport time scales, was also assessed based on SF_6 and CO_2 measurements performed on cryogenically retrieved samples (Engel, 2002). Long-term monitoring of CO_2, CH_4, N_2O and various halocarbons and isotopic analysis of CO_2, CH_4, N_2O have been performed annually for more than a decade (Aoki et al., 2003; Nakazawa et al., 1995, 2002). The stratospheric distribution of methane and its stable isotopes have been performed in order to understand the stratospheric methane sink (Rice, 2003; Röckmann et al., 2011; Sugawara et al., 1997). The stratospheric distribution of N_2O and their position dependent isotopic compositions were determined (Kaiser et al., 2006) and were subsequently used to validate transport models. Engel et al., 2006, reported the observed mesospheric air in polar vortex, improving our understanding of transport in the middle atmosphere. Moreover, these campaigns are essential to validation and comparison of satellite retrievals (e.g. Engel et al., 2016; Stiller et al., 2007).

Trace gas distributions provide a useful tool to obtain an insight in transport properties and chemistry of the stratosphere. (Brenninkmeijer et al., 1995) studied the correlation of CO_2, CH_4 and CO mole fractions and their isotopic composition measurements, and found a high correlation between mole fractions and isotopic compositions. It was shown that the ^{13}C and ^{2}H isotopic composition of stratospheric CH_4 is strongly correlated with its mole fractions (Röckmann et al., 2011) and similar findings were presented for N_2O (Kaiser et al., 2006). A theoretical explanation to the tracer-tracer relations due to rapid mixing of air along isentropic surfaces in the stratosphere was presented by (Plumb, 2007).

Stratospheric tracer observations are essential for validation of General Circulation Models (GCM's). The stratospheric meridional overturning, or the Brewer-Dobson circulation (BDC) was predicted to increase in strength from modelling studies (Butchart, 2014). The mean age of stratospheric air samples was shown to be a good diagnostic for the strength of the BDC

and detected no significant change in the strength of the BDC (Engel et al., 2009, 2017). In spite of all the efforts to make observations of stratospheric tracers, GCM's remain poorly constrained, a problem already pointed out several decades ago (Ehhalt et al., 1983).

Recently, AirCore has been shown to be a viable method for profile measurements of greenhouse gases (Engel et al., 2017; Karion et al., 2010; Membrive et al., 2017). AirCore is much lighter (2 – 9 kg) compared to the cryogenic sampler, and can be launched on weather balloons. The launch of AirCore is also much simpler than the operation of large-payload cryogenic samplers. Being a passive sampling technique, AirCore does not provide large sample amount from the stratosphere. This is problematic for accurate analysis of isotopic compositions or multiple tracers. Sub-sampling of the stratospheric part of the AirCore samples has been used for measurements of $\Delta^{17}O$ in CO_2 (Mrozek et al., 2016) and radiocarbon analysis (Paul et al., 2016). The samples have small sample size, which limits the analytical precision of their analyses. Besides this, the vertical resolution of the samples was low and the altitude registration of these samples was associated with significant uncertainties.

In this work, we present the deployment and field-tests of a new Lightweight Stratospheric Air sampler (LISA). The design of the LISA sampler is described in Section 2. With the LISA sampler, we aim to achieve reasonable accuracy of GHG measurements, which does not necessarily meet the WMO recommended compatibility goals of 0.1 ppm, 2 ppb, 2 ppb for CO_2, CH_4 and CO, respectively, but would be sufficient, e.g. to detect the large vertical gradient of CH_4 in the stratosphere. Besides this, we intend to obtain significantly larger amount of air samples from the LISA sampler than from the AirCore sub-sampler. The accuracy of the CO_2, CH_4 and CO mole fraction measurements of the LISA samples is assessed by the sample storage test that is detailed in Section 3. The vertical resolution and sample amount are both a function of sampling time, and are therefore discussed together in Section 4. Following the development of the sampler, we present the deployment of the sampler in the field and the comparison of the CO_2, CH_4 and CO mole fraction measurements between the LISA sampler and AirCore in Section 5. Finally, we give discussion and conclusions in Section 6 & 7.

2 LISA sampler design and operation

We design the sampler to collect stratospheric air samples during a weather-balloon flight, where the balloon typically bursts at ~ 30 km altitude. The total payload of a weather balloon is usually a few kilograms. Therefore, the sampler needs to be lightweight. To achieve this, we have used bags to contain air samples instead of glass or metal flasks that are commonly used for accurate trace gas measurements, and a diaphragm pump instead of previous cryogenic coolers to pump air. Besides these, a datalogger is used to make the system fully automatic during flight. The payload is housed in a Styrofoam package for thermal insulation and to prevent it from damage during landing. Previously the use of a gas pump and Tedlar bags have been successfully used to sample air from a UAV for methane studies (Greatwood et al., 2017).

Fig. 1 shows the schematic diagram of the sampler. The system consists of a diaphragm pump (KNF, product no. NMP 850.1.2 KNDC B) and four Supel Inert Multi-Layer Foil (MLF) bags (Supelco, product no. 30227-U). The pump has a flow capacity of 8 l/min at STP. Each bag is equipped with a screw cap combo valve that requires a 180-degree turn to be opened or closed. A servomotor (Hitec, product no. HS-65HB+) operates the valve. The pump and bags are connected to a custom-made manifold, which is made from 5 nylon Tees (Swagelok, product no. NY-400-3) connected by Kynar tubing (Cole Palmer, product no. EW-95100-00). A fifth screw cap combo valve is placed at the outflow end as the outlet valve, allowing the manifold to be flushed prior to sampling. The pressure inside the manifold is continuously monitored by a pressure sensor (Honeywell HSCMAND015PASA5). A datalogger (Arduino Mega 2560) operates all the electronics during flight, and logs ambient atmospheric pressure and temperature data, as well as the pressure inside the manifold and temperature within the Styrofoam package. The pump requires 24 volts during operation. The power is therefore supplied by eight 3 V lithium ion batteries (CR123A) connected in series. The Arduino is powered by three batteries out of the eight (9 V). The same applies to the servo motor, powered with 2 batteries (6 V). The sampler is placed in a Styrofoam package, with a total weight of ~ 1 kg excluding the package, and ~2.5 kg including the package.

Because the ascent rate is usually much slower than the descent rate, we take air samples during ascent to optimise the vertical resolution (see Section 4). The sampling process is triggered by starting the pump when the sampler reaches preset ambient pressure levels monitored by the on-board pressure sensor. In practice, when the preset pressure value is reached during ascent, the pump is started, with the outlet valve open and the other valves upstream of the bags closed, to flush the manifold. After 20 seconds, the outlet valve is closed, and the valve upstream of one of the chosen bags is simultaneously opened to allow sampling. The sampling of air into one bag is completed when a preset maximum sampling time is exceeded or the absolute pressure in the manifold is higher than 280 hPa (see Section 4), whichever comes first. The sampling process continues until all four bags are filled. At a certain altitude, the balloon will burst and the sampler falls back to the ground where the samples can be picked up and brought back to the laboratory for analysis.

3 Sample storage tests

The stability of trace gases in the sample container is essential for a sampler to obtain accurate measurements of the trace gases. To this end, we have investigated the stability of CO_2, CH_4, CO and H_2O mole fractions of dry air samples in two types of gas sampling bags: Tedlar and Supel Inert Multi-Layer Foil (MLF). The Tedlar bag is composed of a thin polyvinylfluoride film. The MLF bag consists of several layers: polyethylene (inner layer), aluminum foil, polyethylene, aluminum (metalized) and 60-gauge nylon, which provide a moisture barrier and light protection.

