Stability of Halocarbons in Whole Air Samples
Response to Referee #1

We thank referee#1 for the thorough reading of our manuscript, in particular for spotting the mismatch between the discussed compounds and compounds shown in Figure 3. All suggested changes and raised questions were carefully considered when revising the manuscript and we address them point by point in the following.

Main comments:

– *Figure 3. There seems to be some confusion regarding which species are presented. Panel B shows results for dichloromethane, whereas the text talks about tetrachloroethene (P6 L30, P7 L3). I'm assuming this is simply a mix-up, but it makes the entire section rather difficult to understand.*

Tetrachloroethene was mentioned in the text erroneously as the substance shown is dichloromethane. We have corrected this.

– *With regards to Figure 3, it is also not clear to me as to why the dichloromethane/CFC-12 ratio of the 'orange' sample is higher than the other two samples filled with the exact same ratio of standard/synthetic gas. I suspect that all three are within the measurement uncertainty. In which case it might be good to find some way of showing the error bars which are currently omitted.*

We have modified the figures for the revision of the manuscript now including daily values of the measurement precision for each individual day of measurement.

– *While there were several very interesting results presented, I did not feel that the authors provided much in the way of reasoning for a number of their findings. For instance, why did bromomethane and chloromethane increase in the cylinders over the length of the short-term (and long-term) storage tests? Presumably due to production as a result of the decomposition of more complex chlorinated compounds? The same can be said of H-1301, which would appear to be a strange result. I would not expect to see complex chemical mechanisms in this sort of paper, but it would be useful to have some brief discussion of these points.*
We think that the current experiments do not provide sufficient information to speculate about the mechanisms of the observed changes and this is beyond the scope of the experiment series. We have, however, seen growth of chloromethane and chloromethane in newly welded cylinders of identical shape to the ones used inside HIRES. In addition, we have seen both compounds to be unstable in a high-pressure stainless steel gas bottle, though on longer time periods of the order of months to years. The result for H-1301 is indeed strange and we will look into this further with new cylinders in future experiments with and without the multiposition valves.

- *I think the title needs to be revised. At current, it suggests that the storage tests were conducted on samples collected in the UTLS, while in fact they were conducted using samples prepared in the laboratory.*

We agree and have modified the title which now reads: "*Stability of Halocarbons in Whole Air Samples Collected in Stainless Steel Canisters* "

- *P1 L1. 'Halogenated halocarbons of' should be changed to 'halocarbons in'.*
Changed to: `Measurements of halogenated trace gases in ambient air …`

- *P1 L17. The sentence needs extending. Suggest 'growth was observed during storage for some compounds,…'*
The sentence is modified and now reads: "`Also growth was observed during storage for some species, namely for HFC-152a, HFC-23, and Halon-1301.`"

- *P1 L21. Delete 'the' before stratospheric.*
Done.

- *P2 L7. Remove comma after 'both'.*
- *P2 L24. Remove comma after 'both'.*
Changed.

- *P2 L26. 'Flask' should be plural.*
Done.

- *P2 L33. Start of sentence does not read correctly. Suggest replacing 'got' with 'has been'.*
Changed.

- *P4 L26. 'Details' should be singular.*
Changed.

- *P5 L4. There should be a space between 'Figure' and '2'.*
Modified.

- *P5 L6. This sentence doesn't quite make sense. I think it's supposed to read 'bellows pumps, in this set-up the samples are pressurized…'.*
The sentence was changed to: "`Contrary to the set-up in flight, when the HIRES cylinders are filled with ambient air pressurized by the metal bellows pumps, in this set-up they are pressurized directly from high pressure gas cylinders.`"

- *P5 L15. Purely out of curiosity – how many samples can be obtained from a single whole air sample at a flow rate of 100/150 ml/min? It might be good to include this figure at some point in the text.*

If the samples were exclusively for analysis in our lab, we could obtain 3 enrichments of 1 l from a 4.5bar cylinder (which is 3.5bar above ambient; at pressures below 0.5 bar above ambient the flow rate starts to decrease significantly and we found that measurements with very low enrichment flows are not reliable). From samples from our ground site program we usually do 2 enrichments for quality assurance. This cannot be done with HIRES samples because the air needs to be saved for other analyses. We prefer to not discuss this in the manuscript as it is unrelated to the question of compound stability.

- *P6 L16. The mention of the presence of an air-conditioning unit in the laboratory is fitting given the nature of the gases studied. However, it would be more useful to quote the refrigerant blend used, e.g. R-410A. Very high levels of these gases in the laboratory environment might affect the analysis, if there are small leaks in the system.*

The air conditioning of the laboratory uses water, thus it can be excluded that the results are influenced. We have added the following statement in the revised version of the manuscript: "`The air conditioning uses water and is therefore not expected to adversely influence halocarbon analysis.`"

- *P7 Figure 3 caption. I'm confused by what the solid black line represents. From the caption 'The solid black line represents the value expected from direct measurements of the standard gas and the synthetic air.' Why is the black line a mix of the two gases? I would have thought it would be better if the black line was a direct measurement of the undiluted standard gas? Or is this to account for contamination in the synthetic air. Some additional description would be useful here.*

We look at ratios of all discussed compounds relative to CFC-12, and the black line does indeed represent that ratio for the undiluted standard gas. However, for those compounds which are present as contamination in the synthetic air, i. e. carbonyl sulfide, chloromethane, HFC-152a, and tetrachlorethene, this contamination has to be - and is – taken into account. We have removed that somewhat confusing statement here and refer to the explanation in section 2.3 instead.

- *P7 L9. Throughout the previous paragraph tetrachloroethene is referred to as 'C2Cl4', but here it is referred to be its full name. Suggest using C2Cl4 throughout.*

As noted above the figure shows dichloromethane while the text said tetrachlorethene (for which results are similar). This is corrected in the revised version of the manuscript.

- *P8 L2. Suggest replacing 'right' with 'immediately'.*

Changed to: "`already one day after pressurization`"

- *P8 L19. 'Is' should be 'are'.*

Changed to "`shown is the ratio`" as in the figure caption.

The corresponding paragraph now reads:
"Some substances that were found to be stable during the one week short-term test decreased after longer storage times, for example dichloromethane shown in Figure 4(b). A similar behaviour was observed for trichloromethane (CHCl3), tetrachloromethane (CCl4), trichloroethene (C2HCl3), tetrachloroethene (C2Cl4), tribromomethane (CHBr3), and bromochloromethane (CH2BrCl). Measurements of these compounds should not be evaluated for the HIRES canisters if analysis takes place later than two weeks after sample collection as the long-term test indicates changes of mixing ratios start to occur after that period. In general, the decrease during long-term seems to be independent of the influence of ozone, although the gas mixture that shows the largest depletion (light blue dashed line, mostly cut off in Figure 4) did contain ozone. Ozone could not be monitored during the pressurization of the samples. It can therefore not be excluded that this gas mixture may have been exposed to a different amount of ozone than the one represented by the dashed brown line which could have caused the stronger depletion."

This was added.

Currently we do not have any explanation for this. As we speculate in the original manuscript, a possible source of fluourinated compounds could be valve sealing material as the seals of the Valco multiposition valves are made from PFTE and currently we cannot add any further reasoning on why these compounds grow.

We hope that further tests with new cylinders with and without this type of valves will shed some light on this growth. The result for Halon-1301 is indeed confusing. In an experiment performed with newly welded cylinders only using stainless steel parts (including the valves) we did not observed measurable changes of Halon-1301 over a storage period of 12 days. We will perform further experiments with and without the multiposition valves.

The diamonds are the results of the fast in-situ measurement integrated of the sample period of the canister samples. This information is added to the figure caption which in the revised manuscript reads: "Time series of ozone (red), CFC-12 (yellow) and dichloromethane (blue) during a flight from Munich to Denver on 22 March 2018. Ozone high resolution data represented by the red line were

integrated over the sampling period of each whole air
sample (red diamonds)."

- *P13 Figure 6. It would be useful to include the R value somewhere on each individual plot.*
R² values were added to the plots.

- *P13 Figure 6. There is some overlap of the colour bar with the underlying scatter plot.*
This is on purpose to not interfere with axis labels.

Stability of Halocarbons in Whole Air Samples
Response to Referee #2

We thank referee#2 for the thorough reading of our manuscript and we appreciated the helpful comments and remarks. During revision of the manuscript we considered all suggested modifications and questions which are addressed point by point in the following.

General notes:

- *General: This paper adds valuable information about the stability of halocarbons measured sampled by the CARIBIC project using the HIRES sampler in the UT/LS. It reveals problems for many species with respect to general stability and/or reactivity towards ozone. These tests are welcome, though they should have been performed much earlier. Similar tests for other analyzed species, such as hydrocarbons would be of value as well. In addition to the tests with artificial air mixtures, the HIRES sampler should be tested under flight conditions. That is, several cylinders should be filled with the same UT/LS air and then analyzed over the course of days to weeks in the laboratory.*

  We fully agree that a storage test with parallel filling of several cylinders in flight would yield valuable results. Currently, parallel filling of several samples is technically not possible without major reprogramming of the control unit software. The reason is that to avoid cross-contamination of sample in flight only one valve may be open at a given time. Therefore, while easily possible on the ground, such a test cannot be performed in flight.

- *Otherwise the title should probably be changed to something like "Stability of Halocarbons in Simulated Air Samples from the Upper Troposphere and Lowermost Stratosphere".*

  We agree that the initially chosen title does not accurately reflect the content of the manuscript. The title of the revised manuscript will read "*Stability of Halocarbons in Whole Air Samples Collected in Stainless Steel Canisters* ".

Specific comments:

- *P. 3. Line 9: What kind of stainless steel is the sampler made out of? Is it electropolished? How was it welded?*
  The canisters of the present HIRES were not electropolished. They are made from stainless steel (standard 1.4541), welding was micro plasma welding. Canisters for a new sampling unit currently under construction are made from electropolished steel and are electron beam welded in a vacuum chamber.

- *P. 3. Line 13: How were the leak tests performed? Static with a gas? If so, using what gas at what pressure? Or is it evacuated? Why does the sampler contain either air from the previous flight or gas from the leak test? Also, have the authors considered to precondition the cylinders with moist air? This may have a positive impact on*

storage for several species (unless the water layer is removed quickly by the dry UT/LS air).

