

Reply to Interactive comment of Referee #1 on “LISA: a lightweight stratospheric air sampler” by Joram J. D. Hooghiem et al.

We thank the two reviewers for their helpful and detailed comments on our manuscript. We have addressed the major comments from both reviewers regarding our derivation of the bias estimation in isotopic composition measurements and revised the introduction according to the comments of both reviewers. Below, a detailed point-to-point reply and a revised version of our manuscript with track changes are given.

The paper by Hooghiem presents a new technique for sampling of stratospheric air which may be well suited to add to the available techniques of cryogenic whole air sampling and AirCore. The paper is well written, although the introduction is a bit like a collection of information on sampling techniques and the use of stratospheric trace gas measurements but lacks a clear argumentation line. The subject is very much in line with the scope of AMT. I have a range of minor suggestions/questions and one major observation. The major observation explained below should be clarified before publication.

Major comments:

Major issues My main issue is the discussion of the differences between AirCore and LISA. First, it would be extremely valuable to see the paper by Chen et al., describing the data evaluation of the AirCore system used here. More importantly, I have doubts about the way that the fractional contribution of a contamination source (f_c) is derived in section 6.4. In my view, calculation of f_c from observed CO_2 $[CO_2]$ and deviations between this observation and the expected stratospheric value ($[CO_2]_s$) should be calculated as follows (values in parenthesis are mixing ratios):

*$[CO_2] = f_s * [CO_2]_s + f_c * [CO_2]_c = (1-f_c) * [CO_2]_s + f_c * [CO_2]_c$ With the subscripts as defined in the paper. Solving this for f_c yields: $f_c = ([CO_2] - [CO_2]_s) / ([CO_2]_c - [CO_2]_s)$*

If I assume that $([CO_2] - [CO_2]_s)$ is the difference of 0.84 ppm CO_2 between observed CO_2 in LISA and in AirCore, I need to make an assumption on $([CO_2]_c - [CO_2]_s)$ to calculate f_c . If we assume that $[CO_2]_s$ is stratospheric CO_2 at about 390 ppm (actually 395 is more realistic), and that the contamination is from tropospheric CO_2 with a mixing ratio of around 405 ppm, then I calculate f_c to be $0.84/(405-395) = 0.084$, and not 0.0021 as derived in Table 6.

We thank the reviewer for pointing out the calculation error. We mistakenly assumed that the contamination results from one-way diffusion of ambient CO_2 into the bag. If the observed bias would be entirely caused by diffused contamination air, the fraction of the contamination air is indeed about 8 percent. However, the observed bias is unlikely caused by diffusion alone based on our laboratory experiment results, where we found much smaller biases (~ 0.1 ppm for CO_2 and ~ 2 ppb for CH_4), as shown in Figure 2.

We have further thoughts on the diffusion process. According to the Fick's law, the diffusion depends on the diffusivity and the concentration gradient, which may be different for different species, e.g. the concentration gradient for O_2 and N_2 across the bag's material is negligible, and the concentration gradients for CO_2 and CH_4 depend on their ambient concentrations. We have updated the manuscript with the following analysis of the problem.

“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 storage bias (see Table 3) or the AirCore-LISA

bias (see Table 5), and the estimated isotopic signatures associated with the assumed contamination source.

For any species, the measured number of molecules n_m , is the sum of the number of molecules from the original source, n_s , and the contamination n_c that entered the sampling bag through diffusion:

$$n_m = n_s + n_c \quad (6)$$

Diffusion is governed by Fick's law:

$$J = D \frac{\partial C}{\partial x} \quad (7)$$

Where J is the diffusion flux, D the diffusivity and $\frac{\partial C}{\partial x}$ the concentration gradient of diffusing species, e.g. CO_2 . Each layer of the MLF bag has its own specific diffusivity and sorption characteristics, and for simplicity here we assume that it can be modelled with a single diffusivity constant that is only species-dependent. The process of sorption of gases into the solid material and the interaction governing that process is also ignored for simplicity. Then the total diffusion out of the bag which is of stratospheric origin, denoted by y_{out} . The total amount diffusing into the bag, denoted by y_{in} , is of tropospheric origin. Assuming that these two fluxes can be modelled with a law of mass action:

$$y_{in} = DC_c \quad (8)$$

and

$$y_{out} = DC_s \quad (9)$$

Where C_c is the concentration of ambient air that contaminates the stratospheric sample in the bag denoted by C_s . The bias that we measure is as follows:

$$\text{bias} = y_{in} - y_{out} \quad (10)$$

Assuming that y_{out} is purely stratospheric and y_{in} is purely tropospheric, and that c_{out} and c_{in} are mole fractions outside and inside the bags and are assumed to be constant. We can estimate the fraction of tropospheric contamination in our sample. The measurement (C_m) is the sum of the original stratospheric sample (C_s), minus the sample that is leaving the bag and the tropospheric sample entering the bag:

$$C_m = C_s - y_{out} + y_{in} \quad (11)$$

And the contaminating fraction is then f_c is

$$f_c = \frac{y_{in}}{C_m} = \frac{C_c \cdot \text{bias}}{C_m(C_c - C_s)} \quad (12)$$

Where the right-hand side is obtained by using Eq. (8) to (10). The sample fraction, f_s , is simply

$$f_s = 1 - f_c \quad (13)$$

The isotope composition after the mixing of the tropospheric contamination into the sample air, can be approximated with:

$$\delta_m \approx \delta_s f_s + \delta_c f_c \quad (14)$$

where δ_m is the final isotopic composition, and δ_s and δ_c represent the isotope composition of source and contamination and f_s and f_c are the fractional contributions to the total number of molecules after mixing. We further define the bias of the isotopic composition measurement as

$$\Delta\delta = \delta_s - \delta_m \quad (15)$$

Combining Eq. (8) and Eq. (9), we derive

$$\Delta\delta = (\delta_s - \delta_c) f_c \quad (16)$$

For the calculation, we regard the mean differences between AirCore and LISA measurements (Table 5, e.g. 0.84 ppm for CO_2 and 1.8 ppb for CH_4) as the upper limit of bias induced in the stratospheric samples. Another estimate is performed based on the storage test results, that showed maximum drift of 0.11 ppm CO_2 and 2 ppb CH_4 , presented in Table 3.

The fraction f_c can be calculated according to Eq. (12) with C_s being the typical stratospheric mole fraction, which is taken to 395 ppm for CO_2 and 500 ppb for CH_4 . We use typical tropospheric values of 405 ppm for CO_2 and 1800 ppb for methane. The isotopic compositions δ_c and δ_s are taken from various references, and are presented in Table 7. The resulting bias in the isotopic composition measurements are presented in Table 7.

We can readily see that the estimated uncertainties due to the storage bias are relatively small compared to the typical analytical precisions, also presented in Table 7. Hence the LISA sampler provides a viable sampling tool for accurate measurements of stable isotopes in CO_2 and CH_4 .”

Table 7: Expected bias in stable isotope measurements on samples obtained by LISA, 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). Reported measurement reproducibility's, Re , for stratospheric air are also provided. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are with respect to Vienna Pee Dee Belemnite (VPDB) and $\Delta^{17}\text{O}$ and $\delta^2\text{H}$ are with respect to Vienna Standard Mean Ocean Water (VSMOW). f_c was calculated using a source value 395 ppm (CO_2) and 500 ppb (CH_4). For f_{c1} contamination values of 0.84 ppm (CO_2) and 1.8 ppb (CH_4) based on LISA AirCore observed mean bias, resulting in $\Delta\delta_1$; For f_{c2} the maximum observed drift (Figure 2) of 0.11 ppm (CO_2) and 2 ppb (CH_4) are used, resulting in $\Delta\delta_2$.

Species	δ_c (‰)	δ_s (‰)	Re (‰)	LISA-AirCore		Storage Test	
				f_{c1}	$ \Delta\delta_1 $ (‰)	f_{c2}	$ \Delta\delta_2 $ (‰)
$\delta^{13}\text{C}$ (CO_2) (VPDB)	-7.5 (A)	-8.4 (E)	0.02 (E)		0.077		0.01
$\delta^{18}\text{O}$ (CO_2) (VPDB)	-2 (A)	12 (E)	0.05 (E)	0.086	1.203	0.011	0.158
$\Delta^{17}\text{O}$ (CO_2) (VSMOW)	0 (B)	7 (B)	0.2 (B)		0.602		0.079
$\delta^{13}\text{C}$ (CH_4) (VPDB)	-47 (C)	-20 (F)	0.7 (F)	0.006	0.134	0.006	0.149
$\delta^2\text{H}$ (CH_4) (VSMOW)	-85 (D)	190 (F)	2.3 (F)		1.366		1.517

This might actually also explain the differences observed in April flights with respect to the September flights. During Fall NH CO_2 is expected to be much smaller, thus the difference between contaminant and actual stratospheric mixing ratio is much lower than during spring (when tropospheric CO_2 may be up to 10 ppm higher). This is also in line with the much higher deviations found in the laboratory experiments when having larger concentration differences.

A 0.8 ppm difference was observed during the storage test (Fig. 2) when a rough 250-ppm (assuming room air of about 405 ppm) concentration difference existed across the bags material over 4 hours. According to this storage test result, a seasonal cycle of 10 ppm in CO_2 between winter and summer would cause a difference of $10/250 \times 0.8 = 0.032$. Hence the observed increase of 1 ppm observed from the AirCore LISA difference cannot be fully attributed to the seasonal variability. This is now explicitly mentioned in the revised manuscript.

“The seasonality in tropospheric CO_2 that causes the difference between sampled air and its storage environment could contribute to the observed difference. The northern hemisphere winter CO_2 mole fractions are typically 10 ppm higher those in summer. During the storage test with low mole fractions, e.g. sample nos. 6&7 in Figure 2, a drift of up to 0.8 ppm was observed. Therefore, a typical seasonal difference of 10 ppm could only explain a difference of 0.03 ppm in the observed CO_2 bias.”

We would like to note that citing a publication in preparation, e.g. Chen et al. in prep, is in line with the guidelines of AMT. Nevertheless, we have added a sentence to provide more details about the AirCore measurements.

“The AirCore used during the campaign consists of two pieces of stainless steel tubing (40 m long ¼ in. OD and 60 m long 1/8 in. OD, wall thickness 0.01 in.), with a total weight of ~3.6 kg.”

Minor/specific observations:

p.3. l. 1: the Engel et al. trend is only representative for the mid-latitudes of the Northern Hemisphere, above 24 km altitude.

We have added this in the revised version.

“...however no significant change in the strength of the BDC in the northern hemisphere at mid latitudes was detected (Engel et al., 2009, 2017).”

p.3. l. 3.: A reference from 1983 may not be very good to point to current deficits in GCMs.

We have added a more recent reference (Gerber et al., 2012).

“In spite of all the efforts to make observations of stratospheric tracers, GCM’s remain poorly constrained (Gerber et al., 2012), a problem already pointed out several decades ago (Ehhalt et al., 1983).”

p.3. l. 26.: could you be more specific on the allowed weight?

The total payload of a weather balloon typically ranges between 0.2-12 kg, which represents the range of the weight from radiosondes to medium-weight scientific instrumentation. We have changed the original sentence in the revised version as

“... typically ranges between 0.2-12 kg...”

p. 3. L. 29.: as LISA samples during ascent, has possible outgassing of CO₂ from the Styrofoam be considered?

Yes, this has been considered. Currently, we don’t have data on outgassing under stratospheric conditions.

“Another potential source for the bias in the CO₂ mole fractions is outgassing from the packaging material and balloon. As the balloon ascends the surrounding pressure decreases and gasses desorb from the surface of the packaging material and balloon, which potentially influences the mole fractions. This would, however, not explain the good agreement during the September flights opposed to the April flights. Furthermore, the inlet is located at the top of the payload and any outgassing is flushed away from the inlet during ascent.”

p. 5. section 3.1. Could you comment on how dry the test samples were? This will make a very large difference, especially for CO₂.

Test samples were prepared with air from cylinders that typically contain less than 0.03% H₂O. This value has been added to the revised version. The direct measurements yielded values

below 0.06 % for the MLF bags and 0.12 % for the Tedlar bags, but since we used water vapour correction functions we did not add the absolute water content to the manuscript.

“...with dry air (<0.03% H₂O) from a cylinder”

p.6. l. 13.: How were the bags preconditioned. Why was N₂ used and not ambient air?

A small discussion on the preconditioning procedure has been added in the revised version. In principle, ambient air could be used as well.

“The bags were filled with N₂ from a cylinder and subsequently evacuated with a vacuum pump, prior to filling with test sample. In principle ambient air can be used to flush the bags, as long as it is dry.”

p. 7. Section 4.: At which temperature was the flow characterized? Strat. Temperatures are much lower, which may influence pump performance quite strongly.

Indeed, no laboratory tests were performed at stratospheric temperatures. The pump performance could be affected by the cold environment. First, the batteries could lose capacity and cause the power supplied to the pump decreasing. The temperature inside the thermally insulated package, where the pump is located, during flight ranged between 30 and -15 °C. Secondly, the diaphragm is exposed to the cold air passing through the pump. The elasticity of a rubber is temperature dependent, which could reduce the performance of the pump. On the other hand, heat is released during operation of the pump, which increases the temperature. Finally, the effect of air temperature on sample size follows the ideal gas law, and the sample size increases at low temperatures. As no experimental data is available to determine the performance of the pump at stratospheric temperature, we assume that the pump performs the same during flight as at room temperature for the calculation of the sample size.

We have clarified in the manuscript with the following text in section 6

“During the experiments described in Section 4, the pump was at room temperature. The pump performance could be affected by the cold environment. First, the batteries could lose capacity and cause the power supplied to the pump to decrease. The temperature inside the thermally insulated package, where the pump is located, during flight ranged between 30 and -15 °C. Secondly, the diaphragm is exposed to the cold air passing through the pump. The elasticity of a rubber is temperature dependent, which could reduce the performance of the pump. On the other hand, heat is released during operation of the pump, which increases the temperature. Finally, the effect of air temperature on sample size follows the ideal gas law, and the sample size increases at low temperatures. As no experimental data is available to determine the performance of the pump at stratospheric temperature, we assume that the pump performs the same during flight as at room temperature for the calculation of the sample size.”

p. 7. L 8 sample, not samples

The typo has been corrected in the revised version.