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3.1 Experiments

A total of 7 MLF and 7 Tedlar bags were prepared, with dry air from a cylinder; the mole fractions of CO_2, CH_4 and CO are listed in Table 1. Since the mole fractions of methane are significantly lower in the stratosphere than a typical value of around 2000 ppb in the free troposphere (e.g. Rice et al. 2003; Röckmann et al. 2011), we prepared two samples (nos. 6&7) with low mole fractions (~120 ppm CO_2, ~600 ppb CH_4 and ~75 ppb CO) by diluting air from a cylinder with nitrogen. The CO mole fractions in the stratosphere are also low, but we did not make any storage test for samples with a mole fraction lower than ~75 ppb.

Directly after sample preparation, the air sample is analysed for CO_2, CH_4, CO and H_2O mole fractions on a cavity ring-down spectrometer (CRDS, Picarro Inc., model G2401-m). During an actual balloon flight, it usually takes 3 – 5 hours from sampling until the samples are retrieved and brought back to the laboratory for analysis. Therefore, we have chosen a period of 4 hours as the storage time to represent this time delay, i.e. the bags are stored under laboratory conditions (~ 20°C, ~1000 hPa, ambient mole fractions of CO_2, CH_4, CO and H_2O) for four hours before they are analysed again. The four-hour drift during storage is defined as the difference between the measurement after four hours of storage and the initial measurement: $[X]_{4hours} - [X]_{direct}$, where [X] is the measured mole fraction.

Previous studies show that the material of Tedlar bags is prone to water vapour diffusion (Beghi and Guillot, 2006; Cariou and Guillot, 2006), which leads to humidified air samples after four hours of storage. The CO_2, CH_4 and CO dry mole fractions are obtained by applying the water vapour corrections described in Chen et al., 2013 and Rella et al., 2013.

3.2 The storage test results

The difference between the measured mole fractions after 4 hours and those measured immediately after filling are shown in Fig. 2, which captures the drift over 4 hours of storage. The drift in CO_2 after 4 hours is comparable for both types of sampling bags for sample nos. 1-5, within a range of -0.2 – 0.2 ppm (Fig. 2a). Low mole fractions of CO_2, i.e. samples nos. 6&7, are less stable in both types of sampling bags; however, these low mole fractions are not observed in the stratosphere, and hence the drift observed for samples nos. 1-5 is more representative than that observed for samples nos. 6&7 for the storage of stratospheric air samples. The CH_4 mole fractions are preserved within the range of ± 2 ppb for all cases for both types of sampling bags (Fig. 2b). Although the Tedlar bags perform slightly better than the MLF bags, both are satisfactory for CH_4 measurements when considering its large gradient in the stratosphere (500-2000 ppb e.g. (Röckmann et al., 2011)).

The CO mole fractions appear to be stable in the MLF bags, with no clear indication of drift, independent of the mole fractions (Fig. 2c). The variability of CO differences may be in large part due to the repeatability of the CRDS analyser (1σ 7 ppb). In contrast, the CO mole fractions decrease in the Tedlar bags, coupled with a significant increase of water vapour mole fractions

of up to ~1% (Fig. 2d), which is due to the high permeability of the bag material to water vapour and has been observed in previous studies (Beghi and Guillot, 2006; Cariou and Guillot, 2006). The increase of water vapour mole fractions in the MLF bags is only up to 0.01%. The observed decrease of CO mole fractions in the Tedlar bags, even when its mole fractions are lower than the ambient, cannot be explained by the permeability of the bag material, as diffusion would increase the CO mole fractions. Although mole fractions are corrected for water vapour to obtain dry mole fractions, we cannot exclude that there is still some remaining bias from the water vapour correction function, and this correction function was not tested before with low mole fractions. This would not affect the depicted results for the MLF bags since the water vapour content remains low. Further investigation is needed before Tedlar bags are used to collect samples for analysis of high-precision CO mole fractions at the ambient level.

We found out that it is necessary to precondition the MLF bags before use, because we observed an offset of ~12 ppm CO2, ~8 ppb CH4 and ~30 ppb CO between the immediately analysed results of un-preconditioned MLF bag samples after filling and the assigned cylinder values. This contamination issue could be overcome by preconditioning the bags with N_2.

Based on the storage test results, we choose to use the MLF bags for our sampler. The stability of CO_2 and CH_4 mole fractions in both MLF and Tedlar bags is comparable; however, the observed CO mole fractions in Tedlar bags is less stable than those in MLF bags. In addition, the permeability of water vapour to Tedlar bags causes a significant increase of water vapour, which may affect isotopic compositions, e.g. $\delta^{18}O$ in CO_2. Moreover, the aluminium layers of the MLF bag protect the air samples against radiation that could affect the stability of CO mole fractions. We emphasise the importance of preconditioning the MLF bags before use.

3.3 The uncertainty of the LISA sample measurements

We estimate the measurement uncertainty based on the laboratory storage test results and the uncertainties associated with the sample analysis. The total uncertainty of CO_2, CH_4 and CO mole fraction measurements consists of 3 terms: sampling error, drift due to storage and analysis uncertainty. We do not include any sampling error in the presented evaluation, although it might be significant for high-precision measurements, especially for CO in the stratosphere when the ozone concentration is high. The main factor likely to affect mole fraction measurements of the stratospheric air samples is the drift in the sampling bags, an effect that has been quantified in Section 3.1 & 3.2. In principle, one could correct for the drift as a systematic error. However, detailed information about storage conditions are required to correct for the drift, which is usually unavailable in the field. Therefore, we have not made any correction for the drift, but rather use the maximum observed drift as an estimate of the drift uncertainty, σ_d. The maximum observed drift in these tests were 0.11 ppm, 2 ppb and 2.7 ppb for CO_2, CH_4 and CO, respectively. There are two contributions to the analysis uncertainty: 1) analyser precision (σ_i) and 2) calibration uncertainty (σ_c). Assuming Gaussian error propagation, we compute a total uncertainty on the measurements:

$$\sigma_s = \sqrt{\sigma_d^2 + \sigma_i^2 + \sigma_c^2} \quad (1)$$

The total uncertainty includes the analyser precision (1 sigma 0.04 ppm, 0.2 ppb and 7 ppb for CO_2, CH_4 and CO, respectively), the calibration uncertainty (0.07 ppm, 1 ppb, 2 ppb for CO_2, CH_4 and CO, respectively), and the aforementioned drift. We compute the total uncertainty of the LISA sample measurements to be 0.14 ppm, 2.2 ppb and 7.8 ppb for CO_2, CH_4 and CO, respectively.

4 The vertical resolution and the pump performance

The vertical resolution of each individual air sample depends on the vertical speed of the sampler during flight, and the effective sampling time, i.e. when the flow rate into the sampling bag is positive. On the other hand, the amount of air samples collected into each sampling bag is determined by the sampling time and the sampling flow rate. Due to the trade-off between the vertical resolution and the sample size, we evaluate the pump performance to assist the choice of the sampling time.

Under laboratory conditions the KNF pump can maintain a flow rate of up to 8 l/min at STP. The performance of the small diaphragm pump is to our best knowledge not previously investigated under the atmospheric conditions in the stratosphere, e.g. at low-temperature and low-pressure conditions.

We evaluated the sampling performance using a simplified version of the sampler under simulated conditions in the laboratory. The test version of the sampler consisted of the KNF pump, the outlet valve and one sampling bag, supported by the required electronics (pressure and temperature sensors, a datalogger and batteries). The test version was placed in a 50-litre vessel for testing. The pressure inside the vessel was regulated by a vacuum pump, mimicking the atmospheric pressure levels in the stratosphere. After a desired pressure level was reached, the vacuum pump was switched off, and the sampler sampled air for 153 seconds. The experiment was repeated at 3 different pressure levels. Using the manifold pressure and temperature data within the vessel, logged at 3 Hz, we calculate the sampled air volume at STP using the ideal gas law as a function of sampling time.