Pre-flight leak tests are performed with ambient air passed through a molecular sieve. Evacuation of the cylinders is not possible, therefore there is always air from the previous filling left. The reason is that the canisters are made from stainless steel foil of only 0.25mm thickness. They are mechanically stabilized but nevertheless will fully collapse when evacuated. Tests during the construction phase showed that evacuation below 600 mbar is not save. Preconditioning with moist air was not tested so far.

The corresponding section of the revised manuscript now reads: `"Before a flight, HIRES undergoes leak testing with ambient air passed through a molecular sieve, but cylinders are not preconditioned. On take-off, cylinders will usually hold remnant air from the last research flight or from the leak test. The reason is that due to mechanical stability of the thin-walled flasks they should not be evacuated to absolute pressures below 600 mbar."`

— *P. 3. Line 17: What final pressure is usually achieved after 20 s venting? In other words, what is the dilution factor? If tropospheric/laboratory air is still in the cylinders, more flushing is needed than if previous UT/LS samples are still in the cylinders.*
— *P. 3. Line 18: Again, what is the final dilution? 0.2 to the 8? Is this dilution sufficient to flush out lower tropospheric/laboratory air?*

After 20s venting, ambient pressure is reached which aboard the aircraft is approx. 700 mbar, resulting in a dilution factor of less than 0.2. Tests during the construction phase and monitoring based on NMHC measurements during the first years of operation of the sampler have shown that eight iterations of flushing do reliably dilute remnants of previous fillings of tropospheric air.

The new wording in the revised manuscript reads: `"Tests during the construction phase and monitoring based on NMHC measurements during the first years of operation of the sampler have shown that eight iterations of flushing do reliably dilute remnants of previous fillings of tropospheric air. In flight, canisters are therefore flushed with ambient air eight times, this is achieved by filling a flask to 4 bar followed by venting for 20 s. After this time ambient pressure is reached which aboard the aircraft at flight altitude is 700 mbar. After that, canisters are eventually pressurized to 4.5 bar.`
`The total time needed for this procedure is 4min of which the final pressurization takes 10-20s.`

— *P. 4. Line 1: The flushing/filling procedure should be explained in more details. Are the three flushing iterations in addition to the previous 8 times? Or are those the last three of the eight?*

They are the last of the eight and this has been made more clear in the revised version of the manuscript. P4-L1-3 now read: `"The sampling period is defined as the time interval during which at least 97 % of`

the sample air was collected. This comprises the last
three of the eight flushing iterations and the final
pressurization stage, adding up to a total sampling time
of 1—2 min."

– *P. 4. Line 5: How much time does usually pass (min/max/mean) between sample taking in the airplane and analysis in the lab?*
To answer this question, the following statement was added during revision of the manuscript at the end of subsection 2.1.: "*If a halocarbon analysis is performed it is usually last in a series of measurements and takes place approximately 3 to 5 weeks after the flight. The duration of the long-term storage test time of 8 weeks was deliberately chosen beyond this period."*

– *P. 4. Line 9: What is the effect of heating the Mg(ClO4)2 on the analytes?*

All the tubing is heated to avoid condensation of moisture (relevant for HIRES only for tropospheric samples). In addition, for example bromoform tends to get lost to walls of tubing if these are not heated. We have added the following statement to the text: "*All tubing is heated to avoid condensation of moisture (relevant for HIRES only for tropospheric samples) and to minimize wall losses."*

– *Section 2.2: There does not seem to be any focusing step involved, other than on the pre-column, which at 50 oC probably does not focus very much. How sharp/wide are the peaks of the most volatile peaks? Have the authors considered to add a microfocusing trap?*
At this stage we have not considered adding such a trap as satisfactory measurement precisions are reached. Peak width of the most volatile compounds is typically around 15 seconds (FWHM). At the higher retention times SIM windows are very clean und do usually contain only one peak

– *P. 4. Line 29: Please identify the individual Scripps scales for each compound somewhere.*
– *Please keep in mind scale revisions.*
Information on individual scales for each compound we think can be omitted here, as the results of the storage test do not depend on it as long as the reference gas and the measurements are calibrated on the same scale. In general, scale revisions are taken into account by close collaboration of our lab with the AGAGE network which includes intercalibration and exchange of standards.

– *P. 4. Line 30: What are the calibration scales for CO and O3/how are their measurements calibrated?*
CO is calibrated in-flight at 25 minute intervals with an onboard calibration standard, results are reported on the most recent WMO scale, currently this is WMO CO-X2014A.
The ozone instrument combines two techniques: two-channel UV photometry and dry chemiluminescence detection. The UV photometer is regularly cross-checked to a laboratory standard (a long-path UV photometer standard, UMEG, Germany) which

was referenced to the WMO standard reference photometer (SRP) #15 at EMPA (Switzerland). The chemiluminescence detector is calibrated vs. the UV photometer in post processing.

These details were published by Scharffe et al. (2012) (CO) and Zahn et al. (2012) (Ozone) and are therefore not repeated in the current manuscript but we refer to these specialized publications by the following statement: "*Details of the respective calibration of both instruments were published by Scharffe et al. (2012) and by Zahn at al. (2012)."*

– *Section 2.3: Does your Mg(ClO4)2 drying result in water vapor mixing ratios similar to those in the UT/LS? Please specify the dryness of the standard used for the experiments in comparison to UT/LS dryness. Keep in mind that the drier the samples, the more storage problems are likely to occur for certain halogenated compounds.*

We are aware of the fact that storage issues might arise from the dryness of the samples. As mentioned in the manuscript a dry standard was deliberately chosen for the storage experiments to be comparable to samples from the UT, although stratospheric samples may be much drier.

Unrelated to the HIRES storage tests we found halomethanes to be instable even in a moist stainless steel gas cylinder (large volume, high pressure), likely depending on pressure.

– *P. 5. Line 13: Were the HIRES cylinders flushed the same way as during flight? If not, how? What dilutions were achieved? Did you measure final water vapor in the HIRES cylinders?*

They were flushed the same way as during flight and this point was added in the revised version of the manuscript. Final water vapor was not measured. The standard used had a water vapor content of approx. 200ppm, thus taking into account dilution with dry synthetic air samples would have contained less than this value.

– *P. 5. Line 15: Is one week the typical storage time for actual HIRES samples before halocarbon analysis? In the next sentence you indicate that storage time is usually much longer. Are your tests therefore representative of actual storage effects?*

Typically, the halocarbon analysis takes place approx. 3 to 5 weeks after the flight. The long-term storage test time of 8 weeks was chosen to safely cover this period. The short-term storage test is thus representative for routine operation, but turned out to be crucial for the discussion of the possible influence of ozone.

– *P. 6. Line 6: Have you considered to sample six cylinders at a time, thus increasing the volume and measuring an average storage effect rather than the storage effects in individual cylinders? If you had one rogue cylinder (which behaves much worse) could your tests identify it?*

A laboratory storage test could only identify a cylinder behaving systematically different (for example because of the quality of its individual welding seams) when repeated several times. Long-term an individual odd cylinder would be detected by evaluating measurement results based on canister number. As regular halocarbon measurements have just started, current results do not give indication of any such

behavior, however, we will pay close attention to this issue with the number of measurements increasing.

— *P. 6. Line 17: You cannot assume that synthetic air is free of halocarbons at the ppt level. I see that you have analyzed the zero air. Please rephrase the paragraph. P. 6. Line 30ff: The text refers to C2Cl4, but figure 3b refers to CH2Cl2. Which one is it? Please check the correct chemical names/formulas throughout the text.*

— *P. 7. Line 7: Why are no error bars for the individual data points shown? Please add them.*

We refrain from adding error bars to the individual data points because they overlap and merge into one big error bar for each day of measurement. To compensate for this lack of information the 2-sigma band around the expected value was included. As this came out not sufficiently clear, we have modified the figures. In contrast to the previous version, figures now include the precision of each measurement day rather than the average precision used before. This accounts for the varying measurement uncertainty of our GC-MS system.

— *P. 7. Line 8ff and Figure 3: Why is the spread of the measurements on day 1 (and day 8) so much larger than the gray shaded area?*
The measurement precision achieved has daily variations for example depending on the strength of the instrumental drift during a measurement day or ageing of the sample loop. This is reflected in the observed scatter but was not taken into account by the grey shaded area which was based on an average instrumental precision value. This has now been included in the revised version of the figures by showing the daily precision of each measurement days rather than an average precision as before. If the scatter is larger that the instrumental drift on a measurement day (as derived from the measurements of the laboratory standard) it points to variability of the sample mixing ratio.

— *P. 8. Line 4ff: It seems straightforward that ozone reacts with any of the compounds containing double bonds, but I am very surprised that CH2Cl2 and CH3CCl3 (and CHBr2Cl) were also depleted. CH2Cl2 for example is considered to be inert in organic chemistry. It is used as an inert solvent for ozonolysis of other compounds. Of course, we are talking about very different concentrations, but I just do not see how ozone reacts with CH2Cl2 or CH3CCl3. Do you have any explanation for this? Could you think of any other experimental problem for these compounds? CH2Cl2 for example, shows a very variable behavior in Figure 4.*
Please not that CH3CCl3 was listed erroneously in this line which will be corrected when revising the manuscript.
We do not have an explanation for the depletion of CH2Cl2 and CHBr2Cl. An additional experiment performed in the meantime indicated that both substances could not reliable be retrieved after filling cylinders constructed identically to the ones used in HIRES directly from the reference gas in a much simpler setup with no ozone involved. We can currently not speculate by which mechanism the observed depletion could have been caused. We think that Figure 3b shows convincing evidence that ozone did have an impact, but there likely are additional issues.

— *Have you repeated the storage tests to see if they are reproducible?*

The time-consuming tests could only be performed during a longer operational break of CARIBIC flights in 2016. They could not be repeated since, because this would cause an unacceptable long grounding of the CARIBIC container. For legal reasons, the air sampler has to be part of the instrument package during each flight of the container, even if it was not operated. It can therefore not be removed for laboratory test for the necessary time.

– *The fact that CH2Cl2 is depleted in Figure 5 for all high-ozone periods is compelling, however. Do the other compounds which are affected by ozone also show this (consistently) during actual post-flight analysis? If so, please discuss and add another column to table 1.*
Other compounds affected by ozone in the storage tests do consistently show a behavior similar to dichloromethane. A corresponding statement is included in the revised version of the manuscript and the paragraph now closes: "`A similar behavior was found for tetrachloroethene and trichloromethane and for the tropospheric samples for trichloroethene and for dibromochloromethane. The latter compound was below its detection limit in all stratospheric samples, trichlorethene in several of them.`"

Please note that previously tetrachloromethane was erroneously marked as influenced by ozone in Table 1.