“...of air sample collected into...”

p. 7. L. 11 (and elsewhere in the manuscript): please be consistent in the use of L vs. L STP.

We have made sure that the manuscript is now consistent with the use of L at STP, except for the volume of an object, e.g. the volume of the bag is 2.58 litre.

p.8. l. 25: please restrict this to 30 hPa, as the flow was not measured at lower pressures.

We now clarify in the figure caption that the presented curves are modelled based on the fitted parameters. The extrapolated curves are informative, although they may contain larger uncertainties than those within the tested range. Therefore, we would like to keep the curves outside the tested range, but have made the point clear in the revised version.

“...Atmospheric pressure on the left and corresponding altitude on the right, as a function of modelled sample volume. Note that for atmospheric pressure >120 and <30 hPa, as well as for sampling time >150 s the modelled results rely on extrapolation of the observations.”

p. 9. L. 6.: Is burst pressure of the bag temperature dependent?

No experiments have been performed to show whether the burst pressure of the bag is temperature dependent. All bags survived the four flights. Two bags burst at room temperature at the pressure gradients across the bags of 312 and 331 hPa, respectively. The burst temperature might be temperature dependent; however, we think that the variation of the quality of the bags explains the different burst pressures at room temperature.

p. 9. L. 10: 240 K is actually very warm for the stratosphere.

Changed to 220 K, which is in line with the standard atmosphere.

“...cold e.g. 220 K, the total sampled volume at”

p. 12. L. 17 l. 27: please be consistent in using only one value for the deviations. If the value of 0.84 ppm is used, this is much larger than stated in Engel et al., 2017. Have the authors made an uncertainty estimate for the flight on April 26, considering that no AirCore coils temperature is available?

In the manuscript we have made sure that it is clear which deviation are discussed. The effect of coil temperature on the profile is relatively small.

p. 12 l. 26: It is not only molecular diffusion.

Indeed, we have revised the sentence to include also the effects from Taylor dispersion and air mixing in the cavity of the CRDS analyser. We also state that the altitude registration in pressure coordinates is sensitive to user input.

“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 and Taylor dispersion, and smearing effects in sample renewal of the cavity of the CRDS. Moreover, the AirCore profile suffers from uncertainty in altitude registration.

For more information on the uncertainties associated with AirCore profiles we refer to Engel et al.(2017), Karion et al. (2010) and Membrive et al. (2017)."

p. 12/13. Section 6.1.: This whole section lacks a conclusion. First, which is the best estimate of the deviations, and second what could cause the strong deviations during the April flight (see also my major comment above). Have pollution/outgassing been considered to explain the differences?

A more elaborate discussion has been provided. Outgassing was considered, and we have added this to the discussion.

"Another potential source for the bias in the 26 April 2017 flight is outgassing from the packaging material and balloon. As the balloon ascends the surrounding pressure decreases and gasses desorb from the surface of the packaging material and balloon, which potentially influences our measurements. This would, however, not explain the good agreement during the September flights opposed to the April flights. Furthermore, the inlet is located at the top of the payload and any outgassing is flushed away from the inlet during ascent."

The suggestion of the influence NH seasonality, as in the major comment, has been accounted for.

"The seasonality in tropospheric CO₂ could be another explanation to the observed difference. In northern hemisphere winter CO₂ mole fractions are higher, and hence the difference between sampled air and storage environment is higher. However, during the storage tests with low mole fractions, e.g. sample nos. 6&7 in Figure 2, the mole fractions of CO₂ were much lower than typical stratospheric samples. In that experiment the drift did not exceed 0.8 ppm. Hence, such a large drift cannot be fully attributed to the CO₂ variability in the storage environment that is due to seasonality."

A more detailed discussion on the uncertainties in AirCore has been added, see also the reply to the previous comment. We have no good reason to say that either one of the estimates is better, other than the faulty datalogger, therefore we conclude with deviations as follows:

"Even though the AirCore might have been affected by diffusion and problems with the datalogger, AirCore and Sampler show good agreement in all flights, with mean AirCore sampler differences of 0.84 ppm for CO₂, 1.8 ppb for CH₄ and 6.3 ppb for CO."

p. 13. L. 14.: this sentence is odd. How should a prolonged sampling time result in increased vertical resolution?

The sentence has been rephrased. The explanation why prolonged sampling time compromises vertical resolution was presented in section 4.

"Therefore, the gain in sample amount, for example adding 10 extra seconds of sampling time, is small; however, the decrease in vertical resolution is significant"

p. 14.l. 7.: this sentence is wrong, uncertainty is mentioned twice.

The sentence has been corrected.

“The uncertainty in sounding of the pressure sensors is 1 hPa at 200 hPa (Vaisala, 2013). The total uncertainty after 200 seconds of sampling is 9 mL_{stp}, slightly higher than the effect found above.”

p. 14. Section 6.4. see major comment above. I believe that the contaminating fraction may be much higher.

See our reply to the major comment.

p. 15. L. 24: this is not up to 0.84 ppm. 0.84 ppm is actually an average deviation if all samples are considered.

Correct, we have rephrased the sentence and now use “mean difference” instead of “up to”.

“...showing the mean differences between AirCore and LISA of ...”

Figure 2: the colours for the different bags types are virtually undistinguishable.

The colours of all figures have changed. With respect to Figure 2, we have also increased the marker size to improve visibility.

Figure 3: I wonder if all panels are needed here. I suggest removing panel b.

Panel b shows the linear behaviour observed between sampled volume and ambient pressure. This allows us to model the volume sampled according to Eq. (2) where $a(t)$ is then the only parameter depending on sampling time. To justify our model, we deem it necessary to show panel b. Panel c shows the fit that models the time dependence of the linear coefficient $a(t)$ according to Eq. (3).

Table 6: please explain the different columns on the table heading, not only in the text.

We have provided more detailed explanations of the different columns in the revised version, now it is updated to Table 7:

“Table 7: Expected bias in stable isotope measurements on samples obtained by LISA, 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). Reported measurement reproducibility's, R_e , for stratospheric air are also provided. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are with respect to Vienna Pee Dee Belemnite (VPDB) and $\Delta^{17}\text{O}$ and $\delta^2\text{H}$ are with respect to Vienna Standard Mean Ocean Water (VSMOW). f_c was calculated using a source value 395 ppm (CO_2) and 500 ppb (CH_4). For f_{c1} contamination values of 0.84 ppm (CO_2) and 1.8 ppb (CH_4) based on LISA AirCore observed mean bias, resulting in $\Delta\delta_1$; For f_{c2} the maximum observed drift (Figure 2) of 0.11 ppm (CO_2) and 2 ppb (CH_4) are used, resulting in $\Delta\delta_2$.”

References

Gerber, E. P., Butler, A., Calvo, N., Charlton-Perez, A., Giorgetta, M., Manzini, E., Perlwitz, J., Polvani, L. M., Sassi, F., Scaife, A. A., Shaw, T. A., Son, S. W. and Watanabe, S.: Assessing and understanding the impact of stratospheric dynamics and variability on the earth system, *Bull. Am. Meteorol. Soc.*, 93(6), 845–859, doi:10.1175/BAMS-D-11-00145.1, 2012.

Reply to Interactive comment of Referee #2 on “LISA: a lightweight stratospheric air sampler” by Joram J. D. Hooghiem et al.

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General comments

The authors present a new stratospheric sampling system that can fill a niche between current techniques, as it provides larger air samples with better vertical resolution than AirCore while operating with much lower cost and payload weight than typical cryogenic whole air systems. The manuscript is suitable for AMT and well-written and should be published after addressing the following comments and requests. In particular, a possible error in the calculation of uncertainty for isotopic analysis should be resolved.

Major issue: Section 6.4

I agree with Reviewer 1 that the underlying assumptions used to estimate fraction of sample from contamination (f_c) are incorrect. The ultimate source of the error seems to derive from the expression used to define $f_c = \text{bias}/([X] + \text{bias})$. Here I presume that $[X]$, defined by the authors as “typical mole fraction,” is therefore meant to be $[X]_{\tilde{m}}$, the measured mixing ratio.

If we rearrange equation (7) to $\delta m = \delta s - \Delta\delta$ and rewrite for mixing ratio as $[X]_m = [X]_s - \Delta X$, where $[X]_s$ is the stratospheric mixing ratio and ΔX is the bias, then substitute this into the equation above, we have $f_c = \Delta X / (\Delta X - [X]_s + \Delta X) = \Delta X / [X]_s$. But since the authors also define $f_c = \Delta X / ([X]_s - [X]_c)$ in equation (8), this implies that the authors are assuming the mixing ratio of the contamination is 0 when they calculate the f_c on pg 14, line 28. Instead, they should use measured or typical mixing ratios, nominal 400 ppm and 1800 ppb for CO₂ and CH₄, respectively. This would result in roughly the same estimate as Reviewer 1 has calculated.

We would like to refer to the reply the comments of reviewer 1. We have copied it here for convenience.

We thank the reviewer for pointing out the calculation error. We mistakenly assumed that the contamination results from one-way diffusion of ambient CO₂ into the bag. If the observed bias would be entirely caused by diffused contamination air, the fraction of the contamination air is indeed about 8 percent. However, the observed bias is unlikely caused by diffusion alone based on our laboratory experiment results, where we found much smaller biases (~0.1 ppm for CO₂ and ~2 ppb for CH₄), as shown in Figure 2.

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“The stratospheric air samples can be used for analysis of isotopic composition measurements of trace gases. Here we take CO₂ and CH₄ as an example to estimate the uncertainties of isotopic composition measurements due to the storage bias (see Table 3) or the AirCore-LISA bias (see Table 5), and the estimated isotopic signatures associated with the assumed contamination source.

For any species, the measured number of molecules n_m , is the sum of the number of molecules from the original source, n_s , and the contamination n_c that entered the sampling bag through diffusion:

$$n_m = n_s + n_c \quad (6)$$

Diffusion is governed by Fick’s law:

$$J = D \frac{\partial C}{\partial x} \quad (7)$$

Where J is the diffusion flux, D the diffusivity and $\frac{\partial C}{\partial x}$ the concentration gradient of diffusing species, e.g. CO₂. Each layer of the MLF bag has its own specific diffusivity and sorption characteristics, and for simplicity here we assume that it can be modelled with a single diffusivity constant that is only species-dependent. The process of sorption of gases into the solid material and the interaction governing that process is also ignored for simplicity. Then the total diffusion out of the bag which is of stratospheric origin, denoted by y_{out} . The total amount diffusing into the bag, denoted by y_{in} , is of tropospheric origin. Assuming that these two fluxes can be modelled with a law of mass action:

$$y_{in} = DC_c \quad (8)$$

and

$$y_{out} = DC_s \quad (9)$$

Where C_c is the concentration of ambient air that contaminates the stratospheric sample in the bag denoted by C_s . The bias that we measure is as follows:

$$bias = y_{in} - y_{out} \quad (10)$$

Assuming that y_{out} is purely stratospheric and y_{in} is purely tropospheric, and that c_{out} and c_{in} are mole fractions outside and inside the bags and are assumed to be constant. We can estimate the fraction of tropospheric contamination in our sample. The measurement (C_m) is the sum of the original stratospheric sample (C_s), minus the sample that is leaving the bag and the tropospheric sample entering the bag:

$$C_m = C_s - y_{out} + y_{in} \quad (11)$$

And the contaminating fraction is then f_c is

$$f_c = \frac{y_{in}}{C_m} = \frac{C_c \cdot bias}{C_m(C_c - C_s)} \quad (12)$$

Where the right-hand side is obtained by using Eq. (8) to (10). The sample fraction, f_s , is simply

$$f_s = 1 - f_c \quad (13)$$

The isotope composition after the mixing of the tropospheric contamination into the sample air, can be approximated with:

$$\delta_m \approx \delta_s f_s + \delta_c f_c \quad (14)$$

were δ_m is the final isotopic composition, and δ_s and δ_c represent the isotope composition of source and contamination and f_s and f_c are the fractional contributions to the total number of molecules after mixing. We further define the bias of the isotopic composition measurement as

$$\Delta\delta = \delta_s - \delta_m \quad (15)$$

Combining Eq. (8) and Eq. (9), we derive

$$\Delta\delta = (\delta_s - \delta_c) f_c \quad (16)$$

For the calculation, we regard the mean differences between AirCore and LISA measurements (Table 5, e.g. 0.84 ppm for CO₂ and 1.8 ppb for CH₄) as the upper limit of bias induced in the stratospheric samples. Another estimate is performed based on the storage test results, that showed maximum drift of 0.11 ppm CO₂ and 2 ppb CH₄, presented in Table 3.

The fraction f_c can be calculated according to Eq. (12) with C_s being the typical stratospheric mole fraction, which is taken to 395 ppm for CO₂ and 500 ppb for CH₄. We use typical tropospheric values of 405 ppm for CO₂ and 1800 ppb for methane. The isotopic compositions δ_c and δ_s are taken from various references, and are presented in Table 7. The resulting bias in the isotopic composition measurements are presented in Table 7.

We can readily see that the estimated uncertainties due to the storage bias are relatively small compared to the typical analytical precisions, also presented in Table 7. Hence the LISA sampler provides a viable sampling tool for accurate measurements of stable isotopes in CO₂ and CH₄.”