The pressure readings are initially constant, while the bag is expanding to its full size of 2.58 litres. Afterwards, the pressure starts to increase when air is compressed. We assume that the bag has expanded to its full size when the pressure starts to increase. Furthermore, the results allowed us to create a simple empirical model to calculate the sampled air volume as a function of sampling time at all pressure levels. It provides a useful tool to quickly estimate the expected sample size and vertical resolution during field campaigns.

Fig. 3a shows the sampled air volume at STP as a function of the sampling time in seconds, for three different pressure levels (31.5 hPa, 60.8 hPa and 117.7 hPa) in the vessel. The volume is calculated with the ideal gas law, using the logged manifold pressure and temperature. The volume of the bag is estimated to be 2.58 litres. The 3 Hz pressure data was averaged into 5 s bins, to reduce the random noise of the pressure measurements and to smooth the pressure wave induced by the stroke of the pump. The sampled air volume increases linearly with the sampling time when the bag expands to its full size during the first 19.7 seconds. Afterwards, the increase rate slows down due to reduced flow rates that result from the increasing pressure difference across the pump. The gain in sampled air volume within equal sampling time thus becomes less at longer sampling time.

Furthermore, we show the sampled air volume as a function of the vessel pressure in Fig. 3b. Here the sampling times of 50, 100 and 150 seconds are arbitrarily chosen. For each sampling time, the sampled air volume is interpolated from the data shown in Fig. 3a and appears to be linear to the chamber pressure. Hence, we fit the following linear equation to the derived data in Fig. 3b,

$$V_{stp} = a(t)p_a, \quad (2)$$

Where p_a (in hPa) is the ambient pressure in the vessel, V_{stp} is the sample amount in litre at STP and a is a function of the sampling time (L/hPa). We performed a series of linear fits for the sampling time ranging from 0 to 150 seconds at an interval of 10 seconds, and derived corresponding linear coefficients a as a function of sampling time (see Fig. 3c). To model V_{stp} as a function of pressure p_a and sampling time t, the linear coefficient $a(t)$ in Eq. (2) is empirically modelled using the following function:

$$a(t) = x - b * e^{-(t-t_0)/\tau}, \quad (3)$$

where t is sampling time and x, b and τ are constant parameters used for the fit. t_0=19.7 seconds is the time required to fill the bag up to chamber pressure, and the model is only valid for t>19.7 seconds. Eq. (3) is fitted using the non-linear least squares method to obtain an empirical model for the slope $a(t)$ in Eq. (2), and the fitted parameters are presented in Table 2.

Combining Eq. (1) and Eq. (2), the sampled volume at STP can be modelled for all pressure levels ranging from 200 to 0 hPa for any chosen sampling time. The derived sample volume is shown as a function of ambient pressure or altitude in Fig. 3d for the sampling time of 50, 100, 200 and 1000 seconds, respectively. The International Standard Atmosphere is used to link ambient pressure and altitude. The gain in the sample size from 200 to 1000 seconds of sampling is very small due to the saturation of the pumping capacity; however, the vertical resolution would on the other hand be compromised severely. Assuming an ascent speed of the balloon of 5 m s^{-1}, the corresponding vertical resolutions would be 1 km and 5 km for the sampling time of 200 s and 1000 s, respectively.

An upper limit to the amount of air samples in the MLF bag was found due to its sealing capacity. The bag's seal was observed to break when a differential pressure of ~300 hPa between the inside and the outside of the bag is reached. The maximum allowed pressure serves as a practical limit to the sample size that can be achieved, which is presented in Fig. 3b with a horizontal line, and in Fig. 3d with a vertical line. During flight, the payload is usually lifted up to ~30 km (~10 hPa), which means the pressure inside the MLF bag can be at maximum ~310 hPa. To be on the safe side, we set the maximum absolute pressure in the MLF bag during flight not higher than 280 hPa to avoid any potential loss of sample due to the burst of the bag.

The model provides a good tool to design the sampling strategy in the field. It should be noted that the simplification of the model causes uncertainties in the estimated sample size. On one hand, this model does not take the temperature in the real conditions into account. Since air in the stratosphere is usually cold e.g. 240 K, the total sampled volume at STP would be larger than the modelled, due to thermal expansion. On the other hand, the model assumes a constant upstream pressure, whereas the upstream pressure decreases during flight, and hence the total sampled volume at STP would be then smaller than the modelled.

5 Flights and validation

Following the laboratory experiments described above, we deployed the sampler in the field. A total of 4 flights were performed in Sodankylä, Finland (67.368°N, 26.633°E, 179 m.a.s.l.) at the Finnish Meteorological Institute's (FMI) Total Carbon Column Observing Network (TCCON) facility (Kivi and Heikkinen, 2016). The facility includes a high-resolution Fourier Transform Spectrometer installation to retrieve column-averaged abundances of atmospheric constituents, gas analysers for in situ measurements and both manual and automatic radiosonde systems. The flights were performed on four different days, on 26 April, 4–6 September, 2017, respectively. We aimed to collect four air samples during each flight at four preset pressure altitudes. The settings of the sampling parameters are summarized in Table 3. The sampling parameters varied from flight to flight, to test the capabilities of the sampler.

The payload consisted of an AirCore (H. Chen in prep), LISA Sampler, a payload positioning system that uses both Iridium and GPS/GSM positioning, a lightweight transponder and a Vaisala RS92-SGP radiosonde (Dirksen et al., 2014).This configuration allowed for a direct comparison between AirCore and sampler measurements. The LISA sampler package weighed 2.8 kg. The samples were analysed in the field for CO_2, CH_4 and CO mole fractions using the same CRDS analyser as used in our laboratory, whereas the AirCore sample analysis was done on a second CRDS analyser for CO_2, CH_4 and CO mole fractions. Two different sets of calibration gases were used for the AirCore and the sampler sample analysis. Although both sets of calibration gases are ultimately on the same scales (CO_2: X2007, CH_4: X2004A and CO: X2014A), we cross checked the calibration gases on one CRDS analyser to eliminate any difference that may exist between the two sets of calibration gases.

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During the flights, temperature, air pressure and pressure in the manifold were logged with a frequency of 0.8 Hz. The temperature was measured near the batteries and pump, for diagnostic purposes. Ambient atmospheric temperature was measured with the radiosonde. The logged pressure and radiosonde temperature data allowed us to quantify the sample size (Section 5.2) and to calculate the pressure weighted mean altitude of the samples (Section 5.1). The altitude provided by the radiosonde is used for calculation of the vertical resolution of the samples (Section 5.2).

Fifteen samples were successfully obtained from four flights. During the first flight on 26 April 2017, only time and the start and end time of sampling were logged due to a malfunction in the datalogger. As the time stamp of the datalogger is reported in UTC, we are able to sync the sampling information from the datalogger with atmospheric measurements of temperature, pressure and altitude from the radiosonde on the same payload. This is subsequently used to estimate the vertical resolution and the sample size using the empirical derived function in Section 4. During the same flight, the AirCore datalogger failed to record any data (e.g. coil temperature, valve closing time), and the temperature data from a flight performed two days earlier, on 24 April 2017, has been used to retrieve the AirCore profiles. The detailed information is provided in Chen et al, in prep. During the flight on 4 September 2017, the sampler was unsuccessful to take a sample at the 200 hPa pressure level, because the maximum allowed pressure in the manifold was reached during the short time between the closure of the outlet valve and opening of the sampling bag. Reversing the order of closure of the outlet valve and opening of the sampling bag fixes this problem.