– *P. 8. Line 12ff: It is known that CH3Cl and CH3Br may grow in stainless steel cylinders if they were not filled using particle filters. Whether this is due to sea salt or organic material or other compounds is unclear. Are the HIRES samples filled through a fine particulate filter?*
They are filled through a 2µ filter (Swagelok SS-4F-2). This information has been added in the revised version of the manuscript into subsection 2.1.

– *P. 8. Line 4ff: Which of the observed effects in the ozone experiment do not agree with the long-term storage tests? In other words, could some of the "ozone" problems be general "storage" problems? If so, please discuss this.*

Ozone problems were diagnosed from the measurement that took place right after filling of the samples, therefore they are unlikely to result from storage.

When thinking about the consequences for real UT-LS data, it has to be taken into account that in our experiment the reference gas is mixed with the ozone enriched synthetic air during the filling procedure, right before pressurization of the sample. In flight, stratospheric air masses with high ozone levels will be at some state of mixing and in a continuous chemically processing. A corresponding statement is included in the revised version of the manuscript: "`It should, however, be noted that the experiment does not adequately mimic stratospheric conditions. In the laboratory tests presented here, the reference gas is mixed with the ozone enriched synthetic air during the filling procedure. In flight, stratospheric air masses with high ozone levels will be at some state of mixing and in a continuous`"

chemically processing. In addition contact with hot surfaces such as inside the metal bellows pumps will destroy ozone."

– *Figure 3 and 4: Please add error bars. Figures for all compounds should be shown in the Supplement.*
– *P. 8. Line 22: Please show error bars. Without error bars, the reader cannot put the scatter of the results into perspective.*

Addition of error bars does not add readable information to the figures as they overlap and merge into one big error bar for each day of measurement. However, we have modified the figures such that the 2-sigma range around the expected value - which reflects the combination of error bars on the expected value an the data point – to make it better visible. All points falling into the indicated band agree with the expected value within the measurement precision.

The corresponding part of the text now reads: "*For each measurement day a daily precision value was calculated from the variability of the measurements of the standard. This expected daily uncertainty range is represented by the grey error bars.*
Solid coloured lines stand for canisters pressurized with synthetic air not treated by the UV-lamp, dashed coloured lines represent canisters pressurized with the synthetic air passing the UV-lamp and thus ozone being present. Error bars for the individual data points are not shown as they overlap and merge into one undistinguishable error bar. However, if the symbols fall within the uncertainty range indicated by the grey error bars of the expected value this means, that they agree within 2σ with the expected value."

We refrain from adding a supplement to this paper as we think Table 1 sufficiently summarizes the results.

– *P. 8. Line 22ff: "some scatter" is unscientific. Also, without error bars, the reader cannot evaluate your statement about 2 sigma agreement.*

The statement refers to the 2-sigma band indicated by he grey shaded area in the figures. As this fact did not come out very well, we have made it more clear in the text. The phrase was reworded to: "*HFC-134a variability is smaller than the measurement precision and measured mixing ratios agree within 2σ with the expected value.*"

– *P. 8. Line 24ff: Do you have an explanation why the red and blue experiments are so different? The red, yellow, blue, and dashed brown experiments indicate stability of CH2Cl2, while the other experiments show problems. Is it possible that individual cylinders are worse than others? How would you test that? Please expand your discussion at the end of page 8.*

We do not have an explanation why the measurements indicated by the blue and solid red lines deviate so much from each other, which they do in the case of dichloromethane the most on the last two measurement days. However, compared

to the uncertainty range of the individual days of measurement (cf. revised figures) CH2Cl2 seems not stable also in the other canisters.

It seems likely that individual canisters may perform worse or better than others and we will pay close attention to the behavior of individual canisters when analyzing flight samples, as this should become visible over the course of regular measurements.

We have added the following statement in the revised version of the manuscript: "*In general, the decrease during long-term storage seems to be independent of the influence of ozone, although the gas mixture that shows the largest depletion (light blue dashed line, mostly cut off in Figure 4) did contain ozone. Ozone could not be monitored during the pressurization of the samples. It can therefore not be excluded that this gas mixture may have been exposed to a different amount of ozone than the one represented by the dashed brown line which could have caused the stronger depletion.*"

- *P. 8. Line 28: How do you determine two weeks (rather than one week)?*

The two weeks are estimated from the results of the long-term storage test which indicate that changes to the initial mixing ratios start to become relevant after this time.

The sentence is rephrased to: "*Measurements of these compounds should not be evaluated for the HIRES canisters if analysis takes place later than two weeks after sample collection as the long-term test indicates changes of mixing ratios start to occur after that period.*"

- *P. 9. Line 4: What polymer materials are used inside the sampling and the analytical system? Is Viton used by any chance? This could explain HFC-23 increases.*

During sample enrichment all connectors and tubing used are made from stainless steel with exception of two Valco valves in the sample flow. These do contain PFTE seals (similar to the ones used in HIRES) but this cannot explain increases occurring in the test samples, because during storage those were not connected to the analytical system. During the measurement, contact times with the valves are minimized and all lines are flushed prior to enrichment.

- *Figure 5 and 6: Please add a discussion of evidence for the observed storage tests from actual flights to the discussion.*

The discussion in section 3.3 has been extended in the revised version of the manuscript. In particular, the following statements were added or reworded to:

- *CFC-12 anticorrelates with mixing ratios of ozone and this is also found for the other long-lived compounds which were stable in the storage experiments. Such a behaviour is expected, because ozone-rich stratospheric air masses are aged and should contain lower mixing ratios depending on a substance's stratospheric lifetime and transport pathway. Three of the canisters analysed from this flight were collected in tropospheric air masses characterized by*

lower mixing ratios of ozone levels. Mixing ratios of CFC-12 measured in these samples are around 510 ppt, consistent with current tropospheric mixing ratios observed at ground sites (Schuck et al., 2018). Similarly consistent numbers are measured for the other compounds expected to be stable in the canisters according to the storage experiments.

- *In the tropospheric air samples, dichloromethane varied between 14ppt and 49ppt. This agrees with mixing ratios in tropospheric samples in the dataset presented by Leedham-Elvidge et al. (2015) which were up to 65ppt with an increase observed from 2006 through 2012, but is somewhat lower than mixing ratios at the ground in March 2018 (Schuck et al. 2018) which would be consistent with the result from the storage test, that dichloromethane is not stable in HIRES cylinders long-term.*

- *A similar behaviour was found for tetrachloroethene and trichloromethane and for the tropospheric samples for trichloroethene and for dibromochloromethane. The latter compound was below its detection limit in all stratospheric samples, trichloroethene in several of them.*

– *Please add Figures 5 and 6 for all compounds to the Supplement.*
It cannot be avoided that our selection of compounds is to some extent random and remains uncomplete. We don't agree that adding a supplement to the manuscript does add valuable information which is not contained in the summary Table 1 and therefore we prefer to not add supplementary information to the paper.

– *Figure 5 and 6: Please add correlation lines and R2 values (excluding the tropospheric outliers for CO) to Figures 5 and 6.*
As Figure 5 shows the exemplary time series of flight data, we assume this refers to the scatter plots in Figures 6 and 7. Following your suggestion, we prepared modified versions of Figures 6 and 7 including correlation lines and r² values. The vertical axis of Figure 7(c) was set to the same range as panels (a) and (b).

– *P. 12. Lines 6ff: I do not think that the discussion of correlations for an unstable compound is very informative.*
Although we cannot deduce direct conclusions from this correlation (such as emission ratios or time of chemical processing), we think it an interesting detail that there is a correlation at all. This is despite the compound being unstable during storage and the mixing ratios being depleted in the stratospheric samples.

– *P. 12. Line 30: I think this identifies a general weakness of CARIBIC. Can this be improved? Do the results from this paper have any implications for previously published results?*

We do not see that this could be improved, because no single lab among the collaborators has the capability nor the capacity to perform all different measurements (greenhouse gases, non-methane hydrocarbons, halocarbons, and possibly also isotopic composition analysis) in one place and within shorter times. Halocarbon measurements of HIRES samples were not published up to now, therefore there are no reverse implications on previous results from our tests.

– *P. 15. Line 5ff: It is good to learn that a new sampler is being designed taking into account the lessons learned from this paper and that more rigorous tests will be performed.*
As it turned out in the meantime that the geometry of the cylinders with only one line of tubing of a small diameter does not allow adding a coating on the inside after welding, we removed the statement on tests of a coating.

– *Table 1: Can you exclude that the change of mixing ratios for drifting compounds is NOT caused by drift of the working standard itself? In other words, do you have evidence for stability of the working standard for all compounds over the relevant time scales?*
We can exclude drift of the working standard, because it is regularly compared to a tertiary AGAGE standard during regular sample measurements performed with the GC-MS setup. A corresponding statement is included in the measurement section revised version of the manuscript: "`HIRES samples are measured relative to a laboratory standard which has been collected cryogenically at Jungfraujoch (Switzerland) in December 2007. It is compared to a tertiary standard of the Advanced Global Atmospheric Gases Experiment (AGAGE) network monthly and has been re-calibrated versus several AGAGE standards in December 2018. Drift of the working standard can thus be excluded.`"

Minor comments:

– *P. 1. Line 21: Strike out "the". It should say "responsible for stratospheric ozone depletion".*
Changed.

– *P. 1. Line 23: ".. as an entry point for chlorinated and brominated species into the stratosphere".*
Changed.

– *P. 2. Lines 1/2: The trace gas composition in the ... can be analyzed ... or using air sample collection ...".*
Changed.

– *P. 2. Line 10: Even CO2 is not stable in all cylinders.*
Since a discussion of CO_2 is beyond the scope of this manuscript that sentence will be removed in the revised version.

− *P. 2. Line 23: Flights take place over ...*
Changed to "Measurement flights".

− *P. 2. Lines 33ff: It has been regularly deployed since 2010 for post-flight measurements of greenhouse ...*
Changed.

− *P. 3. Line 1: Please add a few citations.*
References Navarro et al. 2015 and Keber at al. 2019 were added.

− *P. 3. Line 9: HIRES has been defined before.*
The repetitive definition has been removed.

− *P. 4. Line 16: What is 2 x 2 L reference volume? 4 L?*
The reference volume consist of two canisters wit a volume of 2 L each. Therefore, we prefer to write "2 x 2 L" over "4 L".