Table 7: Expected bias in stable isotope measurements on samples obtained by LISA, 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). Reported measurement reproducibility's, R_e , for stratospheric air are also provided. $\delta^{13}C$ and $\delta^{18}O$ values are with respect to Vienna Pee Dee Belemnite (VPDB) and $\Delta^{17}O$ and δ^2H are with respect to Vienna Standard Mean Ocean Water (VSMOW). f_c was calculated using a source value 395 ppm (CO₂) and 500 ppb (CH₄). For f_{c1} contamination values of 0.84 ppm (CO₂) and 1.8 ppb (CH₄) based on LISA AirCore observed mean bias, resulting in $\Delta\delta_1$; For f_{c2} the maximum observed drift (Figure 2) of 0.11 ppm (CO₂) and 2 ppb (CH₄) are used, resulting in $\Delta\delta_2$.

Species	δ_c (‰)	δ_s (‰)	R_e (‰)	LISA-AirCore		Storage Test	
				f_{c1}	$ \Delta\delta_1 $ (‰)	f_{c2}	$ \Delta\delta_2 $ (‰)
$\delta^{13}C$ (CO ₂) (VPDB)	-7.5 (A)	-8.4 (E)	0.02 (E)		0.077		0.01
$\delta^{18}O$ (CO ₂) (VPDB)	-2 (A)	12 (E)	0.05 (E)	0.086	1.203	0.011	0.158
$\Delta^{17}O$ (CO ₂) (VSMOW)	0 (B)	7 (B)	0.2 (B)		0.602		0.079
$\delta^{13}C$ (CH ₄) (VPDB)	-47 (C)	-20 (F)	0.7 (F)	0.006	0.134	0.006	0.149
δ^2H (CH ₄) (VSMOW)	-85 (D)	190 (F)	2.3 (F)		1.366		1.517

An alternative method to estimate f_c would be to solve equation (8) for both CO₂ and CH₄ simultaneously. Since the authors already have estimates for $\Delta\delta$ and δ_s stated (pg 14, lines 26-28), this results in two equations with two unknowns, which can then be solved trivially. This would be a worthwhile exercise to confirm the estimate of f_c provided by Reviewer 1.

Since the diffusion through the bag's material is species dependent (e.g. species dependent diffusivity and concentration gradient.), the fraction f_c is also different for each species. That is why we find different values for f_c as presented in table 7. In a simple mixing scheme with two air masses the suggested calculation would indeed be true.

Finally, it is not clear to me why the authors don't use the storage test results, in addition to the ambient data, to estimate f_c . This should either be performed, or the authors should explain why this analysis is not valid.

In the revised manuscript we have added the estimate based on the storage test results.

Additional general comments

I agree with Reviewer 1 that the introduction is a bit unfocused and broad. I think a more focused discussion of the literature with regards to the particular challenges of making sufficiently accurate and precise mixing ratio measurements in the stratosphere would be more useful. See the introduction offered by Membrive et al., 2017 for an example.

The manuscript presents multiple tables of information (e.g. Table 2 is derived fit coefficients, Table 3 is instrument operational settings) that would be better suited in supplemental materials, as this information is not critical to main discussion here). Meanwhile, there is no table provided that summarizes the instrument specifications (e.g. weight, power requirements, sample resolution at stated altitude) and comparison to the AirCore and other systems. I would be appreciative of such a summary table.

We have added a table summarizing the key components of the sampler in section 2. We like to draw the attention to table 5 where a comparison of sample size and resolution between AirCore and Sampler, which to our best knowledge are to only to instruments with weight lower than 5 kg that can sample from the stratosphere.

In the light of the discussion presented in sections 6.2 about sampling size and vertical resolution we deemed the information in Table 3 relevant. Table 2 is removed from the manuscript, as we agree I does not provide any relevant information.

“Table 1: Components used in the LISA sampler, including manufacturer and product key. The total weight is given for amounts per part. Voltage and power are presented according to manufacturer specification. The total weight for the onboard computer and sensors is given.”

Component	Company	Product key	Amount	Voltage	Power	Weight
			t	(V)	(W)	(g)
Servo motor	Hitec	HS-65HB+	5	4.8-6	1.32	91
Pump	KNF	NMP 850.1.2 KNDC B	1	24	10.8	403.6
Bag (MLF)	Supelco	30227-U	4	(-)	(-)	80.4
Tube	Cole Palmer	EW-95100-02	1	(-)	(-)	30
Union T	Swagelok	NY-400-3	5	(-)	(-)	39
Union Knee	Swagelok	NY-400-9	5	(-)	(-)	33
Battery	(-)	CR123	10	3	(-)	166
Pressure sensor	Honeywell	HSCMAND015PASA 5	2			
Temperature sensor	IST	600C (100Ohm)	1	7-12	(-)	87.4
Datalogger	Arduino	Mega 2560	1			
Battery Casing	TruPower	BH-CR123A	10	(-)	(-)	68.8

Additional comments

p. 1, line 11 - The abstract discusses the stability tests, which include H₂O mole fractions. However, the rest of the abstract only discuss CO₂, CH₄ and CO mole fractions. A phrase noting the significance of H₂O (interferent?) would be appreciated.

We have removed H₂O from the abstract. H₂O was measured and used to obtain dry mole fractions of CO₂, CH₄ and CO, as mentioned in Section 3.1. We are interested in the stability of H₂O in the bags as well, due to its potential effect on isotopic compositions of CO₂. H₂O mole fraction measurements are now only left as a discussion in section 3.

“H₂O measurements are used to obtain dry mole fraction of CO₂, CH₄ and CO using the water vapour corrections described in Chen et al., 2013 and Rella et al., 2013, before assessing drift of these species.”

p. 1, line 29 – “Stratospheric changes in ozone and water vapour levels” is awkwardly phrased. How about “Changes in stratospheric ozone and water vapour levels”?

We have adopted the suggested phrase.

p. 2, line 1 – “stratospheric air up to 35 km” Please define this value (e.g. ASL).

“Above mean sea level (a.m.s.l.)” has been added.

p. 2, line 13 – “remarkable scientific efforts” I would avoid using words like “remarkable” without a substantial defence of this term.

We have adjusted the sentence and avoided the term “remarkable” care has been taken to avoid such terms throughout the text.

p. 2, line 15 – Introducing mean age of air is unnecessary here unless it is discussed later in the text.

We have left out the discussion of mean age since it is indeed not relevant to this manuscript.

p. 3, line 8 – “AirCore does not provide large sample amount” Please quantify this statement.

We have added typical values of 300 to 600 mL of stratospheric air (200 to 0 hPa) sampled with AirCore.

“The volume of air sampled between 0 to 200 hPa (12 to 30 km) by the AirCore ranges from 300 to 600 mL, depending on the geometry of the AirCore.”

p. 4, line 1 – “a diaphragm pump (KNF, product no. NMP 850.1.2 KNDC B)” Please provide a description of wetted surfaces for this pump.

A description has been added in the manuscript, after personal communication with KNF.

“The pump utilizes an EPDM rubber diaphragm (35 mm diameter) and valves, and a small piece of flexible PU tube.”

p. 5, line 20 – Storage test results. Can the authors take advantage of the results of these tests to separate leak and permeability effects for all species?

Diffusion through the bags material is species dependent. Furthermore, the diffusivity through the materials is unknown, and determination of the diffusivities require experiments beyond the scope of this work. Therefore, the experiments do not allow to separate leak and permeability effects. Besides these, most of the time the pressure difference between in and outside the bag is 0, hence there is no driving force for air to leak in or out. Only during ascent, the pressure inside the bag is higher than ambient and air might leak out. Thus, diffusion

through the material and possibly through the septum of the inlet is likely the main cause of the observed drift in mole fractions during the storage tests.

The discussion of the water vapor experiment is nicely done and touches on observed changes in CO₂; can this be extended?

With our current knowledge and data, we can only speculate the different reasons for the observed changes in CO₂. In the manuscript the only remaining correlation we could find from the data is that with water vapour. At this stage we can only postulate a potential bias in the water vapour correction function. Though the water vapour corrections are well quantified, they are not tested with low mole fractions.

p. 6, line 11 – “we observed an offset” Please describe which direction these offsets were (increase or decrease). As a reader, I wondered if this effect could have been a cause of the CO₂ offset observed during the April flight discussed later.

In the revised manuscript the direction, which is positive, has been clarified. There is no difference in preparation between the April and September flights. Due to unavailability of N₂ the bags were preconditioned with our calibration gas in the field prior to each flight. If the offsets would be the cause, it should have been most notable in CO₂, with values higher than AirCore, which is not the case. We therefore conclude that the offsets prior to preconditioning contribute little to the observed AirCore-LISA discrepancies.

“We found out that it is necessary to precondition the MLF bags before use, because we observed a positive 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”

p. 6, line 24 – “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.” This statement was ambiguous to me. Please explain exactly what is meant by “sampling error” and the significance of ozone concentration.

At the time of writing, we hypothesized that ozone might be reacting with the pump materials. However, this was checked later and apparently ozone concentrations of up to 1000 ppm does not have a significant effect on the EPDM material:

http://www.ozoneapplications.com/info/ozone_compatible_materials.htm. The sentence has thus been removed.

The sampling error encompasses any contamination effects or reactions that might alter the mole fraction during the sampling process. This has been adopted in the revised manuscript.

“The sampling error encompasses any contamination introduced by the sampling system itself. This includes chemical production of the species of interest and residual air in any dead volumes of the manifold. The chemical production during sampling is likely to be very small for two reasons. First of all, the wetted surfaces, Kynar and EPDM diaphragm, are chemically inert. Secondly, the high flow rate minimizes exposure of the sample to materials used in the sampler and hence chemical interaction with the wetted surfaces is limited. In addition, the flushing procedure with high flowrates ensures multiple turnovers of the manifold, which

reduces the surface effects on the sample. These effects are thus assumed to have no influence on the CO₂, CH₄ and CO mole fractions.

The dead volumes in the manifold are a potential source of contamination bias. The dead volume is estimated to be 1.5 mL per sample and will be at local ambient pressure prior to sampling. So, the dead volume uncertainty, σ_v , to the contribution to a sample at 200 L_{stp} sampling is very small.”

p. 6, line 28 – “However, detailed information about storage conditions are required to correct for the drift, which is usually unavailable in the field.” Why wouldn’t this be available? The detector used for analysis was in the field (see p. 9, line 27) so this data may have been collected for the samples presented here. Please explain if the data is available and whether it should be collected in future work.

The statement in P. 9, Line 27 (original manuscript) was ambiguous. The samples were analysed in the FMI laboratory at the Sodankylä observatory, which to us, being from Groningen, is “in the field”. The statement has now been modified in the revised manuscript.

“After retrieval of the payload, the samples were analysed in the TCCON laboratory”

The detailed storage information includes 1) ambient mole fractions of different species; 2) ambient temperature; 3) ambient pressure. The ambient temperature and pressure were logged by the datalogger, and the ambient mole fraction measurements of different species were not done as it would require a dedicated precise and accurate analyser. Since a robust correlation between the ambient information and the drift during storage has not been established, we would not recommend collecting this information in future work.

p. 7, line 12 – “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.” This is a nice presentation of this experiment. Was the pump subject to stratospheric temperatures? The manufacturers specification is for ambient temperature between +5°C and +40°C. Any insight that can be provided about the pump performance at stratospheric temperatures would be appreciated.

Indeed, no laboratory tests were performed at stratospheric temperatures. The pump performance could be affected by the cold environment. First, the batteries could lose capacity and cause the power supplied to the pump decreasing. The temperature inside the thermally insulated package, where the pump is located, during flight ranged between 30 and -15 °C. Secondly, the diaphragm is exposed to the cold air passing through the pump. The elasticity of a rubber is temperature dependent, which could reduce the performance of the pump. On the other hand, heat is released during operation of the pump, which increases the temperature. Finally, the effect of air temperature on sample size follows the ideal gas law, and the sample size increases at low temperatures. As no experimental data is available to determine the performance of the pump at stratospheric temperature, we assume that the pump performs the same during flight as at room temperature for the calculation of the sample size. The best insight we have is the comparison of the flight results in Fig. 4.

We have clarified in the manuscript with the following text in section 6.

“During the experiments described in Section 4, the pump was at room temperature. The pump performance could be affected by the cold environment. First, the batteries could lose capacity and cause the power supplied to the pump to decrease. The temperature inside the thermally insulated package, where the pump is located, during flight ranged between 30 and -15 °C. Secondly, the diaphragm is exposed to the cold air passing through the pump. The elasticity of a rubber is temperature dependent, which could reduce the performance of the pump. On the other hand, heat is released during operation of the pump, which increases the temperature. Finally, the effect of air temperature on sample size follows the ideal gas law, and the sample size increases at low temperatures. As no experimental data is available to determine the performance of the pump at stratospheric temperature, we assume that the pump performs the same during flight as at room temperature for the calculation of the sample size.”

p. 8, line 6 – “19.7 seconds.” How precise is this value? I’m a bit surprised that the pumping speed would be so consistent at varying pressure. There are no data points shown in Figure 3 prior to 20 sec, which makes this statement a bit hard to evaluate. The uncertainty of this value under operating conditions should be discussed with respect to the modelled behaviour that follows.

Initially pressure is constant as the bag is expanding. When expanded to its full size, the pressure starts increasing, which was found to be around 19.7 seconds which gave the best fit. This was based on visual inspection of the data. We have added an estimate of the accuracy of this number of about plus or minus 1 second, since we cannot justify otherwise.

“The sampled air volume increases linearly with the sampling time when the bag expands to its full size during the first 20±1 second’s. The moment compression is required, pressure starts increasing rapidly, and this moment was found to be 20 seconds after filling initiated.”

p. 8, line 25 – “The sampled volume at STP can be modelled for all pressure levels ranging from 200 to 0 hPa” It seems inappropriate to model to 0 hPa, given that the data collected ends at 30 hPa.

We have rephrased “modelled” to “approximated”. This was ultimately the goal of the experiment. It provides us with a tool to determine the sampling strategy in the field. And the approximation suffices.