5.1 The weighted mean sampling pressure of the samples

During sampling of each bag, the atmospheric pressure decreases as the payload ascends, and the volume flow rate drops due to a nonlinear increase of pressure in the bag. Therefore, not all atmospheric pressure levels contribute equally to the collected sample in size or mole fractions of trace gases. The integrated sample thus has an associated pressure weighted mean altitude. The contribution of each pressure level to one sample is proportional to the number of moles of air sampled at that pressure level. In general, the first 19.7 seconds of sampling contribute the most and the end of sampling contributes the least to the collected sample. When pressure and temperature within the manifold are measured, the number of moles of air at each pressure level can be computed directly, and the weight of that pressure level will be:

$$w_i = \frac{dn_i}{n}, \tag{4}$$

where dn_i is the number of moles of air sampled at the pressure level p_i, n is the total number of moles of collected air samples. w_i is then the weight of the air samples collected at the pressure level p_i. The altitude weighted mean $\bar{p}$ can be calculated as follows:

$$\bar{P} = \sum_i w_i P_i, \tag{5}$$

The first 19.7 seconds of sampling cannot be calculated directly, since $dp_i = 0$, i.e. no compression and the pressure inside the bag is the same as outside. We assign the first weight that can be calculated to the first 19.7 seconds of sampling.

The temperature of the air samples in the bag was not directly measured. For the calculation of the weighted mean sampling pressure of the samples, we assume constant temperature of the sampled air while sampling. In reality, the temperature of the air samples in the bag would be close to the ambient temperature as the bag is directly exposed to the ambient. Since the observed variability of the ambient temperature during sampling is usually less than 1 Kelvin (1 sigma), the assumption of constant temperature during sampling causes insignificant uncertainty on the weighted mean sampling pressure.

5.2 Vertical resolution and sample size

As the volume of the collected air samples decreases with altitude (Fig. 4a), the vertical resolution increases (Fig. 4b). The sample size achieved by the sampler is close to that estimated based on the empirical model shown in Section 4. The variability of the collected sample size can be mostly explained by the different settings for the sampling time and the maximum allowed pressure during different flights (see Table 3). Furthermore, the cold temperatures in the stratosphere result in denser air, so the observed sample size are slightly higher, especially in the lower stratosphere. The variability in the vertical resolution is the result of three factors: 1) varying sampling time; 2) varying ascending speed; 3) varying maximum allowed pressure. The ascending speed was typically around 7-9 m s^{-1} in the lower stratosphere, and decreased to 4-5 m s^{-1} in the middle stratosphere. In the lower stratosphere (10 to 15) km the maximum allowed pressure inside the bags was usually reached in a period shorter than the preset sampling time, leading to relatively high vertical resolution. In the middle stratosphere, the sampling time was usually the limiting factor to vertical resolution.

While the sampler was still collecting the last sample during the flight on 6 September 2017, the balloon burst at a lower altitude (21.4 km) than previous flights. The vertical resolution of that particular sample was estimated to be 3.1 km (not shown), a number much larger than that of other samples due to the fast descending speed of 16.8 m s^{-1} after burst.

5.3 Comparison with AirCore measurements

The vertical profiles of CO_2, CH_4 and CO mole fractions from both AirCore and LISA measurements are presented in Fig. 5. For the retrieval of the AirCore profiles we refer to (Chen et al. in prep). AirCore and LISA measurements are compared based on the same pressure level. For a fair comparison, we average the AirCore profiles with the same weights that are used to calculate the weighted mean sampling pressure of the samples. The mean differences between AirCore and LISA measurements of CO_2, CH_4 and CO mole fractions are summarized in Table 4.

A relatively large difference in the CO_2 mole fractions (>1 ppm) between LISA and AirCore is clearly visible for the flight on 26 April 2017. The observed difference is much larger than the uncertainty caused by the drift of CO_2 mole fractions due to

storage in the MLF bag (shown in Fig. 2a), and cannot be explained by any known reasons. The differences of the CO_2 mole fractions for other flights are significantly smaller. The summertime stratosphere is only affected by weak diabatic stirring (Holton et al., 1995; Plumb, 2002, 2007), and can be considered relatively stable. Therefore, the flights on 4 - 6 September 2017 can be, to a large extent, considered duplicate measurements. This is supported by the excellent agreement between the AirCore profiles of CO_2 and CH_4 mole fractions during those dates. The AirCore datalogger failure on 26 April 2017 may cause increased uncertainty in the altitude registration of the AirCore measurements, whereas the malfunction of the LISA datalogger during the same flight may cause increased uncertainty in the weighted mean sampling pressure of the samples. Therefore, we also calculated the mean differences excluding the flight on 26 April 2017, which decreases the mean difference in CO_2, but slightly increases the difference in CO.

CO mole fractions agree well during all flights, except that a small decrease with altitude was observed by LISA measurements in September 2017, but not captured by AirCore measurements. A good agreement between AirCore and LISA CO measurements is found for the flight on 26 April 2017. Besides this, an interesting CO plume at 13.5 km is observed by both AirCore and LISA during the flight on 5 September 2017.

6 Discussion

6.1 LISA sampler comparison with AirCore measurements

The deviation between AirCore and sampler results are on average 0.5 ppm or 0.13 % for CO_2, a result that is comparable in magnitude to AirCore inter comparisons, (e.g. Engel et al., 2017; Membrive et al., 2017). For methane, we find a deviation of 5 ppb, or 0.33 %. However, the altitude registration of AirCore measurements is associated with uncertainties, as outlined by (Membrive et al., 2017), especially due to the manual selection of the start and the end of AirCore sample analysis or any potential loss of air samples in case of valve malfunction, which complicates the comparison between AirCore and the sampler.

Two aspects contribute to errors in the AirCore weighted mean. First of all, the AirCore profile needs to be weighted, since not all the pressure levels contribute equally to the sampler samples. The uncertainty in altitude of the AirCore profile adds a level of uncertainty to the AirCore weighted mean. Secondly, the retrieved AirCore profiles are already smoothed due to molecular diffusion of air samples from the time when it is sampled until analysed. Even though the AirCore might have been affected by diffusion, AirCore and Sampler show excellent agreement, with mean AirCore sampler differences of 0.84 ppm for CO_2, 1.8 ppb for CH_4 and 6.3 ppb for CO.

In the first flight on 26 April, an averaged difference of ~1 ppm in CO_2 is observed, which cannot be explained by the associated uncertainties or by smoothing of the AirCore profile due to diffusion. The samples were taken at a distance no more than 1.5 km apart (determined from Vaisala GPS-data) in the stratosphere, with less than 1.5 hours in between LISA and AirCore

sampling. Such large horizontal mole fraction gradients are not expected in the stratosphere, although stratospheric dynamics in winter show a high degree of variability in measured trace gases.

6.2 Vertical resolution and sample size

The vertical resolution of the collected stratospheric air samples ranges from 500 to 1500 m, and the sample size ranges from 800 to 180 mL. The vertical resolution and sample size therefor outperforms the AirCore. The vertical resolution and sample size of the LISA sampler is compared to the performance of AirCore subsampled air in Table 5. Its shows that sampler outperforms the subsample method described in Paul et al., 2016 and Mrozek et al., 2016.

As mentioned previously, the vertical resolution depends on the ascending speed and the effective sampling time, and the sample size also depends on the effective sampling time. To this end, the effort in collecting more air samples by increasing the effective sampling time will compromise the vertical resolution. The vertical resolution can be improved by lowering the ascending speed, and decreasing the sampling time. The pump works most effectively when the pressure difference across it is minimal. From the results shown in Fig. 3d, we see that after 200 seconds of sampling the gain in sample amount decreases fast. Therefore, the gain in sample amount, for example adding 10 extra seconds of sampling time, does not increase, but compromises the vertical resolution. The sample size can be increased by using an alternative pump that can deliver a higher flow rate than the current 8 L/min, and using sampling bags with a larger size than the current 2.58 litres. It will be mostly practical to increase the size of the sampling bag because this does not add significant weight or power consumption. An alternative more powerful pump could potentially increase the sample size, especially for the samples from high altitudes; however, it would also likely add more weight and consume more power that in turn increases the weight due to the need of more batteries.