− *P. 4. Line 18: Please provide the supplier of the helium and the grade.*
Helium grade 6.0 supplied by Praxair is used, this information has been added to the text.

− *P. 4. Line 30: Strike out "in contrast".*
Done.

− *P. 5. Line 5: This sentence is not quite right. Consider changing to "Contrary to ..., when the HIRES cylinders are filled with ambient air pressurized by ..., in this setup, the HIRES cylinders are ...".*
Changed.

− *P. 9. Line 3: "This also occurred for ...".*
Changed.

− *Table 1: The short-term column should be before the long-term column*
We agree and the table is changed correspondingly in the revised manuscript.

− *Figure 1: The CAD drawing of the sampler is nice, but I would also (perhaps rather) like to a drawing of the flow path.*
We have rephrased the figure caption to make clear, that the CAD drawing is deliberately reduced to the main components, not showing any tubing and therefore not indicating sample air flow paths. We finally opted not to include a drawing of the flow path because we don't think it would add any information not contained in Figure 2.

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Stability of Halocarbons in Whole Air Samples ~~from the Upper Troposphere and Lowermost Stratosphere~~ <u>Collected in Stainless Steel Canisters</u>

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Abstract. Measurements of halogenated ~~hydrocarbons~~ trace gases in ambient air frequently rely on canister sampling followed by offline laboratory analysis. This allows for a large number of compounds to be analysed under stable conditions, maximising measurement precision. However, individual compounds might be affected during sampling and storage of canister samples. In order to assess halocarbon stability in whole air samples from the upper troposphere and lowermost stratosphere, we performed

5   stability tests using the air sampling unit High REsolution Sampler (HIRES) which is part of the CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) instrument package. HIRES holds 88 light-weight stainless steel cylinders that are pressurized in flight to 4.5 bar using metal bellows pumps. The HIRES sampling unit was first deployed in 2010, but has up to now not been used for regular halocarbon analysis with exception of chloromethane. The sample collection unit was tested for sampling and storage effects of 28 halogenated compounds. The focus was on

10   compound stability in the stainless steel canisters during storage of up to five weeks and on the influence of ozone, since flights take place in the upper troposphere and lowermost stratosphere with ozone mixing ratios of up to several hundred ppbV. Most of the investigated (hydro)chlorofluorocarbons and long-lived hydrofluorocarbons were found to be stable over a storage time of up to five weeks and were unaltered by ozone being present during pressurization. Some compounds such as for example dichloromethane, trichloromethane and tetrachloroethene started to decrease in the canisters after a storage time of more than

15   two weeks or exhibited lowered mixing ratios in samples pressurized with ozone present. Few compounds such as for example tetrachloromethane and tribromomethane were found to be not stable in the HIRES stainless-steel canisters independent of ozone levels. Also growth was observed during storage for some species, namely for HFC-152a, HFC-23, and Halon-1301.

1 Introduction

Despite their low atmospheric mixing ratios of only a few hundred parts per trillion or less, halogenated trace gases have a

20   significant impact on the Earth's atmosphere. In particular, anthropogenic chlorinated and brominated halocarbons are respon-

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sible for ~~the~~ stratospheric ozone depletion (Engel and Rigby et al., 2018). Of particular interest are the mixing ratios of such species in the upper troposphere as an entry point for ~~transport of~~ chlorine and bromine into the stratosphere.

~~Trace gas measurements~~ The trace gas composition in the upper troposphere and lowermost stratosphere (UTLS) can be ~~performed~~ analysed from aboard aircraft using in-situ instrumentation or using air sample collection followed by post-flight

5   analysis on the ground. Whereas fast in-flight measurements based on gas chromatography/mass spectrometry provide data of halocarbon and non-methane hydrocarbon mixing ratios in the UTLS at a higher spatial resolution (1–4 min) (Apel et al., 2003; Sala et al., 2014; Bourtsoukidis et al., 2017), the number of species quantified is often limited while the instrumentation is complex. Although canister air sampling typically generates data at a much lower spatial coverage, the post-flight analysis allows a wider range of substances to be measured. Thus, air sample collection is a well-established part of the scientific payload

10   of both ~~,~~ campaign-type studies such as for example the HIPPO (Wofsy, 2011) and ATTREX (Navarro et al., 2015; Jensen et al., 2017) projects and long-term projects such as CONTRAIL (Machida et al., 2008) and IAGOS-CARIBIC (Brenninkmeijer et al., 2007; Petzold et al., 2015).

~~The main long-lived greenhouse gases CO$_2$, CH$_4$, N$_2$O and SF$_6$ are usually stable in sampling canisters made of various materials.~~ Literature on compound stability in sampling canisters mainly deals with volatile organics ~~, which are generally more~~

15   ~~reactive~~. For example, Lerner et al. (2017) found alkanes and alkenes to be stable in electropolished stainless steel canisters in a storage experiment over up to four days, but stability of oxygenated compounds was influenced by the level of humidity. Mixing ratios of aldehydes and monoterpenes were found to decrease significantly in stainless steel cylinders even after short storage times of only a few days but exhibited extended stability in humidified cylinders (Batterman et al., 1998). In a storage experiment covering a period of up to 28 days, Ochiai et al. (2002) found polar VOCs to be more stable at elevated relative

20   humidities while non-polar VOCs were also stable in dry canisters. Better stability was found for VOCs in fused-silica-lined cylinders compared to electro-polished stainless steels cylinders (Ochiai et al., 2002; Hsieh et al., 2003).

The CARIBIC project (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container, www.caribic-atmospheric.com) investigates atmospheric composition from aboard a Lufthansa passenger aircraft equipped with a sophisticated air inlet system (Brenninkmeijer et al., 2007). CARIBIC is a long-term scientific project, employing a

25   comprehensive set of instruments for simultaneous measurements of trace gases and aerosol particles inside a 1.5 t air freight container during regular long-distance flights of the aircraft. ~~Measurements~~ Measurement flights take place over 2–4 consecutive days 6–12 times per year. The instrument package consists of remote sensing instruments, fast in-situ instruments and collection of ~~both,~~ particulate matter and air samples (Brenninkmeijer et al., 2007; Petzold et al., 2015).

CARIBIC air sampling initially was limited to 28 glass ~~flask~~ flasks per series of flights. Taking advantage of the large spatial

30   coverage of commercial long-distance flights, measurements from these CARIBIC glass flask samples have provided valuable information on the distribution of halogenated trace gases in the upper troposphere and lowermost stratosphere for example for HFC-227ea (Laube et al., 2010), SF$_5$CF$_3$ (Sturges et al., 2012), perfluorocarbons (Laube et al., 2012), dichloromethane and other short-lived chlorocarbons (Leedham-Elvidge et al., 2015; Oram et al., 2017) and bromocarbons (Wisher et al., 2014), CFC-114 (Laube et al., 2016) and CFC-113a (Adcock et al., 2018). Complementing the two existing sampling units

35   with glass cylinders, ~~a new HIgh REsolution Sampler (HIRES)~~ the new HIRES unit with 88 stainless steel cylinders was

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built for the automated collection of whole air samples at a higher frequency in 2010 (Schuck et al., 2012). ~~It got regularly employed since, being analysed for~~ Since then it has been regularly employed for analysis of greenhouse gases and non-methane hydrocarbons (Baker et al., 2016; Li et al., 2018), but it has not been used for dedicated measurements of halogenated trace gases.

5   Measurements of halocarbons in the tropopause region are sparse. CARIBIC air samples are collected on a regular basis and therefore complement measurements from research aircraft campaigns such as for example the ATTREX (Navarro et al., 2015) or TACTS/WISE/PGS projects (Keber et al., 2019). In order to explore the potential of the HIRES unit for halocarbon measurements, we intensively tested the sampling unit in a series of laboratory experiments. In particular, we investigated the stability of 28 compounds during storage between sampling and analysis over typical processing times. In addition, we investigated the 10 influence of ozone, which may affect sampling of reactive species in the lowermost stratosphere.

2   Technical Details

2.1   The HIgh REsolution Sampler

~~The HIgh REsolution Sampler (HIRES)~~ HIRES holds 88 light-weight cylinders made of stainless steel (wall thickness 0.25 mm), each with a volume of 1 L, total weight is 43 kg. Samples are pressurized to 4.5 bar in flight at pre-set time 15 intervals using two metal bellows pumps (Senior Aerospace Metal Bellows, 28823-7). Coarse particles are filterd by a 2 μ filter (Swagelok SS-4F-2). Each cylinder is connected to one of six 16-position valves (Valco, EMT4LSD16MWE) by which the samples are selected. ~~Thus~~In a laboratory setting, up to six samples can be pressurized simultaneously with identical air mixtures. ~~Due to mechanical stability of the thin-walled flasks they may not be evacuated to absolute pressures below 700 mbar.~~ Figure 1 shows a schematic view of the cylinders and valves.

20   Before a flight, HIRES undergoes leak testing with ambient air passed through a molecular sieve, but cylinders are not preconditioned. On take-off, cylinders will usually hold remnant air from the last research flight or from the leak test. ~~Samples are pressurized to 4.5~~The reason is that due to mechanical stability of the thin-walled flasks they should not be evacuated to absolute pressures below 600 ~~bar in flight at pre-set time intervals using two metal bellows pumps (Senior Aerospace Metal Bellows, 28823-7).~~ mbar. Tests during the construction phase and monitoring based on NMHC measurements during the first 25 years of operation of the sampler have shown that eight iterations of flushing do reliably dilute remnants of previous fillings of tropospheric air. In flight, canisters are therefore flushed with ambient air eight times~~before they are eventually pressurized to 4.5 bar. Flushing~~, this is achieved by filling a flask to 4 bar followed by venting for 20 s. After this time ambient pressure is reached which aboard the aircraft at flight altitude is $\sim$ 700 mbar. After that, canisters are eventually pressurized to 4.5 bar. The total time needed for this procedure is $\sim$ 4 min ~~,~~of which the final pressurization takes 10–20 s. During each flushing about 30 20 % of the air from the previous filling remains in the sample canister. Depending on ambient pressure, 70–80 % of the air is from the final pressurization stage. The sampling period is defined as the time interval during which at least 97 % of the sample air was collected. This comprises ~~three~~ the last three of the eight flushing iterations and the final pressurization stage, adding up to a total sampling time of 1–2 min. Data from continuously measuring instruments, such as ozone (O_3) (Zahn et al., 2012)
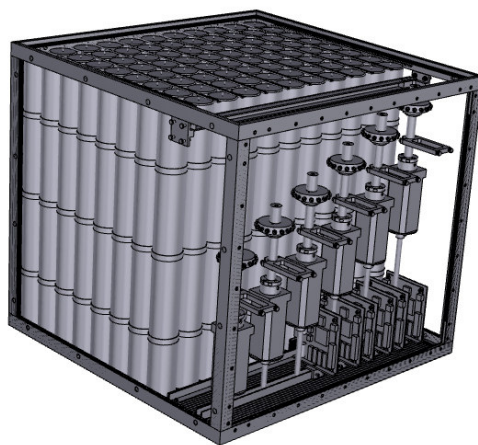
Figure 1. Schematic view of the 88 sample cylinders inside HIRES and the six multi-position valves. For simplicity all tubing is omitted to illustrate only the positioning of these main components. Drawing: Laurin Merkel.

and carbon monoxide (CO) (Scharffe et al., 2012), are integrated over the sampling intervals for comparison with canister measurements.