“Combining Eq. (1) and Eq. (2), the sampled volume at STP can be approximated for all pressure levels ranging from 200 to 0 hPa for any chosen sampling time.”

p. 9, line 5 – “To be on the safe side,” should be rephrased “Conservatively,”

The sentence has been rephrased according to the suggestion made by the reviewer.

“Conservatively, 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.”

p. 11, line 10 – “the vertical resolution increases” The vertical resolution decreases since the vertical height increases. There are several significant deviations from the relationship between altitude and vertical resolution, as shown in Figure 4b: 26-Apr at 150 hPa, 4-Sep at 100 hPa and 5-Sep at 30 hPa. Could these data points be explained in the context of the discussion of the variability in vertical resolution starting at p. 11, line 14?

Indeed, the vertical resolution decreases with altitude. As explained in P. 11, Line 28 there were 3 factors that explained all the existing variability 1) varying sampling time; 2) varying ascending speed; 3) varying maximum allowed pressure.

We have highlighted the samples mentioned by the reviewer above in the manuscript.

“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. The varying ascending speed accounts for the observed deviations from the otherwise linear trend in Fig. 4b. In the lower stratosphere (10 to 15) km the maximum allowed pressure inside the bags was usually reached in a period shorter than the pre-set sampling time, leading to relatively high vertical resolution. In the region 10 to 15 km two samples deviate (4-Sep 17 km and 26-April 14 km), with lower resolution, which is due to a higher ascending speed. In the middle stratosphere, the sampling time was usually the limiting factor to vertical resolution. One sample in the middle stratosphere has a relatively good vertical resolution (5-Sep, 25 km), which is due to the relatively slow ascent speed.”

p. 11, line 25 – While the vertical profiles of the mixing ratios are shown in Figure 5, I don't see the actual values presented. Could this be added to Table 3 or as a Supplemental Table (along with individual uncertainties of both mixing ratio and vertical height)?

The data is available on request.

p. 12, line 8 - While there are significant differences between the LISA and AirCore retrieved mixing ratios for CO₂, the CH₄ and CO mixing ratios show good agreement. Can this allow the authors to make a statement about the validity of their assumptions for estimating altitudes and pressures for the failed data loggers? And does this indicate that the offset CO₂ measurement is a result of the measurement of mixing ratio rather than altitude? This comment is also for p. 12 line 30 to p. 13, line 2.

This is a very good suggestion, which we have added in our discussion (section 6.1). The CO is not a good diagnostic since virtually no gradient is observed in CO (within measurement uncertainty). CH₄ however is a good diagnostic and indeed the observed LISA and AirCore CH₄ profiles show that the altitude registration is reliable. The CO₂ offset must be related to a difference in measurement and cannot be attributed fully to altitude registration.

“The AirCore valve did not close during the 26 April 2017 flight. This complicates the altitude registration of the AirCore. However, the large degree of agreement in CH₄ profiles between AirCore and LISA shows that AirCore altitude registration is reliable for the flight on 26 April 2017. The bias in CO₂ cannot be attributed to a failure in altitude registration and hence must be related to mole fraction measurement.”

p. 12, line 17 – “0.5 ppm or 0.13%” I'm not sure that the percentage reported here is appropriate, as it implies greater analytical precision that is achieved. If the CO₂ mixing ratio varies only 20 ppm or less between the troposphere and the top of the sampling region, then 0.5 ppm is a more significant deviation. I would suggest simply removing these percentages.

We agree that depiction of a percentage leaves room for interpretation. The percentages are thus removed from the manuscript.

p. 13, line 13 – “decreases fast.” Should be “decreases quickly.” In the following sentence, “the gain in sample amount, for example adding 10 extra seconds of sampling time, does not increase” is not correct, but rather the gain in sample amount is very small in comparison to the decrease in vertical resolution. This should be restated.

The sentence in the original manuscript was indeed ill phrased and has been updated according to the reviewer’s comment.

“From the results shown in Fig. 3d, we see that after 200 seconds of sampling the gain in sample amount decreases quickly. Therefore, the gain in sample amount, for example adding 10 extra seconds of sampling time, is small, however the decrease in vertical resolution is significant.”

p. 13, line 16 - As an aside, I would suggest additional bags as an alternative to larger bags, as the altitude profiles presented in Figure 5 indicate that there are periods during the ascent when no sample is collected, i.e. the system is sitting idle.

We agree that additional bags would be a good option to increase the vertical density of the sampling, and the system presented in this manuscript can indeed be easily adapted for that. However, for other scientific needs, e.g. for more precise $^{14}\text{CO}_2$ measurements, larger samples are preferred. We have modified the text to include both cases.

“Alternatively, to increase the amount of sample retrieved during one flight, additional bags can be considered. Currently the system is idle during several stages of the ascent as can be inferred from Figure 5. This will however be more demanding on battery power. Furthermore, care has to be taken to avoid overlapping sampling schemes i.e. sampling of a sample at altitude P_1 is still ongoing while the set-point altitude for sample two, P_2 is reached. This is complicated further with variable ascent speed, that is typical for these balloon flights.”

p. 13, line 28 – It is not clear why the uncertainty in the sample amount is important. Could the authors explain the importance of this?

The sample amount is important because it often significantly influences the precision of the measurements by instruments. Since we aim to obtain larger sample amount and the sample amount was only determined indirectly from pressure and temperature measurements, we think it logical to estimate the uncertainty of the sample size. We have added the uncertainty to the captions of Figures 3 - 4.

p. 23 – Figure 3b. I found the reuse of marker shapes between 3a and 3b confusing (I was looking for a relationship between the same marker shape in both figures). Could the authors change the marker shapes in Figure 3b to avoid this? For Fig 3c, it is not clear if the units on the vertical axis use volumetric liters or standard liters. This should be standard liters for consistency. Also, in Fig 3d please extend the vertical line at 0.76 L for the full vertical height of the figure, as was done in Fig 3b.

We have adjusted the marker shapes so that 3a and 3b are now compatible. The vertical line is extended.

p. 25 – Figure 4 and Figure 5. As a color-blind reader I cannot distinguish between the colors used for the 26-Apr and 4-Sep flight data. Could the 26-Apr color be changed to a different color (e.g. blue)?

Yes, we have updated the figures with colour blind friendly palettes, and tested them with the following simulator:

<http://www.color-blindness.com/coblis-color-blindness-simulator/>

p. 27 – Table 6. Please define the acronyms VPDB and VSMOW.

The definitions have been added in the revised version, and now it is table 7.

Reference: Membrive, O., Crevoisier, C., Sweeney, C., Danis, F., Hertzog, A., Engel, A., Bönisch, H., and Picon, L.: AirCore-HR: a high-resolution column sampling to enhance the vertical description of CH₄ and CO₂, Atmos. Meas. Tech., 10, 2163-2181, <https://doi.org/10.5194/amt-10-2163-2017>, 2017.

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 CO₂, CH₄ 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 CO₂, CH₄ and CO 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 three species CO₂, CH₄ and CO. 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 CO₂, CH₄ and CO mole fractions, and evaluated against AirCore retrieved profiles, showing mean differences of 0.84 ppm for CO₂, 1.8 ppb for CH₄ 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. Changes in stratospheric ozone and water vapour levels in turn affect climate and climate

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variability (Baldwin et al., 2007). The distribution of trace gases in the atmosphere provides useful insights in atmospheric transport and chemistry. 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; however, no significant change in the strength of the BDC in the northern hemisphere at mid latitudes was detected (Engel et al., 2009, 2017). In spite of all the efforts to make observations of stratospheric tracers, GCM's remain poorly constrained (Gerber et al., 2012), a problem already pointed out several decades ago (Ehhalt et al., 1983).

In order to determine the vertical distribution of trace gases, both remote sensing techniques and airborne platforms are utilized. Remote sensing is performed either from the ground, e.g. TCCON (Wunch et al., 2011), and from satellite instruments like SCIAMACHY (Frankenberg et al., 2011) and IASI (Crevoisier et al., 2013). Although remote sensing techniques have a high spatial and temporal coverage, they are subjected to systematic bias and need to be calibrated. Calibration requires in situ measurements, of which the availability relies on infrequent campaigns (e.g. Engel et al., 2016)

In situ measurements of stratospheric air up to 35 km above mean sea level (a.m.s.l.) can currently only be achieved on balloon-borne platforms. To this end, both airborne analysers (e.g. Daube et al., 2002) as well as sampling techniques have been developed specifically for balloon-borne platforms. Of these techniques, the cryogenic sampling method (Lueb et al., 1975) is the most employed technique. It has been used for the analysis of many trace gases like SF₆, CO₂, CH₄, N₂O and halocarbons (Aoki et al., 2003; Engel, 2002; Laube et al., 2010; Nakazawa et al., 1995, 2002) and isotopic composition measurements (Kaiser et al., 2006; Rice, 2003; Röckmann et al., 2011; Sugawara et al., 1997). 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). This makes the cryogenic sampling technique suitable for multi-tracer and isotopic composition analysis. Secondly, the cryogenic technique provides a way of contamination-free sampling.

Inasmuch as their accuracy, these samplers and airborne analysers are 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 light cryogenic sampler (22 kg) using liquid neon (Morimoto et al., 2009) was developed, and launched from a research vessel to retrieve stratospheric air samples in the tropics (Fuke et al., 2014); however, it is capable of retrieving one sample per flight.

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

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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. The volume of air sampled between 0 to 200 hPa (12 to 30 km) by the AirCore ranges from 300 to 600 mL, depending on the geometry of the AirCore. 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 $\Delta^{17}\text{O}$ 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.

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In this work, we present the deployment and field-tests of a new Lightweight Stratospheric Air sampler (LISA). With the LISA sampler, we aim to develop a sampling technique complementary to AirCore. With LISA we aim for a 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. Moreover, we intend to obtain significantly larger amount of air samples from the LISA sampler than from the AirCore sub-sampler.

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The design of the LISA sampler is described in Section 2. 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.

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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 typically ranges between 0.2-12 kg. 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).

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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. The pump utilises an EPDM rubber

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diaphragm (35 mm diameter) and valves, and a small piece of flexible polyurethane tube. 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) and 5 union elbows (Swagelok, product no. NY-400-9), connected by Kynar tubing (Cole Palmer, product no. EW-95100-02). 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 servo motors, powered with 2 separate 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. The key components are summarised in Table 1.

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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 pre-set ambient pressure levels monitored by the on-board pressure sensor. In practice, when the pre-set 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 pre-set 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 CO₂, CH₄, CO and H₂O 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), aluminium foil, polyethylene, aluminium (metalised) 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 (<0.03% ppm H₂O) from a cylinder; the mole fractions of CO₂, CH₄ and CO are listed in Table 2. Since the mole fractions of methane are significantly lower in the stratosphere than a typical value of around 2000 ppb in the free troposphere

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(e.g. Rice et al. 2003; Röckmann et al. 2011), we prepared two samples (nos. 6 & 7) with low mole fractions (~120 ppm CO₂, ~600 ppb CH₄ 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.

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Directly after sample preparation, the air sample is analysed for CO₂, CH₄, CO and H₂O 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 CO₂, CH₄, CO and H₂O) 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: $[X]_{4\text{hours}} - [X]_{\text{direct}}$, where $[X]$ is the measured dry 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. H₂O measurements are used to obtain dry mole fraction of CO₂, CH₄ and CO using the water vapour corrections described in Chen et al., 2013 and Rella et al., 2013, before assessing drift of these species.

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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 CO₂ 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 CO₂, 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 CH₄ 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 CH₄ measurements when considering its large gradient in the stratosphere (500-2000 ppb e.g. (Röckmann et al., 2011)).

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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

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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 a positive 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 N₂. The bags were filled with N₂ from a cylinder and subsequently evacuated with a vacuum pump, prior to filling with test sample. In principle ambient air can be used to flush the bags, as long as it is dry.

Based on the storage test results, we choose to use the MLF bags for our sampler. The stability of CO₂ and CH₄ 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. $\delta^{18}\text{O}$ in CO₂. 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 CO₂, CH₄ and CO mole fraction measurements consists of 3 terms: sampling error, drift due to storage and analysis uncertainty. There are two contributions to the analysis uncertainty: 1) analyser precision (σ_i) and 2) calibration uncertainty (σ_c).

The sampling error encompasses any contamination introduced by the sampling system itself. This includes chemical production of the species of interest and residual air in any dead volumes of the manifold. The chemical production during sampling is likely to be very small for two reasons. First of all, the wetted surfaces, Kynar and EPDM diaphragm, are chemically inert. Secondly, the high flow rate minimizes exposure of the sample to materials used in the sampler and hence chemical interaction with the wetted surfaces is limited. In addition, the flushing procedure with high flowrates ensures multiple turnovers of the manifold, which reduces the surface effects on the sample. These effects are thus assumed to have no influence on the CO₂, CH₄ and CO mole fractions.

The dead volume in the tube connecting the bag to the manifold is a potential source of contamination bias. The dead volume is estimated to be 1.5 mL per sample and will be at local ambient pressure prior to sampling. The dead volume uncertainty, $\sigma_{p,v}$, is estimated using a dead volume of 1.5 mL_{stp}, which prior to sampling is assumed to be at 50 hPa and 220 K. This volume might remain unflushed, hence the air is of tropospheric origin, with concentrations of 400 ppm CO₂, 1800 ppb CH₄ and 150 ppb CO. The total

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sample volume is 200 mL_{stp} and has mole fractions of 395 ppm CO₂, 500 ppb CH₄ and 30 ppb CO. The bias is then calculated as the resulting deviation after mixing the contamination with sample air.

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. The drift, a consequence of diffusion through the bag's material, is governed by Fick's first and second law. A systematic correction for the drift would require the determination of the species-dependent diffusivity, which usually depends on pressure and temperature. Secondly, since diffusion depends on the concentration gradient, mole fractions of the sampler environment are needed. Hence, detailed information about storage conditions over the 3-5 hour period between sampling and analysis are required to correct for the drift. Moreover, the information required is usually unavailable in the field. Therefore, we have not determined a correction function 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 CO₂, CH₄ and CO, respectively.