6.3 Uncertainty in sample amount and vertical resolution

The accuracy in sounding of the Vaisala RS92-SGP pressure sensors is 1 hPa respectively at 200 hPa, and 0.6 hPa in the range 100-3 hPa, (Vaisala, 2013). The uncertainty of RS92-SGP pressure altitude is discussed in detail by Dirksen et al. (2014). The uncertainty of the vertical position of the RS92-SGP radiosonde is 20 m and hence is also the uncertainty of the pressure weighted altitude mean. Since the vertical resolution is calculated as the altitude where sampling stops minus the altitude at which sampling starts, the uncertainty in vertical resolution of the sampler is 29 m, calculated using Gaussian error propagation.

The uncertainty in the estimated sample amount is a result of the uncertainty in pressure and temperature measurements. The pressure sensor in the manifold has an uncertainty of 2.6 hPa (Honeywell, n.d.) whereas the radiosonde temperature measurements have an 1 sigma uncertainty of 0.25 K in sounding (Vaisala, 2013). This results in an error in estimated sample amount of 7.6 mL.

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Since the manifold pressure was not logged during the flight on 26 April, the pressure weighted altitude mean of the samples had to be estimated using Eq (2) and (3). As mentioned earlier Eq (3) assumes a constant upstream pressure, which is not the case during flight where the pressure decreases. This results in errors in both the estimated sample amount and the estimated mean pressure altitude. Using the parameters presented in Table 3. The error in p_b (Eq (1)) can be calculated using the uncertainties of the fit (Eq (2) and the pressure and measurements can be calculated using standard error propagation. The error in sounding of the pressure sensors is 1 hPa respectively at 200 hPa (Vaisala, 2013). The total uncertainty after 200 seconds of sampling the uncertainty is 9 ml, slightly higher than the effect found above.

6.4 Uncertainty of potential isotopic composition measurements

The stratospheric air samples can be used for analysis of isotopic composition measurements of trace gases. Here we take CO_2 and CH_4 as an example to estimate the uncertainties of isotopic composition measurements due to the sampling and storage errors (see Table 4). The uncertainties are calculated based on the estimated sampling and storage errors and the estimated isotopic signatures associated with the mole fraction changes of CO_2 and CH_4.

As CO_2 and CH_4 are stable molecules, we only consider contamination of the stratospheric air samples due to the sampling and the storage. The isotope ratio after the mixing of two originally separated air parcels of source and contamination (denoted by the subscripts s and c) can be approximated with:

$$\delta_m \approx \delta_s f_s + \delta_c f_c \quad (6)$$

were δ_m is the final isotopic composition, and δ_s and δ_c represent the isotope ratios of the two separated air parcels and f_s and f_c are the fractional contributions to the total mass after mixing. We further define the bias of the isotopic composition measurement as

$$\Delta\delta = \delta_s - \delta_m \quad (7)$$

Combining Eq. (6) and Eq. (7), we derive

$$\Delta\delta = (\delta_s - \delta_c) f_c, \quad (8)$$

For the calculation, we regard the differences between AirCore and LISA measurements (Table 4, e.g. 0.84 ppm for CO_2 and 1.8 ppb for CH_4) as the upper limit of the sampling and storage errors of the stratospheric samples, and take typical stratospheric CO_2 and CH_4 mole fractions of 390 ppm and 500 ppb, respectively. The fraction f_c can be calculated according to $f_c = \frac{bias}{[X]+bias}$ where [X] is the typical mole fraction. We use typical tropospheric values for δ_c and typical observed stratospheric values for

δ_s. The resulting bias in the isotopic composition measurements are presented in Table 6, together with typical tropospheric and stratospheric composition values used.

We can readily see that the estimated uncertainties due to the sampling and storage errors are relative small compared to the typical analytical precisions, also presented in Table 6. Hence the LISA sampler provides an excellent sampling tool for accurate measurements of stable isotopes in CO_2 and CH_4.

7 Conclusions

We have developed a new lightweight stratospheric air sampler, named LISA. The LISA sampler weighs ~2.5 kg, and is designed to collect four bag samples in the stratosphere during a balloon flight for CO_2, CH_4 and CO mole fraction measurements. Laboratory test results show that both MLF and Tedlar bags can maintain the sample mole fractions of CO_2, CH_4 reasonably well for at least 4 hours; however, we choose the MLF bag because it outperforms the Tedlar bag in the stability of both CO and water vapour. Accounting for the storage drift and analysis uncertainty, we estimate the uncertainty of the LISA sample measurements to be 0.14 ppm for CO_2, 2.2 ppb for CH_4 and 7.8 ppb for CO, respectively.

To assist the choice of the sampling strategy in terms of the sample vertical resolution and the sample size, we have evaluated the performance of the sampling pump in a pressure-controlled chamber. Based on the test results, we have estimated the expected sample size for each altitude and for each sampling time, and found that the increase of the sample size is saturated around 200 seconds of sampling. A further increase of the sampling time would collect little additional air sample but decrease the vertical resolution.

The LISA sampler was successfully flown four times during balloon flights in Sodankylä, Finland, in April and September 2017, retrieving a total of 15 samples. The sample size ranges between 800 mL to 180 mL for the altitude between 12 km and 25 km, with the corresponding vertical resolution ranging from 0.5 to 1.5 km. The collected air samples were analysed for CO_2, CH_4 and CO mole fractions, and evaluated against AirCore retrieved profiles, showing differences of up to 0.85 ppm for CO_2, 1.8 ppb for CH_4 and 6.3 ppb for CO, respectively.

The LISA sampler is thus a viable low-cost tool for retrieving stratospheric air samples, providing a complementary method to AirCore. Furthermore, The LISA sampler is advantageous to perform routine stratospheric measurements of isotopic compositions of trace gases.

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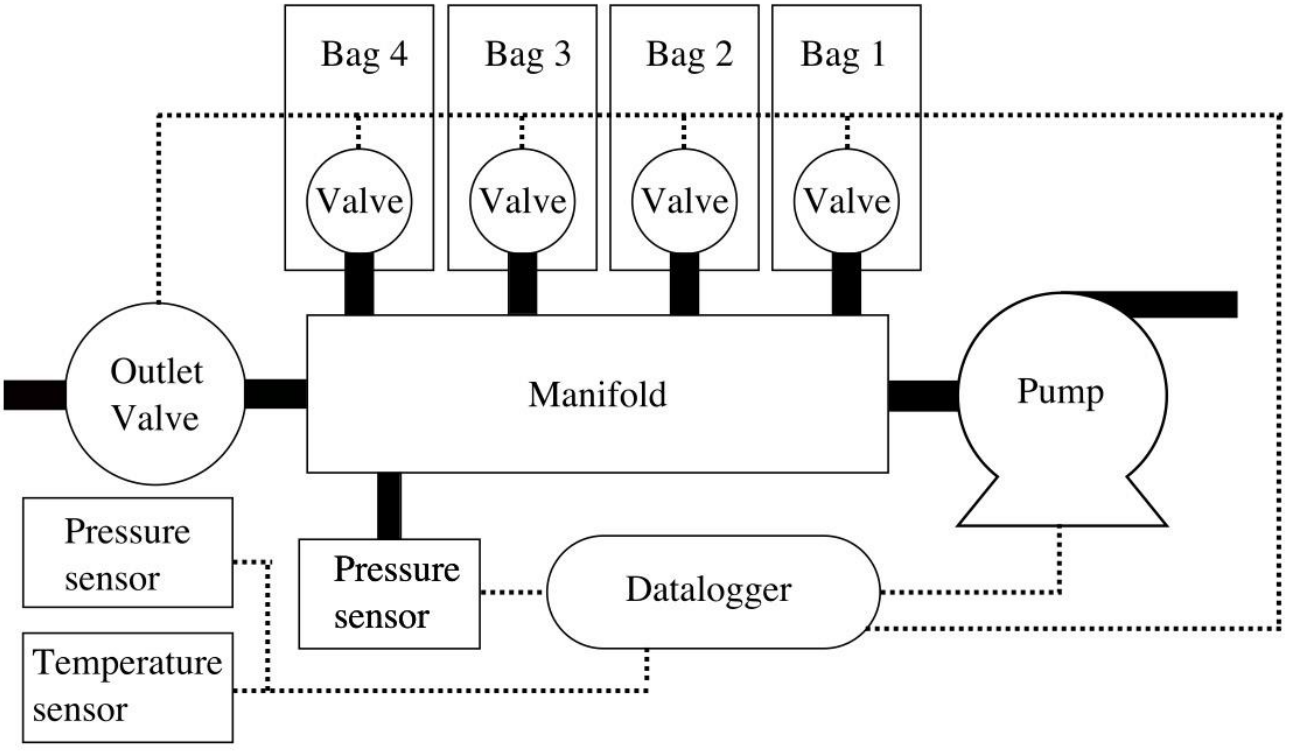