Upon return of the instrument container, the sample collector is de-installed, and post-flight gas chromatography analyses are performed in the laboratory for greenhouse gases (Schuck et al., 2009) and non-methane hydrocarbons (Baker et al., 2010).

5 If a halocarbon analysis is performed it is usually last in a series of measurements and takes place approximately 3 to 5 weeks after the flight. The duration of the long-term storage test time of 8 weeks was deliberately chosen beyond this period.

2.2 Halocarbon Measurements

The halocarbon measurements are based on adsorption-desorption gas chromatography / mass spectrometry (GC/MS) (Hoker et al., 2015; Schuck et al., 2018). As halocarbon mixing ratios in the atmosphere are in the ppt range, pre-concentration of

10 the sample air prior to gas chromatographic separation and detection is required (Obersteiner et al., 2016). In addition, the sample air is dried by passing over a heated (80 °C) tube filled with magnesium perchlorate $Mg(ClO_4)_2$. Mixing ratios are therefore reported as dry mole fractions. All tubing is heated to avoid condensation of moisture (relevant for HIRES only for tropospheric samples) and to minimize wall losses. Following the drying unit, the sample flow is directed through a 1/16" stainless steel sample loop (inner diameter 1 mm) filled with HayeSep D over a length of 10 cm. During the adsorption phase

15 the sample loop is kept at -80 °C (Stirling Cooler, Global Cooling, M150). Depending on the pressure of the HIRES air samples at the time of measurement, the enrichment flow is set to either 100 ml/min or 150 ml/min controlled by a mass flow controller mounted behind the sample loop in order to exclude sample contamination from the controller. The enriched sample volume is determined by monitoring the pressure inside a 2 x 2 L reference volume which gets evacuated prior to sample enrichment.

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Typically a volume of 0.8–1.0 L of air is used. For desorption, the sample loop is heated to approx. 200 °C for 4 min while the carrier gas flow is directed through it (~~purified Helium~~ Helium grade 6.0 (Praxair), Purification System: Vici Valco HP2).

Gas chromatography is performed with an Agilent 7890A instrument equipped with a 7.5 m pre-column and a 22.5 m main column (both GasPro PLOT, inner diameter 0.32 mm). The temperature program of the GC starts at 50 °C kept for 2 min after which the oven is heated to 95 °C at a rate of 15 °C/min. Then it is heated to 135°C at 10 °C/min, and finally to 200 °C at a rate of 22 °C/min. This temperature is kept for another 2.95 min. The complete runtime adds up to 17.95 min. Backward flushing of the pre-column is started after 12.6 min to avoid contamination of the subsequent chromatographic run with high-boiling substances. Mass spectrometric detection is with a quadrupole (QP) mass spectrometer (Agilent 5975C) operated in selected ion monitoring mode, scanning pre-selected masses at a given retention time. Ionisation is via electron impact at 70 eV. Data from a time-of-flight-mass spectrometer operated in parellel to the QP-MS are not discussed here. The experimental setup was described in more detail by Hoker et al. (2015) and Obersteiner et al. (2016).

HIRES samples are measured relative to a laboratory standard which has been collected cryogenically at Jungfraujoch (Switzerland) in December ~~2007 and has been calibrated against standards~~ 2007. It is compared to a tertiary standard of the Advanced Global Atmospheric Gases Experiment (AGAGE) network monthly and has been re-calibrated versus several AGAGE standards in December 2018. Drift of the working standard can thus be excluded. Mixing ratios are reported in ppt on Scripps Institution of Oceanography (SIO) scales except for Trichloroethene, Dibromochloromethane, Tetrachloroethene, and Tribromomethane (reported on scales defined by University of Bristol, University of East Anglia and the National Oceanic and Atmospheric Administration). Mixing ratios of CO and Ozone from CARIBIC in-flight measurements ~~in contrast~~ are reported in ppb per Volume (ppbV). Details of the respective calibration of both instruments were published by Scharffe et al. (2012) and by Zahn et al. (2012).

2.3 Storage Experiments

To test a possible influence of ozone on reactive halocarbon species, HIRES sample canisters were pressurized in the laboratory with a mixture of a well-characterized laboratory standard and synthetic air. The standard was filled with an oil-free compressor at Taunus Observatory (50.22 ° N, 8.44° E , 825 m.a.s.l) in 2015 and contained typical tropospheric mixing ratios of halocarbons. During pressurization it had been dried using magnesium perchlorate. This standard was chosen for the storage experiments, as air from the UTLS usually contains water vapour mixing ratios of less than 100 ppmV.

Figure 2 shows the set-up used for the pressurization of HIRES for storage tests. Samples could be filled with either the standard gas, synthetic air or a mixture of both. Contrary to the set-up in flight, when ~~ambient air is~~ the HIRES cylinders are filled with ambient air pressurized by the metal bellows pumps, in this set-up they are pressurized directly from high pressure gas cylinders. On path I the synthetic air flow passed a quartz glass tube exposed to UV light from a mercury lamp generating ozone. On average, ~ 1200 ppbV of ozone was generated as determined by a separate measurement (API Photometric Ozone Analyzer T400), but it was not monitored during the filling of the cylinders. After mixing of the ozone enriched synthetic air with the standard gas (path III), ozone mixing ratios were approx. 400–600 pbbV, being characteristic of the lowermost
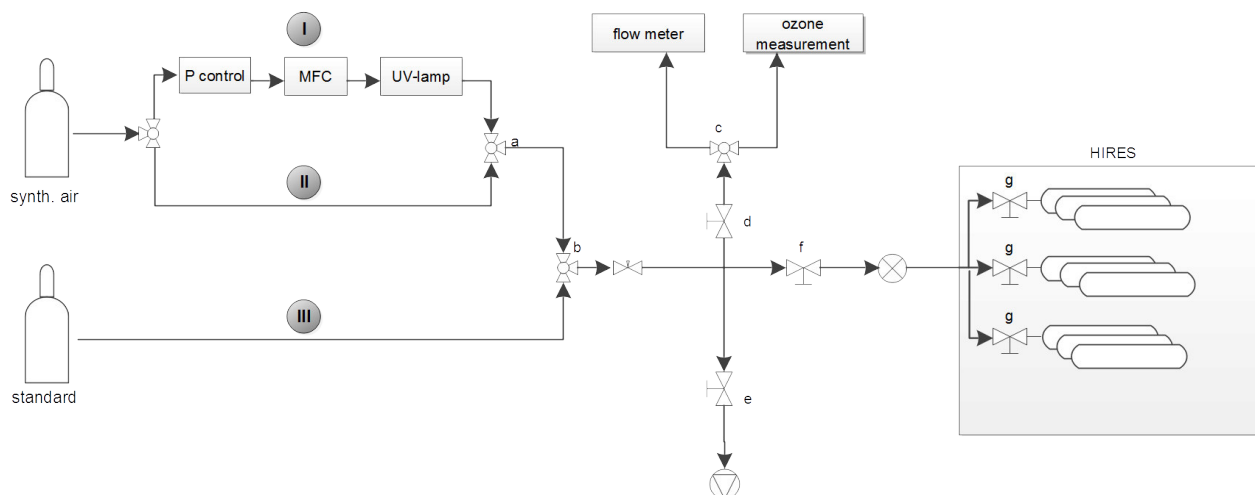
Figure 2. Schematic view of the gas flows for filling HIRES canisters for the storage experiments. Samples could be pressurized with either pure air from a standard gas bottle (flow path III), pure synthetic air (path II), or with a mixture of both. Alternatively, the flow of synthetic air could be directed to pass an ozone generating UV lamp (path I).

stratosphere as typically sampled by the CARIBIC aircraft. This procedure was chosen, because generating ozone directly in the flow of the standard gas could have altered mixing ratios of the reactive halogenated compounds contained in the standard.

For a short-term storage test, six individual canisters were pressurized consecutively to an absolute pressure of 4 bar using 1.7 bar of synthetic air and 2.3 bar of the standard gas. For three of the canisters, the synthetic air was enriched in ozone by directing its flow via the UV lamp. All samples were analysed one day after filling and again one week later.

5   Because of the large number of cylinders, measurement of all samples of one CARIBIC flight series takes several days, depending on the type of analysis performed. The halocarbon measurements described here add up to approx. 53 hours total measurement time, not including blank measurements and preparation work. In addition, HIRES needs to circulate between different laboratories in different institutions, therefore the time between in-flight sampling and post-flight sample analyses can be much longer than one week.

10   Canisters have a volume of 1 l and were pressurized up to 4 bar. Due to mechanical stability of the thin-walled flasks they may not be evacuated during the measurement. For a corresponding long-term storage test with six measurements of one gas mixture the sample volume of one cylinder would not be sufficient. Therefore, six cylinders were simultaneously filled, and on each measurement day, the next canister of such a series was measured. Canisters were pressurized to an absolute pressure of 4 bar with one of the following gas mixtures:

15   – synthetic air (4 bar)

       – synthetic air (1 bar) + standard (3 bar)

- synthetic air (1.7 bar) + standard (2.3 bar)

- synthetic air (1.7 bar) + ozone + standard (2.3 bar)

- synthetic air (4 bar) + ozone

5   With each of the mixtures two subsets of six canisters each were pressurized simultaneously, thus containing identical composition. One canister out of each subset was analysed after a storage time of 1, 8, 15, 29, 51, and after 57 days. The full measurements series for the long-term storage test comprises analyses of 60 individual canisters. Between measurements, the sampling unit was stored in an air conditioned laboratory at temperatures around 22 °C. The air conditioning uses water and is therefore not expected to adversely influence halocarbon analysis.