Assuming Gaussian error propagation, we compute a total uncertainty on the measurements:

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

The total uncertainty includes the analyser precision (1 sigma 0.04 ppm, 0.2 ppb and 7 ppb for CO₂, CH₄ and CO, respectively), the calibration uncertainty (0.07 ppm, 1 ppb, 2 ppb for CO₂, CH₄ and CO, respectively), and the aforementioned drift.

The different uncertainties are summarised in Table 3. We compute the total uncertainty of the LISA sample measurements to be 0.14 ppm, 2.3 ppb and 7.8 ppb for CO₂, CH₄ and CO, respectively.

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25 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 sample 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_{stp}/min. 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

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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 experiments were performed at room temperature.**

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The pressure readings are initially constant, while the bag is expanding to its full size of 2.58 litre. 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.

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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 litre. 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 20 ± 1 second. **The moment compression is required, pressure starts increasing rapidly, and this moment was found to be 20 seconds after filling initiated.** 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.

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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,

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

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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_{stp}/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:

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

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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).

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Combining Eq. (1) and Eq. (2), the sampled volume at STP can be approximated 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.

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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. Conservatively, 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.

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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. 220 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.

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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 pre-set pressure altitudes. The settings of the sampling parameters are summarized in Table 4. The sampling parameters varied from flight to flight, to test the capabilities of the sampler.

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The payload consisted of an AirCore, 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 AirCore used during the campaign consists of two pieces of stainless steel tubing (40 m long ¼ in. OD and 60 m long 1/8 in. OD, wall thickness 0.01 in.), with a total weight of ~3.6 kg. The LISA sampler package weighed 2.8 kg. After retrieval of the payload, the samples were analysed in the TCCON laboratory for CO₂, CH₄ 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 CO₂, CH₄ 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 (CO₂: X2007, CH₄: 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. 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.

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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:

$$w_i = \frac{dn_i}{n}, \quad (4)$$

5 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:

$$\bar{P} = \sum_i w_i P_i, \quad (5)$$

10 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.

15 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

20 Both, the volume of the collected air samples (Fig. 4a) and vertical resolution decreases (Fig. 4b) with increasing altitude. 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 4). Furthermore, the cold temperatures in the stratosphere result in denser air, so the observed sample size are slightly higher, especially in the lower stratosphere.

25 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. The varying ascending speed accounts for the observed deviations from the otherwise linear trend in Fig. 4b. In the lower stratosphere (10 to 15) km the maximum allowed pressure inside the bags was usually reached in a period shorter than the pre-set sampling time, leading to relatively high vertical resolution. In the region 10 to 15 km two samples deviate (4-Sep 17 km and 26-April 14 km), with lower resolution, which is due to a higher ascending speed. In the middle stratosphere, the sampling time was usually the limiting factor to vertical resolution. One sample in the middle stratosphere has a relatively good vertical resolution (5-Sep, 25 km), which is due to the relatively slow ascent speed.

35 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

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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 CO₂, CH₄ 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 CO₂, CH₄ and CO mole fractions are summarized in Table 5.

A relatively large difference in the CO₂ 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 CO₂ 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 CO₂ 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 CO₂ and CH₄ 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 CO₂, 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 0.84 ppm for CO₂, 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 mean deviation of 1.8 ppb, within the uncertainties of both AirCore and LISA (see Section 3.3). CO also shows a good agreement within the measurement uncertainty of CO by the CRDS analyser.

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Several aspects are considered that could explain the observed differences. First of all, 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. Secondly, there are uncertainties associated with the calculation of AirCore weighted mean. The AirCore profile needs to be weighted for a fair comparison, since air samples at different altitudes (or pressure levels) do not contribute equally to the sampler samples. The uncertainty in altitude of the AirCore profile adds a level of uncertainty to the AirCore weighted mean. Finally, the retrieved AirCore profiles are already smoothed due to molecular diffusion and Taylor dispersion, and smearing effects in sample renewal of the cavity of the CRDS. For more information on the uncertainties associated with AirCore profiles we refer to Engel et al. (2017), Karion et al. (2010) and Membrive et al. (2017).

In the first flight on 26 April, an averaged difference of ~1 ppm in CO₂ 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 higher degree of variability in measured trace gases. The AirCore valve did not close during the 26 April 2017 flight. This complicates the altitude registration of the AirCore, especially on the lowest part of the profile. The influence on the stratospheric part of the profile is limited, which can be seen from the large degree of agreement in CH₄ profiles between AirCore and LISA.

Another potential source for the bias is outgassing from the packaging material and the balloon. As the ambient pressure decreases during ascent of the balloon flight, the desorption of trace gasses from the surface of the packaging material and the balloon occurs, which potentially influences the mole fractions of the air samples. This would, however, not explain the good agreement during the September flights. Furthermore, the inlet is located at the top of the payload and any outgassing from the packaging material would be flushed away from the inlet during ascent.

The seasonality in tropospheric CO₂ that causes the difference between sampled air and its storage environment could contribute to the observed difference. The northern hemisphere winter CO₂ mole fractions are typically 10 ppm higher those in summer. During the storage test with low mole fractions, e.g. sample nos. 6&7 in Figure 2, a drift of up to 0.8 ppm was observed. Therefore, a typical seasonal difference of 10 ppm could only explain a difference of 0.03 ppm in the observed CO₂ bias.

As seen from Table 5, the mean deviation for CO₂ reduces from 0.84 to 0.55 ppm, when the 26 April 2017 flight is excluded. Still, the sampler shows consistently higher CO₂ mole fractions than AirCore, which suggests that a small unexplained bias might exist in the LISA CO₂ mole fraction measurements compared to AirCore. CH₄ and CO on the other hand show an excellent agreement within measurement uncertainties, which suggests that no significant bias exist within the measurement uncertainties for CH₄ and CO.

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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_{stp}. The vertical resolution and sample size thus outperform the AirCore. The vertical resolution and sample size of the LISA sampler is compared to the performance of AirCore subsampled air in Table 6. It 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 quickly. Therefore, the gain in sample amount, for example adding 10 extra seconds of sampling time, is small, however the decrease in vertical resolution is significant.

During the experiments described in Section 4, the pump was at room temperature. The pump performance could be affected by the cold environment. First, the batteries could lose capacity and cause the power supplied to the pump to decrease. The temperature inside the thermally insulated package, where the pump is located, during flight ranged between 30 and -15 °C. Secondly, the diaphragm is exposed to the cold air passing through the pump. The elasticity of a rubber is temperature dependent, which could reduce the performance of the pump. On the other hand, heat is released during operation of the pump, which increases the temperature. Finally, the effect of air temperature on sample size follows the ideal gas law, and the sample size increases at low temperatures. As no experimental data is available to determine the performance of the pump at stratospheric temperature, we assume that the pump performs the same during flight as at room temperature for the calculation of the sample size.

The sample size can be increased by using an alternative pump that can deliver a higher flow rate than the current 8 L_{stp}/min and using sampling bags with a larger size than the current 2.58 L. 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 for more batteries.

Alternatively, to increase the amount of sample retrieved during one flight, additional bags can be considered. Currently the system is idle during several stages of the ascent as can be inferred from Fig. 5. This will however be more demanding on battery power. Furthermore, care has to be taken to avoid overlapping sampling schemes i.e. sampling of a sample at altitude P₁ is still ongoing while the set-point

Deleted: The deviation between AirCore and sampler results are on average 0.5 ppm or 0.13 % for CO₂, 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 CO₂, 1.8 ppb for CH₄ and 6.3 ppb for CO.

In the first flight on 26 April, an averaged difference of ~1 ppm in CO₂ 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.

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altitude for sample two, P_2 is reached. This is complicated further with variable ascent speed, that is typical for these balloon flights.

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_{stp}.

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. The error in the fit parameters, is included in the calculation. 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 is 9 mL_{stp}, 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 CO₂ and CH₄ as an example to estimate the uncertainties of isotopic composition measurements due to the storage bias (see Table 3) or the AirCore-LISA bias (see Table 5), and the estimated isotopic signatures associated with the assumed contamination source.

For any species, the measured number of molecules n_m is the sum of the number of molecules from the original source, n_s , and the contamination n_c that entered the sampling bag through diffusion:

$$n_m = n_s + n_c \quad (6)$$

Diffusion is governed by Fick's law:

$$J = D \frac{\partial C}{\partial x} \quad (7)$$

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	Where J is the diffusion flux, D the diffusivity and $\frac{\partial C}{\partial x}$ the concentration gradient of diffusing species, e.g. CO_2 . Each layer of the MLF bag has its own specific diffusivity and sorption characteristics, and for simplicity here we assume that it can be modelled with a single diffusivity constant that is only species-dependent. The process of sorption of gases into the solid material and the interaction governing that	Formatted ... [3]
5	process is also ignored for simplicity. Then the total diffusion out of the bag which is of stratospheric origin, denoted by v_{out} . The total amount diffusing into the bag, denoted by v_{in} is of tropospheric origin. Assuming that these two fluxes can be modelled with a law of mass action:	Formatted ... [4] Formatted ... [5]
	$v_{\text{in}} = DC_c$ (8)	Formatted ... [6]
	and	
10	$v_{\text{out}} = DC_s$ (9)	Formatted ... [7]
	Where C_c is the concentration of ambient air that contaminates the stratospheric sample in the bag denoted by C_s . The bias that we measure is as follows:	Formatted ... [8] Formatted ... [9]
	bias = $v_{\text{in}} - v_{\text{out}}$ (10)	Formatted ... [10]
15	Assuming that v_{out} is purely stratospheric and v_{in} is purely tropospheric, and that c_{out} and c_{in} are mole fractions outside and inside the bags and are assumed to be constant. We can estimate the fraction of tropospheric contamination in our sample. The measurement (C_m) is the sum of the original stratospheric sample (C_s), minus the sample that is leaving the bag and the tropospheric sample entering the bag:	Formatted ... [11] Formatted ... [12] Formatted ... [13]
	$C_m = C_s - v_{\text{out}} + v_{\text{in}}$ (11)	Formatted ... [14]
	And the contaminating fraction is then f_c is	Formatted ... [15]
20	$f_c = \frac{v_{\text{in}}}{C_m} = \frac{C_c \cdot \text{bias}}{C_m(C_c - C_s)}$ (12)	Formatted ... [16] Formatted ... [17]
	Where the right-hand side is obtained by using Eq. (8) to (10). The sample fraction, f_s is simply	Formatted ... [18]
	$f_s = 1 - f_c$ (13)	Formatted ... [19]
	The isotope composition after the mixing of the tropospheric contamination into the sample air, can be approximated with:	Formatted ... [20]
25	$\delta_m \approx \delta_s f_s + \delta_c f_c$ (14)	Formatted ... [21]
	where δ_m is the final isotopic composition, and δ_s and δ_c represent the isotope composition of source and contamination and f_s and f_c are the fractional contributions to the total number of molecules after mixing. We further define the bias of the isotopic composition measurement as	Formatted ... [22] Formatted ... [23] Formatted ... [24]
	$\Delta\delta = \delta_s - \delta_m$ (15)	Formatted ... [25]
30	Combining Eq. (8) and Eq. (9), we derive	Formatted ... [26]
	$\Delta\delta = (\delta_c - \delta_s) f_c$ (16)	Formatted ... [27]
	For the calculation, we regard the mean differences between AirCore and LISA measurements (Table 5, e.g. 0.84 ppm for CO_2 and 1.8 ppb for CH_4) as the upper limit of bias induced in the stratospheric samples. Another estimate is performed based on the storage test results, that showed maximum drift of of 0.11	Formatted ... [28]
35	ppm CO_2 and 2 ppb CH_4 presented in Table 3.	
	The fraction f_c can be calculated according to Eq. (12) with C_c being the typical stratospheric mole fraction, which is taken to 395 ppm for CO_2 and 500 ppb for CH_4 . We use typical tropospheric values of 405 ppm for CO_2 and 1800 ppb for methane. The isotopic compositions δ_c and δ_s are taken from various	Formatted ... [29] Formatted ... [30] Formatted ... [31] Formatted ... [32]

references, and are presented in Table 7. The resulting bias in the isotopic composition measurements are presented in Table 7.

We can readily see that the estimated uncertainties due to the storage bias are relatively small compared to the typical analytical precisions, also presented in Table 7. Hence the LISA sampler provides a viable sampling tool for accurate measurements of stable isotopes in CO₂ and CH₄.

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 CO₂, CH₄ and CO mole fraction measurements. Laboratory test results show that both MLF and Tedlar bags can maintain the sample mole fractions of CO₂, CH₄ 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 CO₂, 2.3 ppb for CH₄ 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 CO₂, CH₄ and CO mole fractions, and evaluated against AirCore retrieved profiles, showing mean differences of 0.84 ppm for CO₂, 1.8 ppb for CH₄ 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.

Data availability

The data presented here is available on request. (huilin.chen@rug.nl)

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As CO₂ and CH₄ 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:

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

where 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 CO₂ and 1.8 ppb for CH₄) as the upper limit of the sampling and storage errors of the stratospheric samples, and take typical stratospheric CO₂ and CH₄ mole fractions of 390 ppm and 500 ppb, respectively. The fraction f_c can be calculated according to $f_c = \frac{\text{bias}}{[X] + \text{bias}}$ where [X] is the typical mole fraction. We use typical tropospheric values for δ_s and typical observed stratospheric values for δ_c . 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 CO₂ and CH₄.