Figure 1: A schematic diagram of the sampler. Four bags are connected to a custom-made manifold. A small servomotor operates the screw cap combo valve. The outlet valve is the same as that of the bags, but is normally open when the sampler is idle during flight, allowing air pressure to equilibrate with outside air. Pressure inside the manifold is monitored by a pressure sensor. A datalogger is used to control all of the electronics. Electric connections are shown with dashed lines.

Table 1: A total of 7 sampling bags of each type (Tedlar and MLF) were prepared with the mole fractions presented below. Sampling bag nos. 6 & 7 were filled with cylinder air and were subsequently diluted using nitrogen. The results of the CRDS analysis directly after measurement are presented for those samples.

sample number		CO_2 (ppm)	CH_4 (ppb)	CO (ppb)
1		449.85	2086.2	260.5
2		398.12	1969.5	121.5
3		398.12	1969.5	121.5
4		449.85	2086.2	260.5
5		449.85	2086.2	260.5
6	MLF	127.04	597.5	74.8
	Tedlar	110.89	520.4	62.1
7	MLF	138.01	649.9	79.1
	Tedlar	125.89	591.1	71.7

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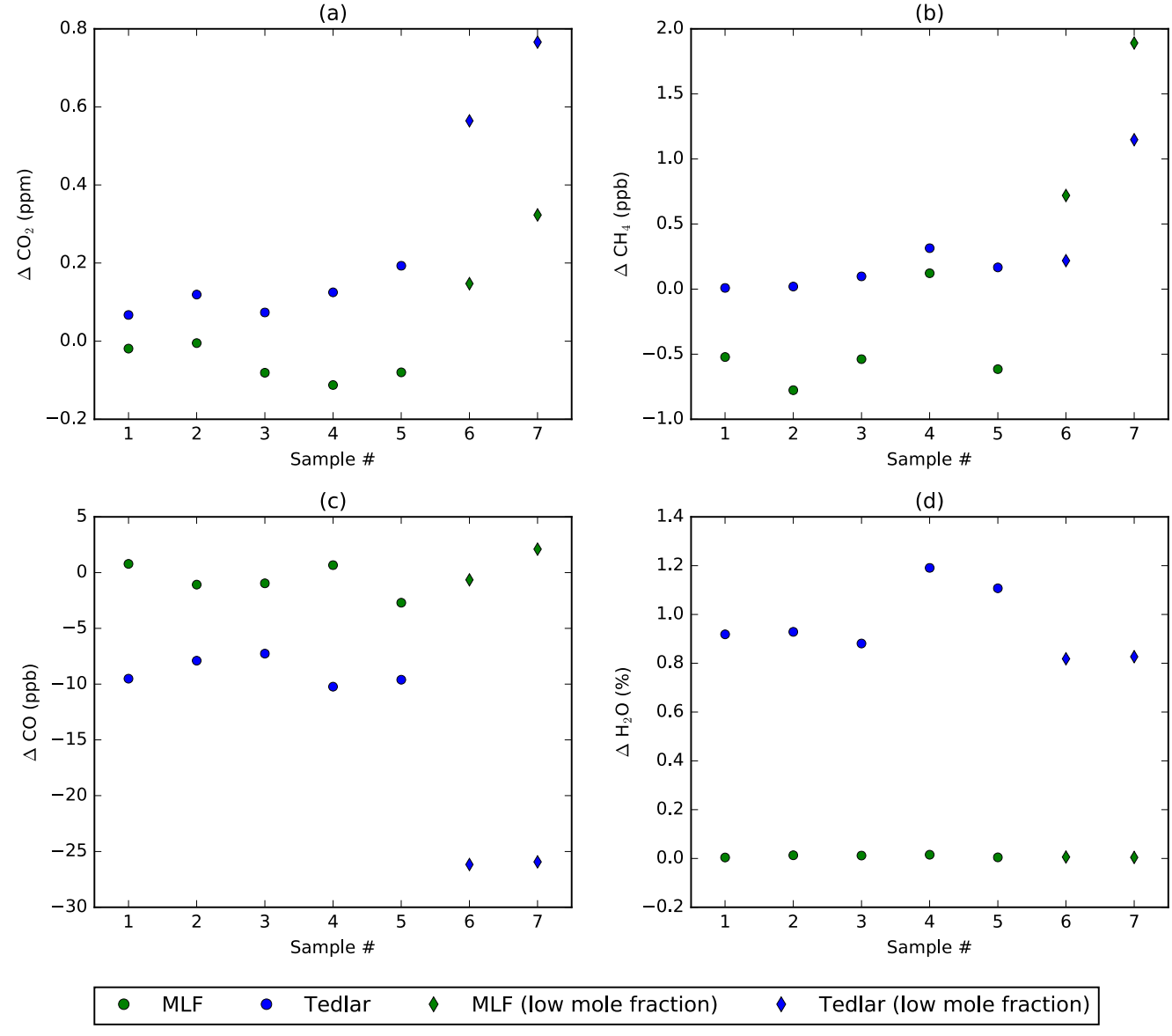

Figure 2: The observed drift of the mole fractions of CO_2 (a), CH_4 (b), CO (c) and H_2O (d) in each of 7 samples in both Tedlar and MLF bags. The drift is defined as the difference between the measured mole fractions after 4 hours and those measured immediately after filling. For CO_2, the mole fractions of samples nos. 1-5 are representative for stratospheric mole fractions. Samples nos. 6&7 contain low mole fractions and represent a typical mole fraction of stratospheric CH_4.