10   Assuming the synthetic air to be free of any of the compounds of interest, mixing ratios in the canisters should be identical to the original mixing ratios weighted by the relative contribution of each gas, i. e. trace gas mixing ratios in the HIRES canisters should be about 75 % of the original mixing ratios of the standard in the case of 1 bar of synthetic air mixed with 3 bar of the standard gas and about 57.5 % in the case of 1.7 bar of synthetic air mixed with 2.3 bar of the standard gas. Measurements of the pure synthetic air, however, revealed contamination of the synthetic air with carbonyl sulfide (12.8 ppt), chloromethane (24.3 ppt), HFC-152a (2.8 ppt), and tetrachloroethene (1.1 ppt). This needs to be taken into account for calculation of the trace gas mixing ratios expected in the HIRES canisters after mixing synthetic air and standard gas. To reduce uncertainties related to the mixing of synthetic air and standard gas, which are mainly caused by the uncertainty of the pressure readings of approx. 0.1 bar, all compounds were evaluated relative to CFC-12 (CCl_3F). CFC-12 was found to be stable in the canisters.

3   Results

3.1   Ozone interference and short-term stability

The short-term storage test was performed to investigate the influence of ozone being present during pressurization. HIRES is usually operated in the UTLS region and ozone mixing ratios are commonly up to 800 ppbV, depending on flight route and season. Figure 3 shows as examples the results of the test for HFC-134a (CH_2FCF_3) (panel (a)) and ~~tetrachloroethene (C~~dichloromethane (CH_2Cl~~$_4$~~$_2$) (panel (b)). Plotted is the ratio of the mixing ratio of the respective substance to CFC-12 (CCl_3F) as described in the previous section. The solid black line represents the value expected from the known mixing ratios of the standard gas~~, taking into account dilution with synthetic air. For C_2Cl_4 the contamination of 1.12 ppt of the synthetic air has been taken into account. The standardgas contains 12.51 ppt of C_2Cl_4. The grey shaded area represents the 2-σ uncertainty range of the measurements, not including the error of the mixing ratio of the standard gas~~. For each measurement day a daily precision value was calculated from the variability of the measurements of the standard. This expected daily uncertainty range is represented by the grey error bars. Solid coloured lines stand for canisters pressurized with synthetic air not treated by the UV-lamp, dashed coloured lines represent canisters pressurized with the synthetic air passing the UV-lamp and thus ozone being present. Error bars for the individual data points are not shown ~~,~~ as they overlap and merge into one undistinguishable
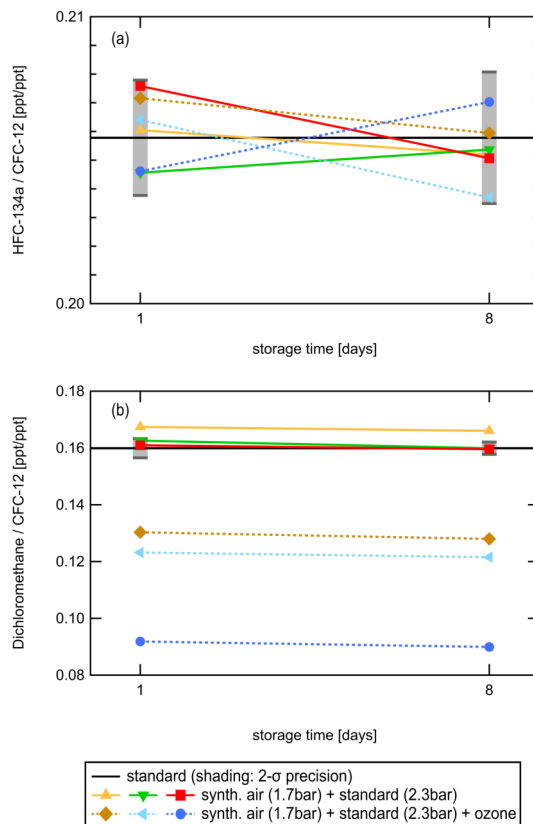
Figure 3. Results of the ozone and short-term storage test for HFC-134a (a) and dichloromethane (b). Shown is the ratio of mixing ratios of the respective compound relative to that of CFC-12 to cancel dilution uncertainties. The solid black line represents the value expected from direct measurements of the standard gas and the synthetic air. Shading indicates the 2-σ experimental uncertainty range around the expected value, error bars of individual data points are omitted for clarity.

error bar. However, if the symbols fall within the uncertainty range indicated by the grey error bars of the expected value this means, that they agree within 2-σ with the expected value.

For HFC-134a, the ratio of mixing ratio agrees with the expected value within the experimental uncertainty on the first day and on day 8. For ~~tetrachloroethene~~ dichloromethane, samples influenced by ozone (dashed lines) show a significantly lower ratio ~~of tetrachloroethene~~ to CFC-12 than expected. No systematic change from day 1 to day 8 was measured for either of the two compounds. While ~~tetrachloroethene~~ dichloromethane was stable over a storage time of one week, it was influenced by ozone and exhibited depleted mixing ratios in the canisters ~~right~~ already one day after pressurization. It can thus not be reliably measured from HIRES canisters from the lowermost stratosphere.

~~Other substances~~ Substances that were found to be depleted in HIRES canisters when pressurized in the presence of ozone were: ~~dichloromethane~~ dichloromethane (CH_2Cl_2), ~~111-trichloroethane ($C_2H_3Cl_3$),~~ trichloroethene (C_2HCl_3), ~~tetrachlorethene~~

tetrachloroethene (C$_2$Cl$_4$), and dibromochloromethane (CHBr$_2$Cl). Carbonyl sulfide (COS) showed higher mixing ratios in samples that had been exposed to ozone. While there is clear evidence, that the mixing ratios of these substances are modified in the canisters when they are pressurized at elevated levels of ozone, it is not possible from these experiments to deduce an ozone threshold above which results become unreliable. We will thus consider all UTLS samples characterized as stratospheric by ozone mixing ratios above the respective ozone chemical tropopause, potential vorticity or low mixing ratios of nitrous oxide as not suited for post-flight analysis of these compounds in samples from the current HIRES sampling unit.

It should, however, be noted that the experiment does not adequately mimic stratospheric conditions. In the laboratory tests presented here, the reference gas is mixed with the ozone enriched synthetic air during the filling procedure. In flight, stratospheric air masses with high ozone levels will be at some state of mixing and in a continuous chemically processing. In addition contact with hot surfaces such as inside the metal bellows pumps will destroy ozone.

Among the substances influenced by ozone, dibromochloromethane (CHBr$_2$Cl) additionally showed decreasing mixing ratios already after one week of storage (depleted by 94 %), while bromomethane (CH$_3$Br, +46 %) and chloromethane(CH$_3$Cl, +14 %) were found to grow. Trichloroethene (C$_2$HCl$_3$) exhibited a variability which did not allow to draw stringent conclusions in the short-term storage test. Tribromomethane (CHBr$_3$), which was unaffected by ozone, was depleted by 70 % after one week of storage. Table 1 summarizes these results.

3.2 Long-term stability

The long-term storage test comprised measurements of pressurized canisters after storage times of 1, 8, 15, 29, 51, and 57 days. While for the short-term test, individual canisters were measured on day 1 and day 8, this was not possible for the long-term test. For the long-term test, six cylinders were simultaneously filled, and on each measurement day, the next canister of such a series was measured. Thus, it cannot be fully excluded that stability might not only depend on the substance investigated, but it might be a feature of an individual canister, for example related to the quality of welding seams.

Figure 4 shows as an example results of the long-term storage test for HFC-134a, dichloromethane and HFC-152a. As before, shown is the ~~ratios~~ ratio of mixing ratios of the respective substance and CFC-12. The black line indicates the expected ratio and the grey shaded area represents the experimental 2-σ uncertainty range. Solid lines are for measurements of the gas mixture without ozone, dashed line for those with ozone. Error bars for individual data points are not shown. Like most long-lived halogenated tracers, HFC-134a ~~exhibits some scatter but~~ variability is smaller than the measurement precision and measured mixing ratios agree within 2 σ with the expected value.

Some substances that were found to be stable during the one week short-term test decreased after longer storage times, for example dichloromethane shown in Figure 4(b). ~~In general, this seems to be independent of the influence of ozone, although the gas mixture that shows the largest depletion (light blue dashed line, mostly cut off in Figure 4) did contain ozone.~~ A similar behaviour was observed for trichloromethane (CHCl$_3$), tetrachloromethane (CCl$_4$), trichloroethene (C$_2$HCl$_3$), tetrachloroethene (C$_2$Cl$_4$), tribromomethane (CHBr$_3$), and ~~bromochloromethane~~ bromochloromethane (CH$_2$BrCl). Measurements of these compounds should not be evaluated for the HIRES canisters if analysis takes place later than two weeks after sample collection ~~.~~ ~~None of the substances that showed sensitivity to high ozone levels was stable in the~~ as the long-term ~~test~~ test indicates changes
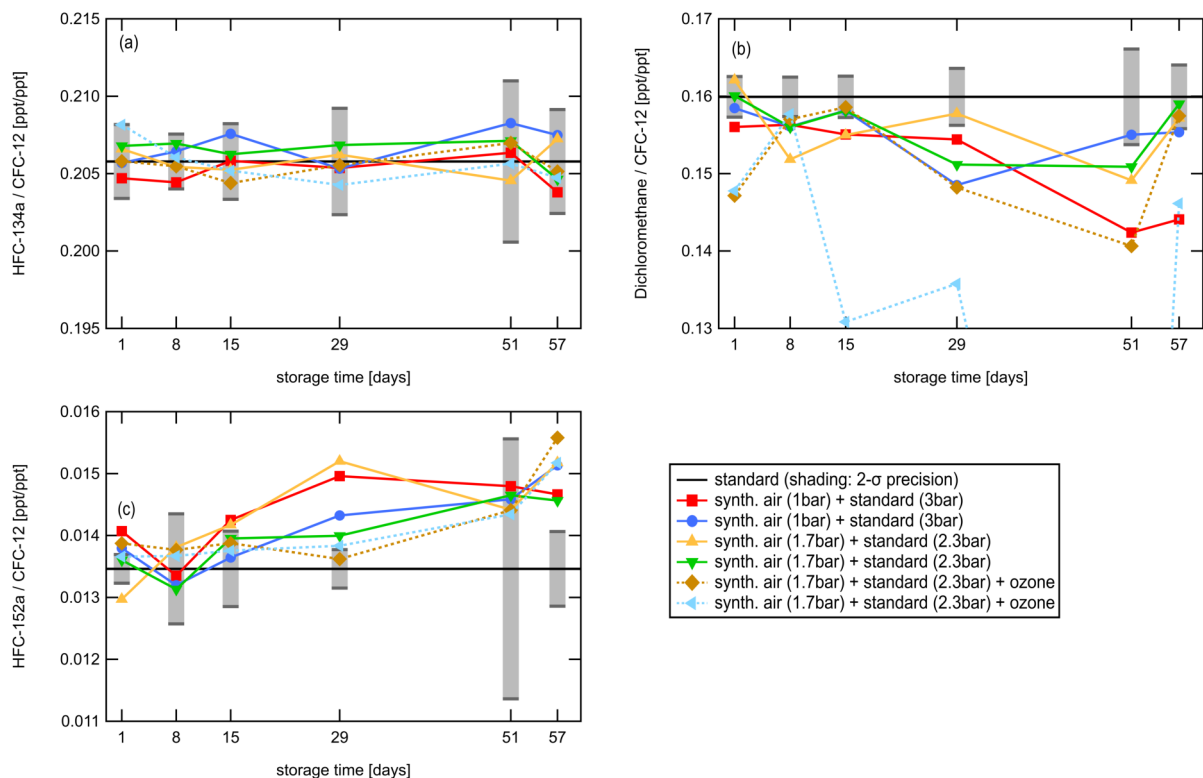
Figure 4. Results of the ozone and ~~short-term~~ long-term storage test for HFC-134a (a)~~and~~, dichloromethane (b), and HFC-152a (c). Shown is the ratio of mixing ratios of the respective compound relative to that of CFC-12 to cancel dilution uncertainties. For dichloromethane the vertical scale has been adjusted cutting off samples that were strongly depleted. The solid black line represents the value expected from direct measurements of the standard gas and the synthetic air. Shading indicates the 2-σ experimental uncertainty range around the expected value, error bars of individual data points are omitted for clarity.