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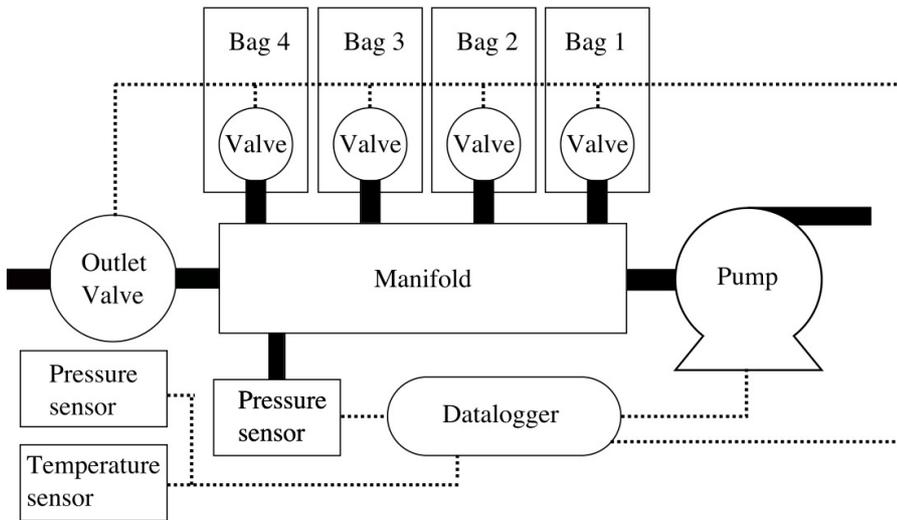


Figure 1: A schematic diagram of the sampler. Four bags are connected to a custom-made manifold. A small servomotor operates the screw cap combo valve. The outlet valve is the same as that of the bags, but is normally open when the sampler is idle during flight, allowing air pressure to equilibrate with 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.

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Table 1: Components used in the LISA sampler, including manufacturer and product key. The total weight is given for amounts per part. Voltage and power are presented according to manufacturer specification. The total weight for the onboard computer and sensors is given.

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Component	Company	Product key	Amount	Voltage (V)	Power (W)	Weight (g)
Servo motor	Hitec	HS-65HB+	5	4.8-6	1.32	91
Pump	KNF	NMP 850.1.2 KNDC B	1	24	10.8	403.6
Bag (MLF)	Supelco	30227-U	4	(-)	(-)	80.4
Tube	Cole Palmer	EW-95100-02	1	(-)	(-)	30
Union T	Swagelok	NY-400-3	5	(-)	(-)	39
Union Knee	Swagelok	NY-400-9	5	(-)	(-)	33
Battery	(-)	CR123	10	3	(-)	166
Pressure sensor	Honeywell	HSCMAND01SPASA5	2	(-)	(-)	(-)
Temperature sensor	IST	600C (100Ohm)	1	7-12	(-)	87.4
Datalogger	Arduino	Mega 2560	1	(-)	(-)	(-)
Battery Casing	TruPower	BH-CR123A	10	(-)	(-)	68.8

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Table 2: 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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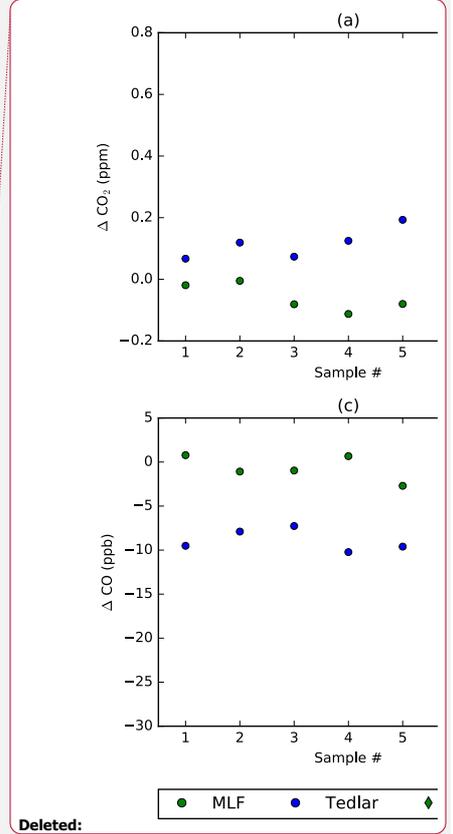
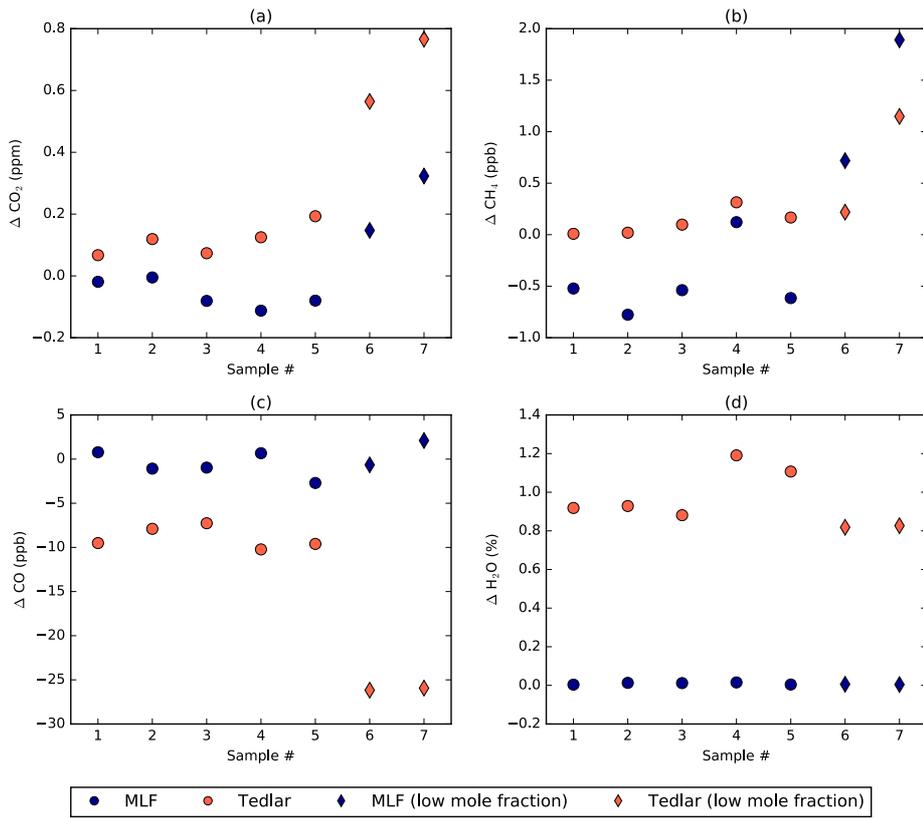
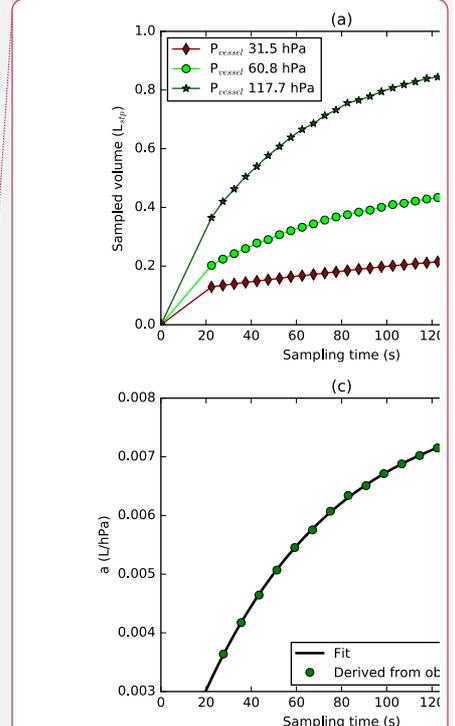
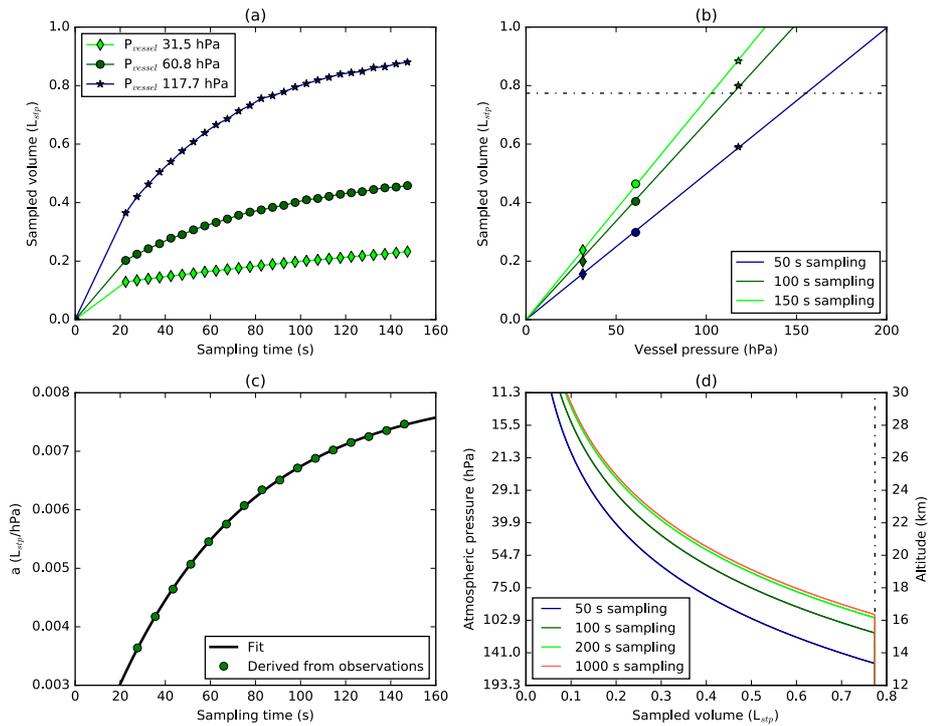


Figure 2: The observed drift of the mole fractions of CO₂ (a), CH₄ (b), CO (c) and H₂O (d) in each of 7 samples in both Tedlar and MLF bags. The drift is defined as the difference between the measured mole fractions after 4 hours and those measured immediately after filling. For CO₂, the mole fractions 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 CH₄.

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Figure 3 a) Sample volume as a function of the sampling time in seconds. The first 19.7 ± 0.3 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 (markers correspond to those presented in 3a). 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 dashed 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 data 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, as a function of modelled sampled volume. Note that for atmospheric pressure > 120 and < 30 hPa, as well as for sampling time > 150 the depicted model relies on extrapolation of the observations. The International Standard Atmosphere is used to link pressure and altitude. The cut-off at the sample size of $0.77 L_{stp}$ is due to the practical fill limit of 300 hPa which consequently means that the sampling time is less. The uncertainty in volume presented in a and b is 7.6 mL_{stp} .

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Table 3: Uncertainty based on the different error sources for CO₂, CH₄ and CO. The total uncertainty is calculated using Gaussian error propagation. ¹The dead volume bias is estimated using a dead volume of 1.5 mL_{STP}, which prior to sampling is assumed to be at 50 hPa and 220 K. This volume might remain unflushed, hence the air is of tropospheric origin, with concentrations of 400 ppm CO₂, 1800 ppb CH₄ and 150 ppb CO. The total sample volume is 200 mL_{STP} and has mole fractions of 395 ppm CO₂, 500 ppb CH₄ and 30 ppb CO. The bias is then calculated as the resulting deviation after mixing.

Source	CO ₂	CH ₄	CO
Analyser	0.04	0.2	7
Calibration transfer	0.07	1	2
Dead volume ¹	0.002	0.605	0.056
Storage drift	0.11	2.0	2.7
Total	0.14	2.3	7.8

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Table 4: 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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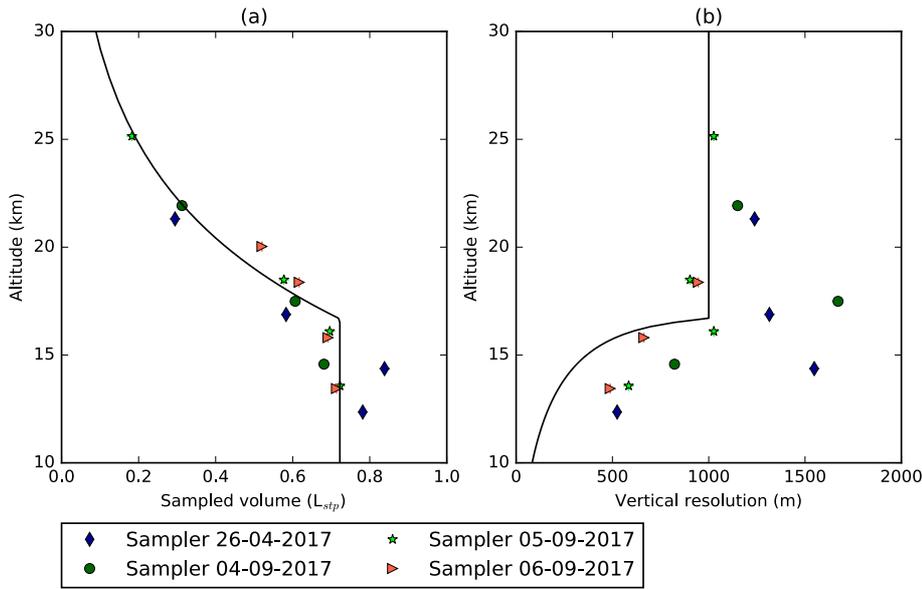


Figure 4: a) The altitude profile of the sample size of the collected 15 air samples. The estimated sample size with the sampling time of 200 seconds, and a maximum allowed bag pressure of 280 hPa, using the empirical relations used in Section 4 is shown in blue line, the same as in Fig. 3d. The uncertainty in volume presented is 7.6 mL. 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. The black solid line shows the expected vertical resolution, assuming an ascent speed of 5 m s^{-1} . Sampling time is calculated using the empirical relations discussed in Section 4, with a maximum allowed pressure of 280 hPa. If this is not reached we have used the maximum sampling time of 200 seconds, which corresponds to a vertical resolution of 1 km.

