

## 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(ClO<sub>4</sub>)<sub>2</sub> 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 and 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 O<sub>3</sub>/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 et al. (2012).”*

- *Section 2.3: Does your Mg(ClO<sub>4</sub>)<sub>2</sub> 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 C<sub>2</sub>Cl<sub>4</sub>, but figure 3b refers to CH<sub>2</sub>Cl<sub>2</sub>. 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 than 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 CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CCl<sub>3</sub> (and CHBr<sub>2</sub>Cl) were also depleted. CH<sub>2</sub>Cl<sub>2</sub> 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 CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CCl<sub>3</sub>. Do you have any explanation for this? Could you think of any other experimental problem for these compounds? CH<sub>2</sub>Cl<sub>2</sub> for example, shows a very variable behavior in Figure 4.*  
Please note that CH<sub>3</sub>CCl<sub>3</sub> was listed erroneously in this line which will be corrected when revising the manuscript.  
We do not have an explanation for the depletion of CH<sub>2</sub>Cl<sub>2</sub> and CHBr<sub>2</sub>Cl. An additional experiment performed in the meantime indicated that both substances could not reliably 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 CH<sub>2</sub>Cl<sub>2</sub> 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 CH<sub>3</sub>Cl and CH<sub>3</sub>Br 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 2 $\mu$  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 and 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  $2\sigma$  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 the 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  $2\sigma$  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 CH<sub>2</sub>Cl<sub>2</sub>, 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) CH<sub>2</sub>Cl<sub>2</sub> 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 PTFE 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 incomplete. 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  $r^2$  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 Jungfraujoeh (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 CO<sub>2</sub> is not stable in all cylinders.*

Since a discussion of CO<sub>2</sub> 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.

## References:

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