of mixing ratios start to occur after that period. In general, the decrease during long-term storage seems to be independent of the influence of ozone, although the gas mixture that shows the largest depletion (light blue dashed line, mostly cut off in Figure 4) did contain ozone. Ozone could not be monitored during the pressurization of the samples. It can therefore not be excluded that this gas mixture may have been exposed to a different amount of ozone than the one represented by the dashed brown line which could have caused the stronger depletion.

5   Panel (c) of Figure 4 shows the result of the long-term storage test for HFC-152a (CH_3CHF_2). While mixing ratios measured on day 1 and 8 were within the expected range, they started to significantly increase after storage day 15. This also occurred for samples influenced by ozone and independent of the gas mixture. A similar result was found for Halon-1301 ($CBrF_3$) and HFC-23 (CHF_3). HFC-23 is known to degas from certain materials, thus degassing from valve seals might be a possible source. The
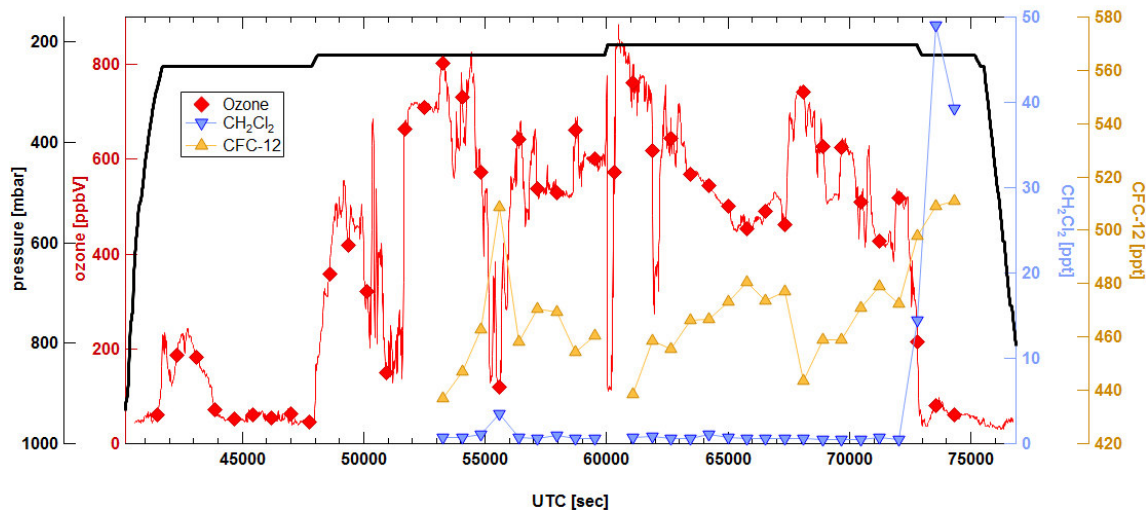
Figure 5. Time series of ozone (red), CFC-12 (yellow) and dichloromethane (blue) during a flight from Munich to Denver on 22 March 2018. Ozone high resolution data represented by the red line were integrated over the sampling period of each whole air sample (red diamonds).

rotors of the Valco multi-position valves are made of Valcon E, a polyaryletherketone/PTFE composite, therefore degassing of fluorinated compounds could occur. Of the shorter-lived compounds investigated bromomethane (CH_3Br) exhibited an increase in the long-term storage experiment. Table 1 summarizes the results of ~~both,~~ the long-term and the short-term test.

3.3 Air samples from the UTLS

As an example of air collected in the atmosphere under real conditions, samples from CARIBIC flight 544 which took place on 22 March 2018 travelling from Munich (Germany) to Denver (US) were analysed. These measurements were performed approximately 5 weeks after the flight, thus only substances that were shown to be stable in the long-term stability experiment are expected to yield reliable results. Figure 5 shows a time series of ozone and CFC-12 , which was found to be stable in all experiments, and of dichloromethane, which was found to be depleted in samples pressurized at elevated ozone and decreased with time during storage.

~~While~~ CFC-12 anticorrelates with mixing ratios of ozone ~~, dichloromethane mixing ratios are~~ and this is also found for the other long-lived compounds which were stable in the storage experiments. Such a behaviour is expected, because ozone-rich stratospheric air masses are aged and should contain lower mixing ratios depending on a substance's stratospheric lifetime and transport pathway. Three of the canisters analysed from this flight were collected in tropospheric air masses characterized by lower mixing ratios of ozone levels. Mixing ratios of CFC-12 measured in these samples are around 510 ppt, consistent with current tropospheric mixing ratios observed at ground sites (Schuck et al., 2018). Similarly consistent numbers are measured for the other compounds expected to be stable in the canisters according to the storage experiments.

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Table 1. Results of ozone interference, short-term (8 days) and long-term (57 days) storage tests. Arrows indicate whether mixing ratios were increasing (↗) or decreasing (↘). Numbers indicate the maximum deviation measured for substances not stable in HIRES cylinders.

substance		stable ~~long-term~~ short-term	stable ~~short-term~~ long-term	influenced by O$_3$
CFC-12	CCl$_3$F	X	X	
CFC-11	CCl$_2$F$_2$	X	X	
HCFC-22	CHClF$_2$	X	X	
HCFC-141b	CH$_3$CCl$_2$F	X	X	
HCFC-142b	CH$_3$CClF$_2$	X	X	
HFC-125	CHF$_2$CF$_3$	X	X	
HFC-134a	CH$_2$FCF$_3$	X	X	
HFC-143a	CH$_3$CF$_3$	X	X	
HFC-152a	CH$_3$CHF$_2$	~~↗ (16 %)~~ X	↗	
HFC-23	CHF$_3$	~~↗ (15 %)~~ X	↗	
HFC-227ea	CF$_3$CHFCF$_3$	X	X	
HFC-245fa	CHF$_2$CH$_2$CF$_3$	X	X	
HFC-32	CH$_2$F$_2$	X	X	
Halon-1211	CBrClF$_2$	X	X	
Halon-1301	CBrF$_3$	~~↗ (5 %)~~ X	↗	
Halon-2402	C$_2$Br$_2$F$_4$	X	X	
Chloromethane	CH$_3$Cl	~~variable~~ ↗	↗ (14 %)	
Dichloromethane	CH$_2$Cl$_2$	~~↘ (-77 %)~~ X	↘	↘
Trichloromethane	CHCl$_3$	~~↘ (-97 %)~~ X	↘	↘
Tetrachloromethane	CCl$_4$	↘ (-47 %)	~~X~~ ↘	
1,1,1-Trichloroethane	CCl$_3$CH$_3$	X	X	
Trichloroethene	C$_2$HCl$_3$	↘ (-97 %)	~~variable~~ ↘	↘
Tetrachloroethene	C$_2$Cl$_4$	~~↘ (-97 %)~~ X	↘	↘
Bromomethane	CH$_3$Br	↗ (46 %)	↗ (35 %)	
Tribromomethane	CHBr$_3$	↘ (-93 %)	↘ (-70 %)	
Bromochloromethane	CH$_2$BrCl	~~↘ (-45 %)~~ X	↘	
Dibromochloromethane	CHBr$_2$Cl	↘ (-88 %)	↘ (-94 %)	↘
Carbonyl sulfide	OCS	~~↗ (20 %)~~ X	↗	↗
Sulfuryl fluoride	SO$_2$F$_2$	X	X	

Dichloromethane mixing ratios are below 1 ppt in most samples, close to the limit of detection of 0.4 ppt as derived from the 3-fold noise level. Only three samples have mixing ratios above 5 ppt, they are at the same time characterised by higher mixing ratios of CFC-12 and low mixing ratios of ozone which is indicative of tropospheric air. Leedham-Elvidge et al. (2015) reported stratospheric dichloromethane mixing ratios measured from glass samples collected during CARIBIC flights in 2001/2002, 2009/2010 and 2011/2012 to vary around 5–35 ppt. The mixing ratios measured from the HIRES stainless steel cylinders from CARIBIC flight 544 are significantly lower, which is consistent with the storage test results. A similar behaviour was found for all compounds which were not stable in the storage tests.