Table 5: Comparison of CO_2 , CH_4 and CO mole fractions between AirCore and LISA measurements. The difference is calculated as AirCore - LISA. The correlation coefficient between LISA and averaged AirCore is also presented. *Excluding the April 26 flight

Species	Mean $\pm\sigma$	R^2	Mean $\pm\sigma$	R^2
CO_2 (ppm)	-0.84 ± 0.47	0.93	-0.55 ± 0.13	0.97
CH_4 (ppb)	-1.8 ± 16.2	0.99	5.1 ± 13.1	0.99
CO (ppb)	6.3 ± 6.6	0.58	9.2 ± 5.2	0.59

This sidebar contains a smaller version of Figure 4(a) at the top, showing the altitude profile of sample size. Below it is a list of document actions:

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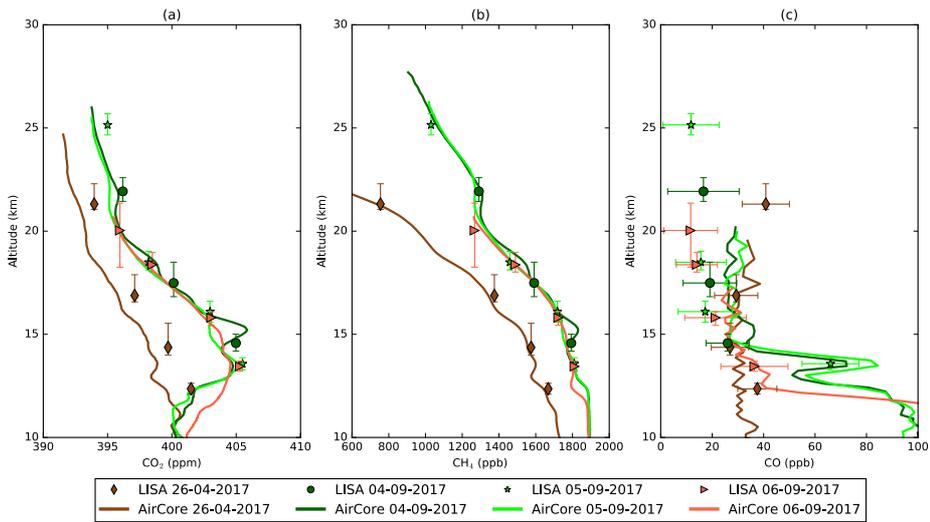


Figure 5: Comparison of AirCore and LISA measurements of (a) CO₂, (b) CH₄ and (c) CO mole fractions. The AirCore CO profiles are averaged in 100 m bins to smooth the relatively large noise of the measurements due to the analytical precision of 7 ppb (1 σ) of the CRDS analyser. Different colours and symbols are used to label the samples from different flights shown in the legend.

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Table 6: 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

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Table 7: Expected bias in stable isotope measurements on samples obtained by LISA, due to the limited accuracy of the LISA sampler. Typical values for the troposphere and stratosphere are taken from the indicated references: A) (Troler 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). Reported measurement reproducibility's, Re , for stratospheric air are also provided. $\delta^{13}C$ and $\delta^{18}O$ values are with respect to Vienna Pee Dee Belemnite (VPDB) and $\Delta^{17}O$ and δ^2H are with respect to Vienna Standard Mean Ocean Water (VSMOW). f_c was calculated using a source value 395 ppm (CO₂) and 500 ppb (CH₄). For f_{c1} contamination values of 0.84 ppm (CO₂) and 1.8 ppb (CH₄) based on LISA AirCore observed mean bias, resulting in $\Delta\delta_1$; For f_{c2} the maximum observed drift (Fig. 2) of 0.11 ppm (CO₂) and 2 ppb (CH₄) are used, resulting in $\Delta\delta_2$.

Species	δ_s (‰)	δ_a (‰)	Re (‰)	LISA-AirCore		Storage drift	
				f_{c1}	$ \Delta\delta_1 $ (‰)	f_{c2}	$ \Delta\delta_2 $ (‰)
$\delta^{13}C$ (CO ₂) (VPDB)	-7.5 (A)	-8.4 (E)	0.02 (E)	0.077	0.077	0.010	
$\delta^{18}O$ (CO ₂) (VPDB)	-2 (A)	12 (E)	0.05 (E)	0.086	1.203	0.011	0.158
$\Delta^{17}O$ (CO ₂) (VSMOW)	0 (B)	7 (B)	0.2 (B)	0.602	0.602	0.079	
$\delta^{13}C$ (CH ₄) (VPDB)	-47 (C)	-20 (F)	0.7 (F)	0.006	0.134	0.149	15
δ^2H (CH ₄) (VSMOW)	-85 (D)	190 (F)	2.3 (F)	0.006	1.366	1.517	

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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 SF₆ and CO₂ measurements performed on cryogenically retrieved samples (Engel, 2002). Long-term monitoring of CO₂, CH₄, N₂O and various halocarbons and isotopic analysis of CO₂, CH₄, N₂O 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 N₂O 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. (Brennkmeijer et al., 1995) studied the correlation of CO₂, CH₄ 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 ¹³C and ²H isotopic composition of stratospheric CH₄ is strongly correlated with its mole fractions (Röckmann et al., 2011) and similar findings were presented for N₂O (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).

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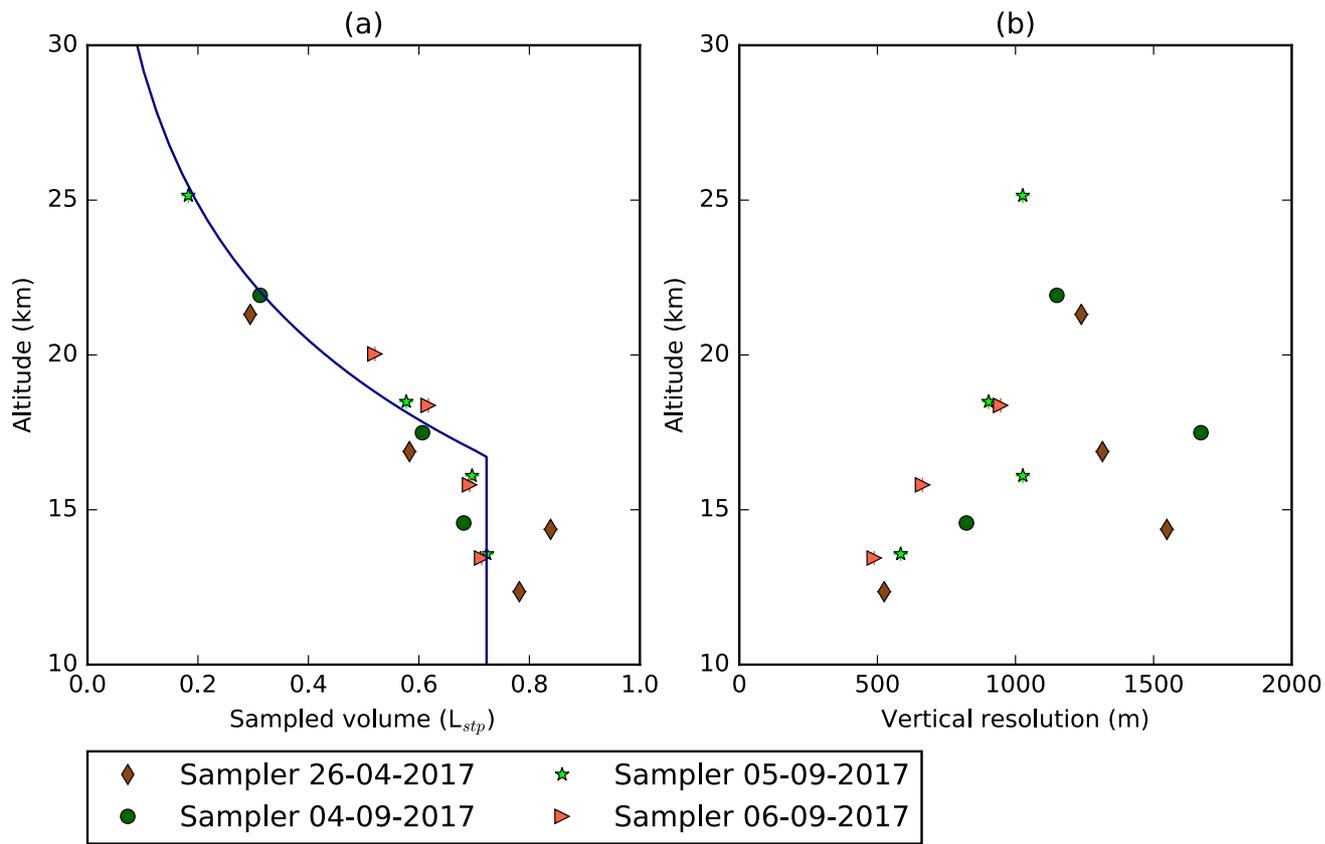
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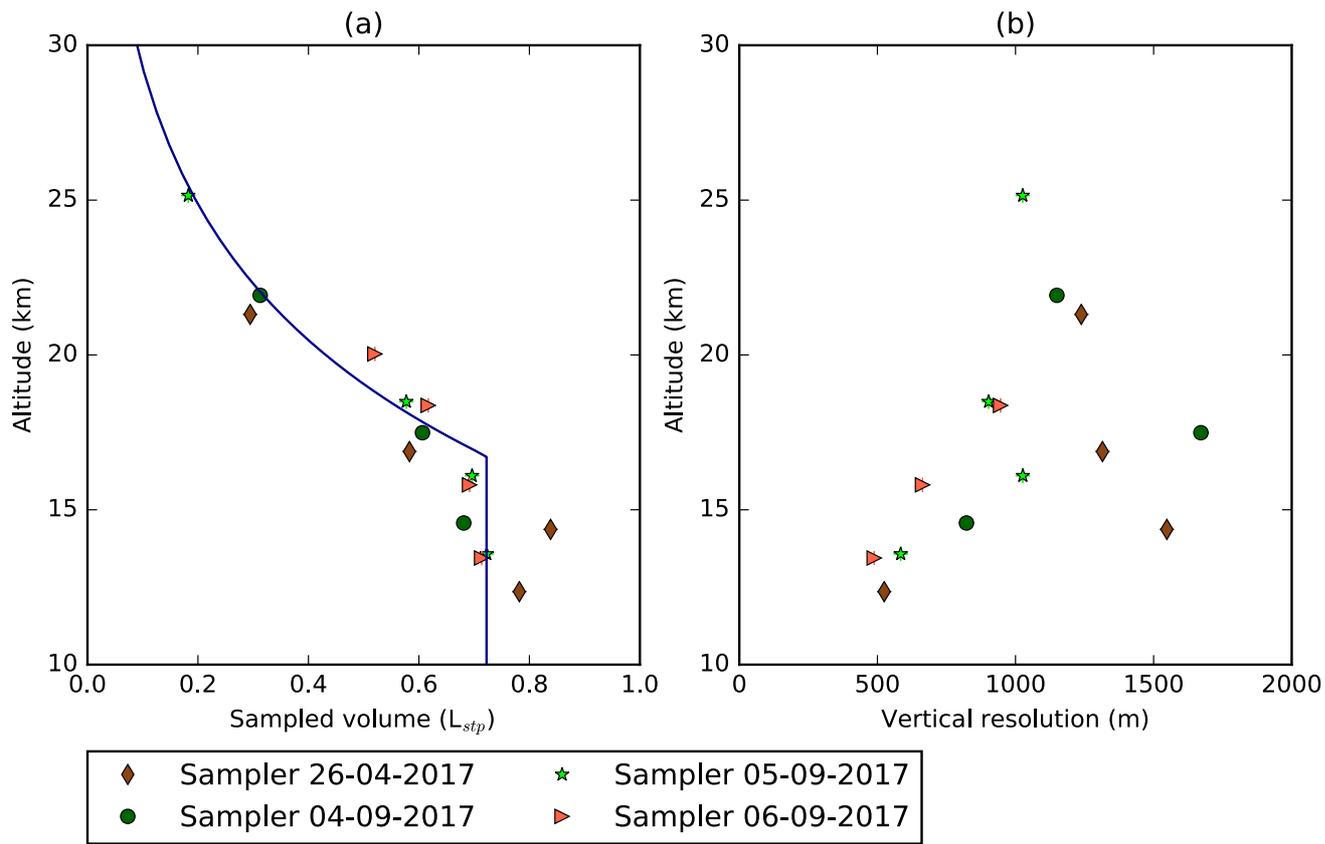
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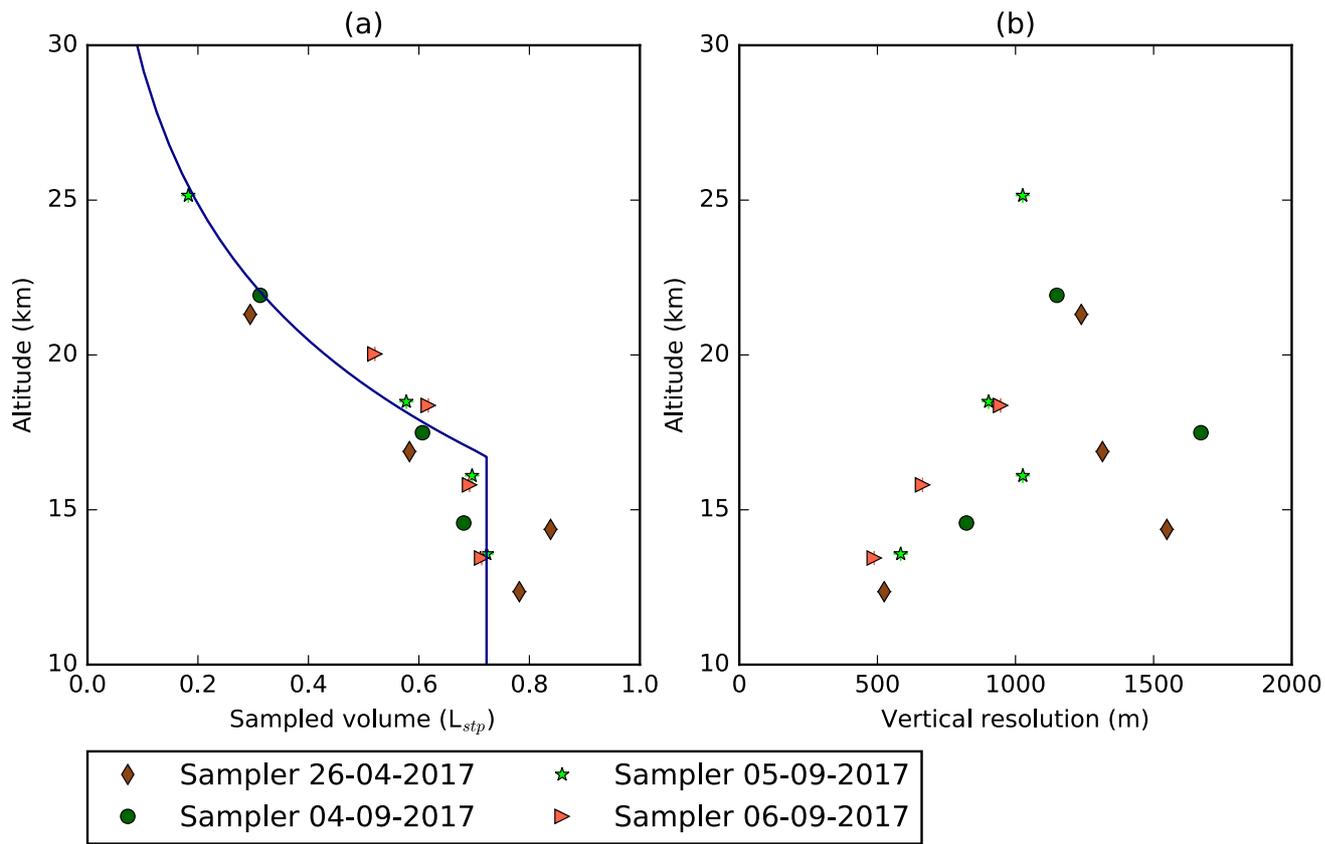
Table 2: Fit constants for Eq. (3) and standard error of the fit.