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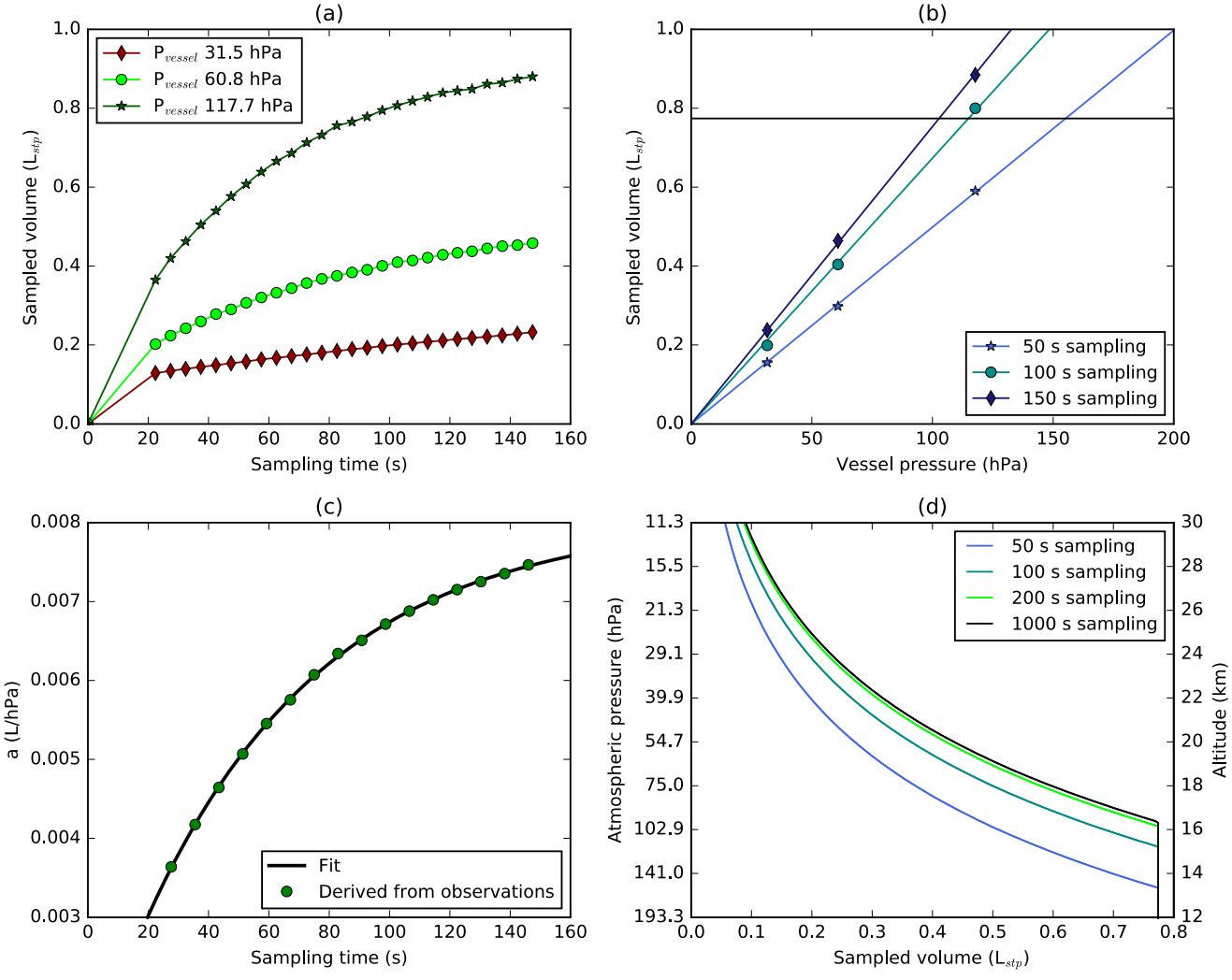

Figure 3 a) Sample volume as a function of the sampling time in seconds. The first 19.7 seconds fill the bag up to the pressure in the vessel. The sampled volume in the first 19.7 seconds linearly interpolated starting at zero, e.g. assuming that sampled volume increases linear with time. After the first 19.7 seconds, the bag is not expanding and air needs to be compressed and the flow rate drops. b) Sampled volume in litre at STP as a function of chamber pressure. The sampling times of 50 seconds, 100 seconds and 150 seconds are arbitrarily chosen. The lines are a linear fit to the data as in Eq. (1). For a given sampling time, the sampled amount at STP decreases linear with vessel pressure. The bags cannot withstand a pressure difference larger than 300 hPa. The practical limit is presented with a black line. c) The slope $a(t)$ (Eq. (1)) as a function of sampling time. The data points are derived values of (t) from the pressure date and the black line is the applied fit to the data, according to Eq. (2), with t_0=19.7 seconds. The fit constants can be found in Table 2. d) Atmospheric pressure on the left and corresponding altitude on the right. The International Standard Atmosphere is used to link pressure and altitude. The cut-of at the sample size of 0.76 L is the due to the practical fill limit of 300 hPa which consequently means that the sampling time is less.

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Table 2: Fit constants for Eq. (3) and standard error of the fit.

Parameter	Value	Error (1 σ)
x	0.0080	0.00003
b	0.0050	0.00002
τ	59.61	0.82

Table 3: Preset sampling parameters. Sampling is completed after either the maximum pressure in the manifold or the maximum sampling time is reached. P1-P4 are the preset targeted pressure altitudes.

Date	Maximum sampling time (s)	Maximum pressure (hPa)	P1 (hPa)	P2 (hPa)	P3 (hPa)	P4 (hPa)
26-Apr-2017	250	250	200	150	100	50
04-Sep-2017	180	275	200	150	100	50
05-Sep-2017	220	280	170	120	80	30
06-Sep-2017	250	280	170	120	80	50

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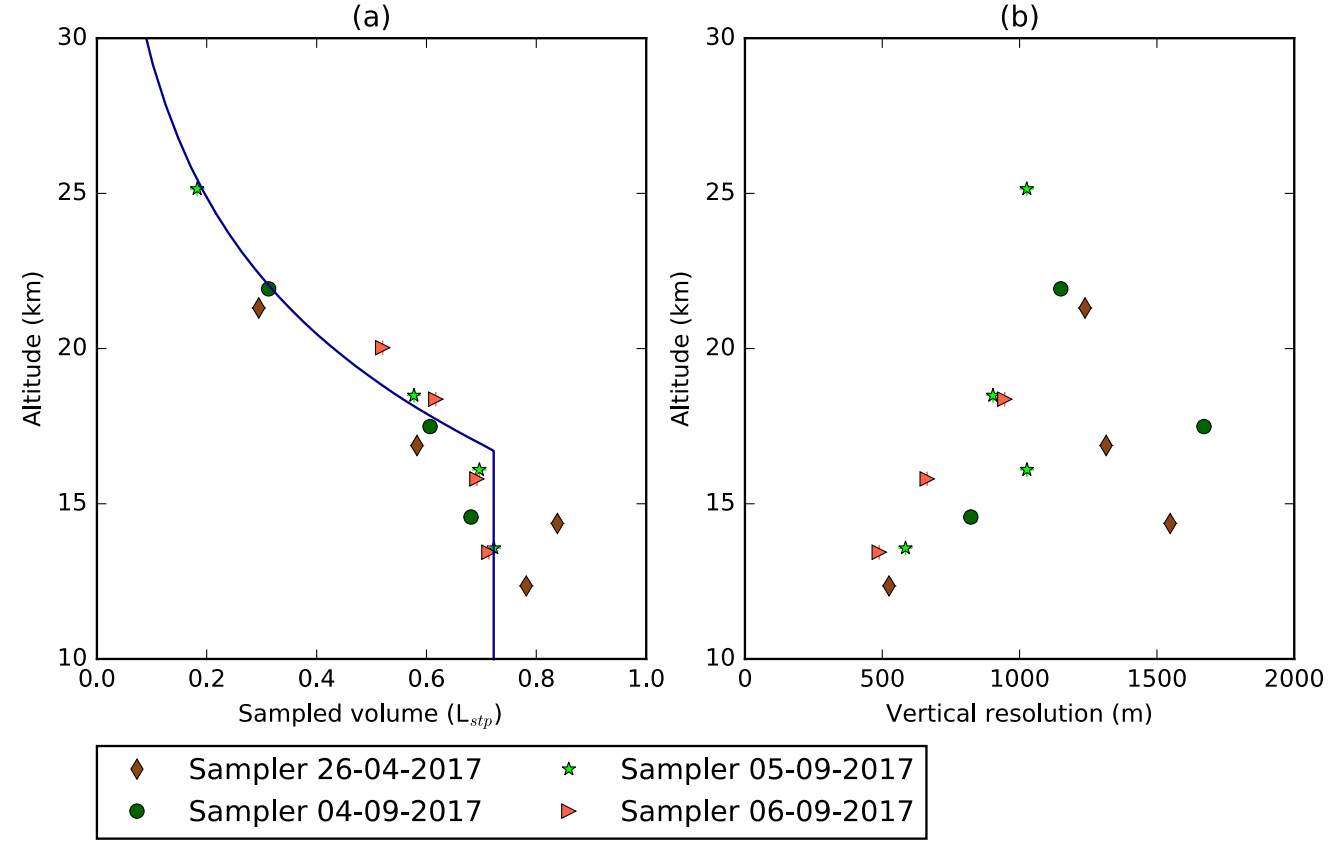