Three of the canisters analysed from this flight were collected in tropospheric air masses characterized by lower mixing ratios of ozone levels. Dichloromethane In the tropospheric air samples, dichloromethane varied between 14 ppt and 49 ppt. This agrees with mixing ratios in tropospheric samples in the dataset presented by Leedham-Elvidge et al. (2015) which were up to 65 ppt with an increase observed from 2006 through 2012. 2012, but is somewhat lower than mixing ratios at the ground in March 2018 (Schuck et al., 2018) which would be consistent with the result from the storage test, that dichloromethane is not stable in HIRES cylinders long-term.

Figures 6 and 7 show correlations of CFC-12, HFC-134a and dichloromethane with ozone and CO, respectively. For the stable long-lived compounds CFC-12 and HFC-134a a tight correlation with ozone ($r^2 = 0.98$ and $r^2 = 0.99$) with ozone is found. Correlation with CO is also tight for stratospheric samples with CO mixing ratios below 40 ppbV ($r^2 = 0.98$ for both, CFC-12 and HFC-134a), but it is less tight in the troposphere and with CO ($r^2 = 0.80$ and $r^2 = 0.79$) is found. For one tropospheric sample there is no corresponding integrated CO mixing ratio, because it was collected during one of the regular in-flight calibration phases of the CO instrument.

Dichloromethane does not correlate with ozone nor with CO in the stratosphere (panel (c) in Fig. 6 and 7), but it does show a correlation with CO for samples with CO mixing ratios of more than 40 ppbV . This with a value of r^2 of 0.99. Although the value of r^2 has a limited meaning owing to the small number of samples, this might be an indication that despite the analysis taking place within five weeks after the flight and dichloromethane being found to decrease with storage time in HIRES canisters, results may still reflect initial mixing ratios. If the decrease rate was the same for all tropospheric samples, the correlation of dichloromethane with CO might still persist, even if mixing ratios of dichloromethane have decreased. A similar behaviour was found for tetrachloroethene and trichloromethane and for the tropospheric samples for trichloroethene and for dibromochloromethane. The latter compound was below its detection limit in all stratospheric samples, trichloroethene in several of them.

4 Conclusions

In order to assess the potential of halocarbon analysis from samples collected in the HIgh REsolution air Sampler (HIRES) with the HIRES unit from the CARIBIC instrument package, the sample collection unit was intensively tested focusing on compound stability in the stainless steel canisters and the influence of ozone. Sampling during CARIBIC flights takes place in the upper troposphere and the lowermost stratosphere with ozone mixing ratios of up to several hundred ppbV. Therefore
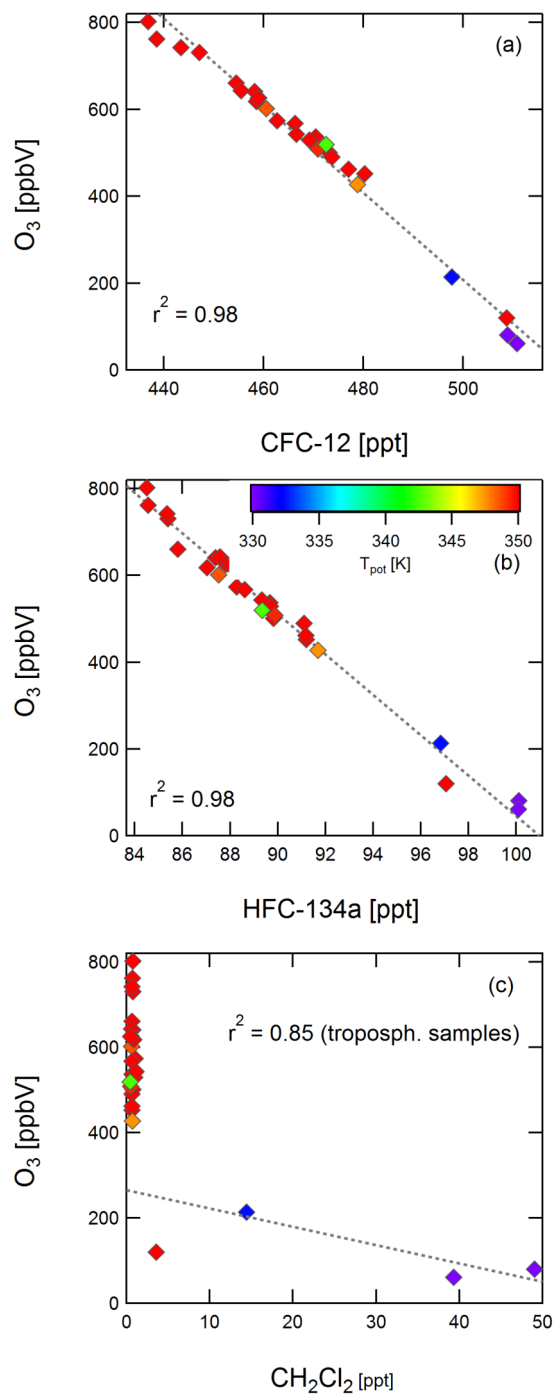
Figure 6. Correlation of CFC-12 (a), HFC-134a (b), and dichloromethane (c) with ozone. Colour coding is by potential temperature. Values of r^2 are given for the correlation of all samples for CFC-12 and HFC-134a, and for three tropopsheric samples in the case of dichloromethane.
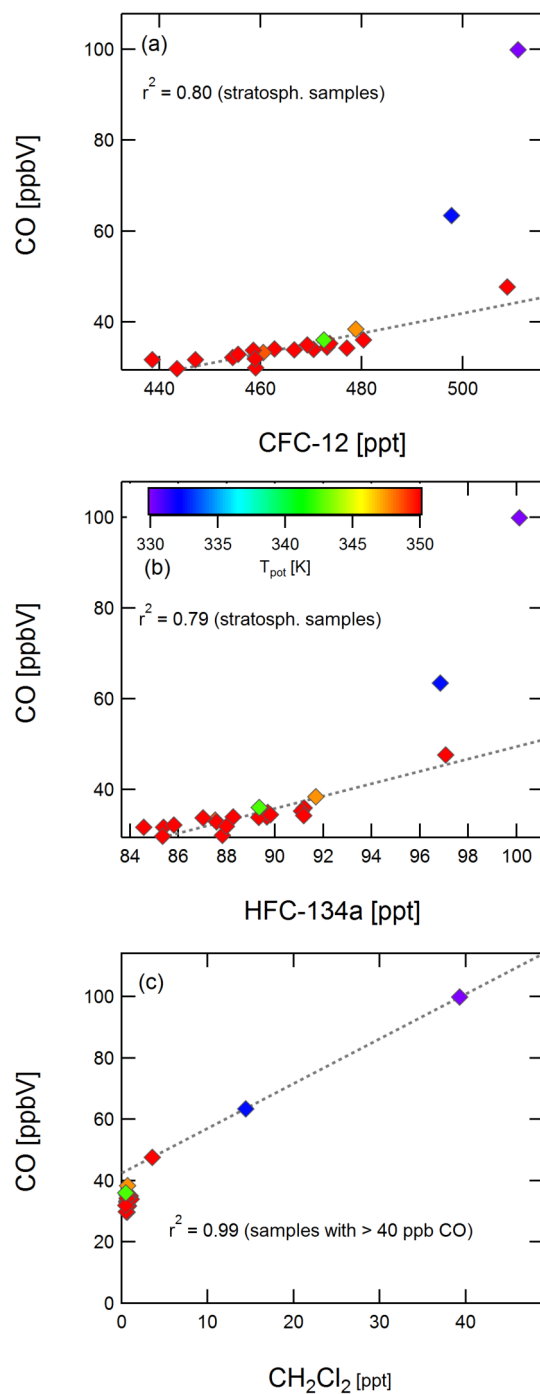
Figure 7. Correlation of CFC-12 (a), HFC-134a (b), and dichloromethane (c) with CO. Colour coding is by potential temperature. Values of r^2 are given for the correlation of stratospheric samples for CFC-12 and HFC-134a, and for three samples with a CO mixing ratio above 40 ppb in the case of dichloromethane.

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samples were pressurized with a mixture of a dry standard gas, containing typical tropospheric mixing ratios of a wide range of halogenated hydrocarbons, and synthetic air. The synthetic air could be enriched in ozone by passing an ozone-generating UV lamp. Final ozone mixing ratios were estimated to range from 400 ppbV to 600 ppbV. This is representative of the mixing ratios typically encountered at flight levels in the lowermost stratosphere. Several short-lived halocarbons were found to be depleted in canisters pressurized in the presence of ozone. COS was found to exhibit higher mixing ratios in this case.

In one experiment samples were analysed one day after pressurization and again after a storage time of one week. While bromomethane and chloromethane were found to grow already after this short period, tribromomethane ~~, tetrachloromethane~~ and trichloroethene had decreased, tetrachloromethane was found to be stable but its mixing ratio was significantly below the value expected. Of the 28 compounds investigated, 23 were found to be stable over storage of up to one week.

This changed in the long-term stability test which was conducted over up to 57 days. All compounds influenced by high levels of ozone were found to show the same behaviour (decreasing or increasing) during the long-term test. In addition, dichloromethane, trichloromethane, tetrachloroethene, tetrachloromethane, and bromochloromethane also showed a tendency to decrease after storage for longer than two weeks. HFC-152a, HFC-23, and Halon-1301 started to increase significantly. The tests showed, that for a number of halogenated tracers reliable measurement results can only be achieved if measurements are performed within few days after a flight. If this is not possible, which for CARIBIC samples is often the case as they circulate several laboratories at different institutions, results must be interpreted with care.

Measurements of samples from a CARIBIC flight in March 2018 that took place about five weeks after the flight confirmed the results from the stability tests. Mixing ratios of compounds found to decrease in the stability tests were in general very low, often below their respective detection limits. Also the results of the ozone test were confirmed, as mixing ratios of compound found to be sensitive to ozone were low in canisters sampled in the stratosphere at high ozone mixing ratios. With the current HIRES sampler it is not possible to study for example vertical gradients of mixing ratios above the tropopause for short-lived species. Compounds that had grown during the storage test were not evaluated.

Currently, we are in the process of constructing a second high resolution air sampler for use inside the CARIBIC container. Based on the measurements presented here, close attention will be given to the manufacturing of the stainless steel cylinders ~~. The new ones~~ which will be made of electro-polished stainless steel foil and welding will be done under vacuum~~. Ochiai et al. (2002) reported better compound stability for fused-silica-lined cylinders in comparison to electro-polished stainless steel. We will therefore test an additional coating in order to enhance stability also of short-lived compounds inside the canisters~~.

Data availability. Data are available from the corresponding author upon individual request.

Competing interests. The authors declare that there are no competing interests.

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