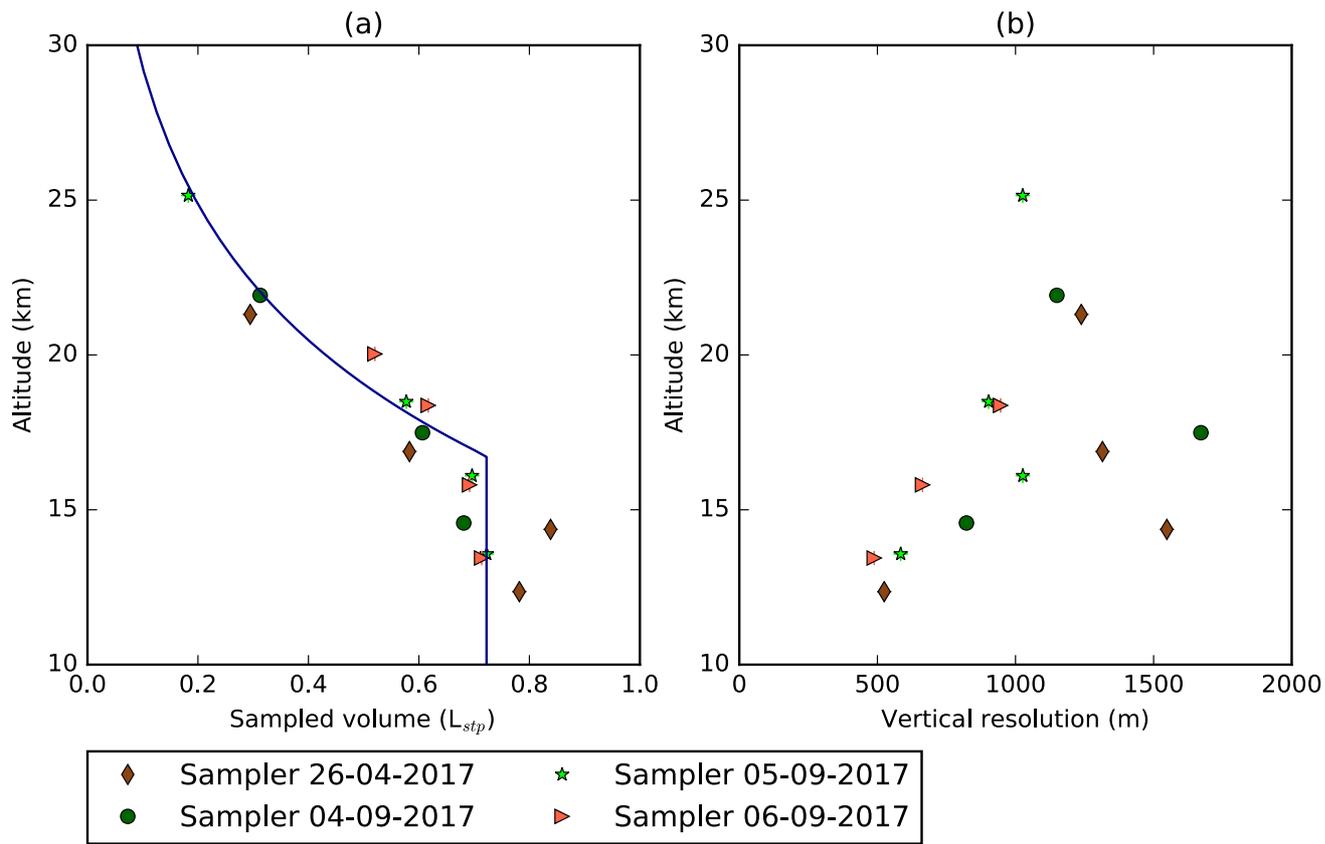
Parameter	Value	Error (1 σ)
x	0.0080	0.00003
b	0.0050	0.00002
τ	59.61	0.82

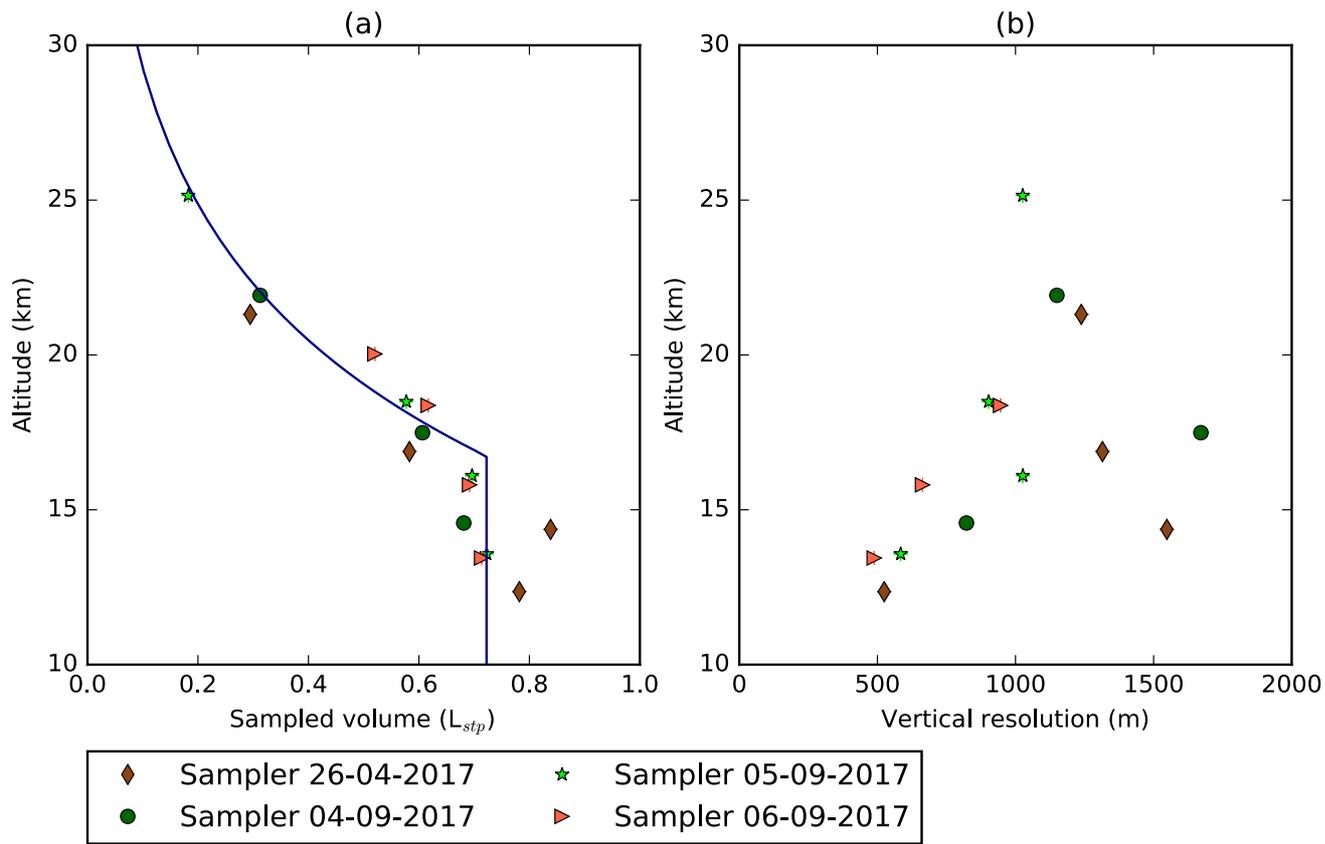
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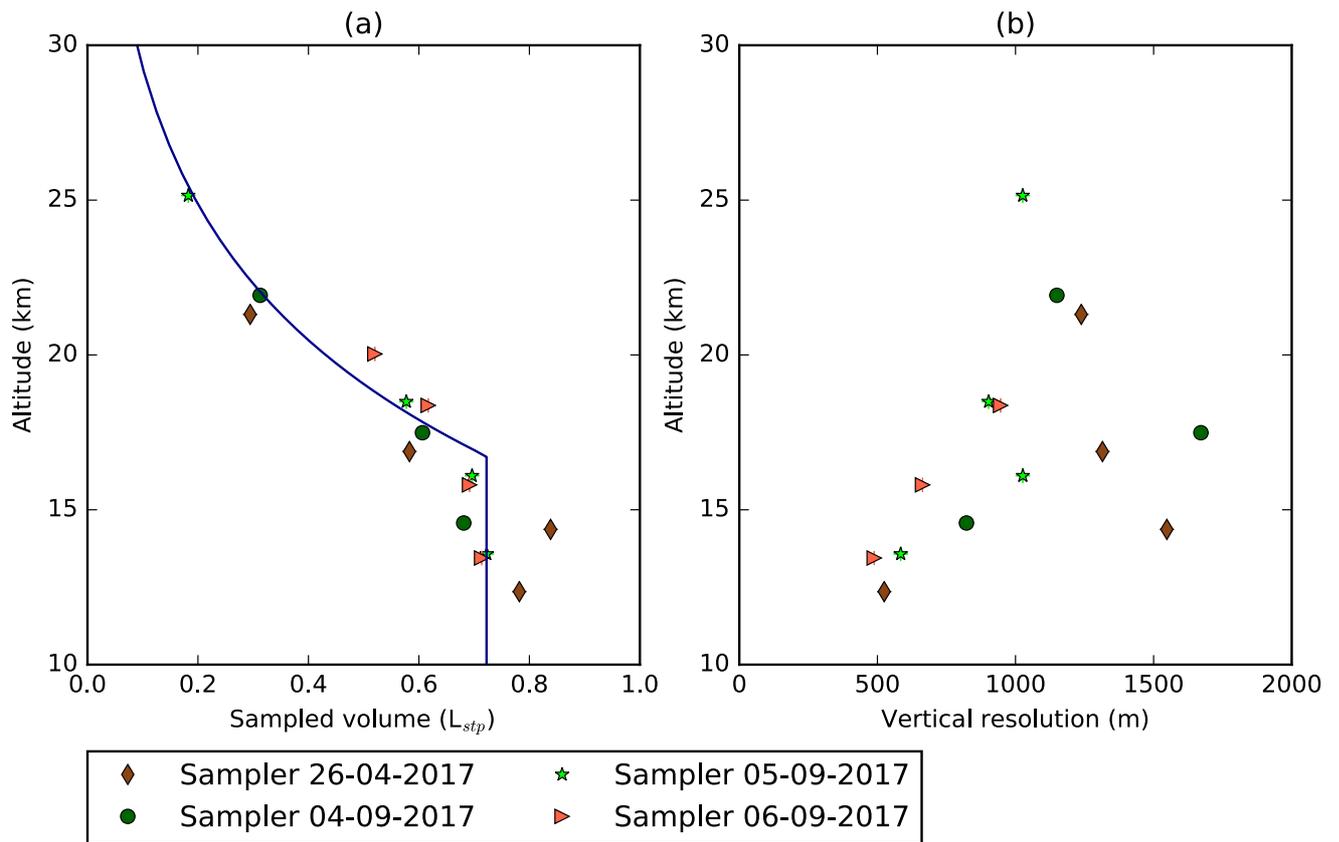












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Table 6: Expected bias due to the limited accuracy of the LISA sampler. Typical values for the troposphere and stratosphere are taken from the indicated references: A) (Trolier et al., 1996) B) (Mrozek et al., 2016) C) (Nisbet et al., 2016) D) (Bergamaschi et al., 2001) E) (Aoki et al., 2003) and F) (Röckmann et al., 2011). f_c was calculated using a source value 390 ppm (CO₂) and 1000 ppb (CH₄); contamination values of 0.55 ppm (CO₂) and 5.1 ppb (CH₄). Reported measurement reproducibility's for stratospheric air are also provided.

Measurement Reproducibility (‰)
0.02 (E)
0.05 (E)
0.2 (B)
0.7 (F)
2.3 (F)

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