Figure 4: a) The altitude profile of the sample size of the collected 15 air samples. The estimated sample size with the sampling time of 200 seconds, and a maximum allowed bag pressure of 280 hPa, using the empirical relations used in Section 4 is shown in blue line, the same as in Figure 3d. b) The altitude profile of the vertical resolution of the collected samples. Different colours and symbols are used to label the samples from different flights. The vertical resolution of the highest sample from the flight on 6 September 2017 is not shown as the number is abnormally large caused by fast descending speed after the burst of the balloon.

Table 4: Comparison of CO_2, CH_4 and CO mole fractions between AirCore and LISA measurements. The difference is calculated as AirCore – LISA.

Species	Mean±σ	R^2	Mean±σ (excluding the April 26 flight)	R^2 (excluding the April 26 flight)
CO_2 (ppm)	-0.84±0.47	0.93	-0.55±0.13	0.97
CH_4 (ppb)	-1.80±16.16	0.99	5.1±13.10	0.99
CO (ppb)	6.34±6.58	0.58	9.19±5.18	0.59

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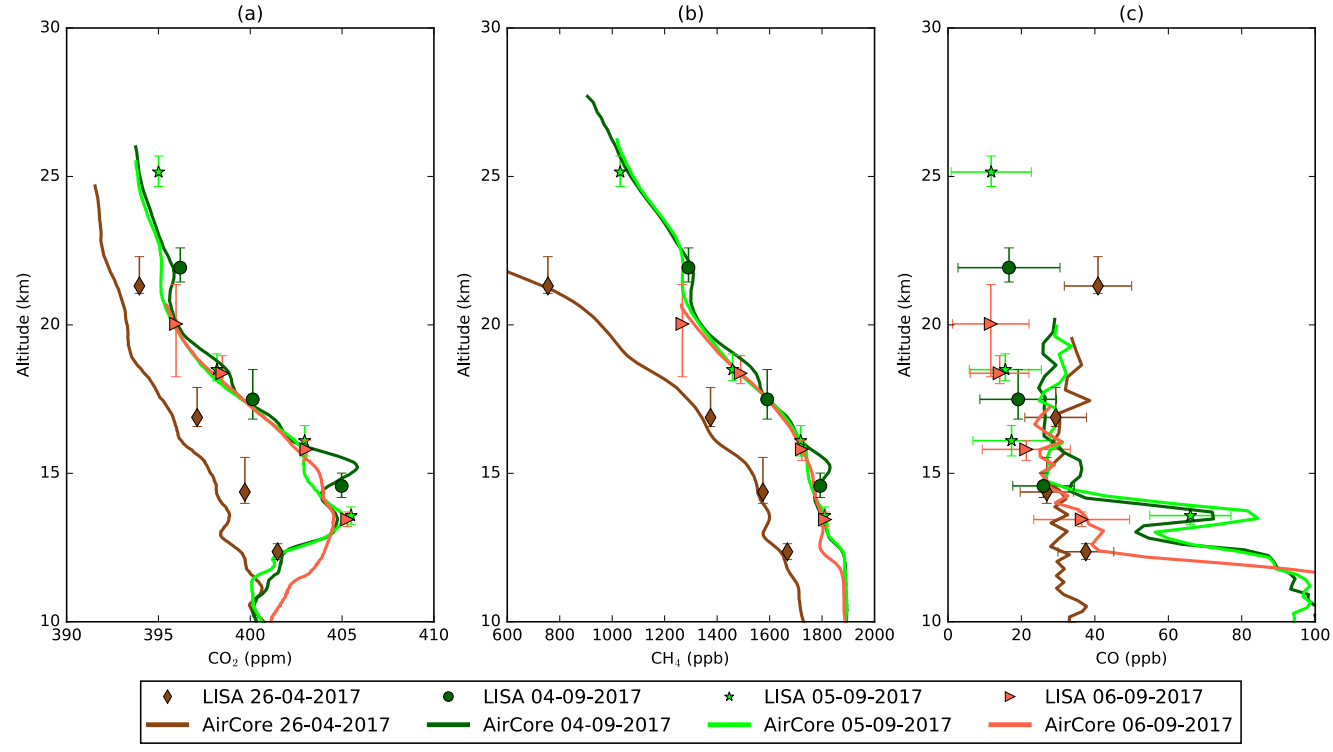

Figure 5: Comparison of AirCore and LISA measurements of (a) CO_2, (b) CH_4 and (c) CO mole fractions. The AirCore CO profiles are averaged in 100 m bins to smooth the relatively large noise of the measurements due to the analytical precision of 7 ppb (1 σ) of the CRDS analyser. Different colours and symbols are used to label the samples from different flights shown in the legend.

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Table 5: Comparison of the vertical resolution and sample size between the LISA sampler and samples sampled from AirCore. References: A Mrozek et al., 2016; B Paul et al., 2016; C this study.

Altitude (km)	Method	Resolution (m)	Sample size (mL)	Reference
12	AirCore	800	25	A
	AirCore	1000	50	B
	LISA	580	720	C
15	AirCore	1500	25	A
	AirCore	2000	50	B
	LISA	820	680	C
20	AirCore	2000	25	A
	AirCore	3000	50	B
	LISA	1100	312	C
25	AirCore	3000	25	A
	AirCore	5000	50	B
	LISA	1000	182	C

Table 6: Expected bias due to the limited accuracy of the LISA sampler. Typical values for the troposphere and stratosphere are taken from the indicated references: A) (Trolier et al., 1996) B) (Mrozek et al., 2016) C) (Nisbet et al., 2016) D) (Bergamaschi et al., 2001) E) (Aoki et al., 2003) and F) (Röckmann et al., 2011). f_c was calculated using a source value 390 ppm (CO_2) and 1000 ppb (CH_4); contamination values of 0.55 ppm (CO_2) and 5.1 ppb (CH_4). Reported measurement reproducibility's for stratospheric air are also provided.

Species	δ_c(‰)	δ_s(‰)	f_c	$\lvert\Delta\delta\rvert$(‰)	Measurement Reproducibility (‰)
$\delta^{13}C$ (CO_2) (VPDB)	-7.5 (A)	-8.4 (E)	0.0021	0.002	0.02 (E)
$\delta^{18}O$ (CO_2) (VPDB)	-2 (A)	12 (E)	0.0021	0.030	0.05 (E)
$\Delta^{17}O$ (CO_2) (VPDB)	0 (B)	5 (B)	0.0021	0.011	0.2 (B)
$\delta^{13}C$ (CH_4) (VPDB)	-47 (C)	-20 (F)	0.0036	0.097	0.7 (F)
$\delta^{2}H$ (CH_4) (VSMOW)	-85 (D)	190 (F)	0.0036	0.986	2.3 (F)